

Transport Phenomena of Non-Newtonian Fluids
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Lecture - 31
Basics of MT; Diffusion through Stagnant Gas Film

Welcome to the MOOCs course Transport Phenomena of Non-Newtonian Fluids. Till now what we have seen? We have seen different aspects of momentum transfer and then heat transfer individually, also we have seen when both momentum and heat transfer are combined how to solve the problems, then heat transfer combined with the reaction, then how to solve the problems; those details we have seen.

Now in this lecture we are going to discuss a few basics of a mechanisms of a mass transfer; the mass transfer by molecular transport as well as the bulk motion. And then we see a standard simple problem diffusion through stagnant gas film how to solve using the transport equation for the mass transfer that we are going to develop in this lecture ok.

So, the basics of mass transfer though all of them are known through your UG classes, UG transport phenomena classes so, but however, it is essential to have a kind of recapitulation because this equations transport equations for the mass transfer whatever we are going to develop in today's lecture are going to be useful in the coming two weeks ok. We understand that mass transfer can occur by both molecular transport as well as the convective transport mechanism.

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Introduction

- Mass transfer by molecular transport and convective transport mechanisms

Fick's law of diffusion (molecular mass transport):

- Diffusion of helium in a thin fused silica horizontal plate of area S and thickness Y is considered
- At $t < 0$, both horizontal surfaces of plate are in contact with insoluble air

Thickness of slab of fused silica (substance B) is Y .

For $t < 0$

- In this system, helium \rightarrow species A and Silica \rightarrow species B
- Mass fraction of A $\rightarrow w_A$ and mass fraction of B $\rightarrow w_B$

So, whether not only mass transfer if it is momentum or heat transfer, then also and they occur both by molecular mechanism as well as the convective bulk motion mechanism as well transport occur. So, the same is true for the mass transfer also. So, we see a few basics of a mass transfer by molecular transport mechanism, then mass transfer by convective transport mechanism.

So, first molecular mass transport that is well explained by the Fick's law of diffusion so, that we see. Here what we do? In order to understand the diffusion or in order to obtain the Fick's law of diffusion; what we consider? We consider a diffusion of helium in a thin fused silica horizontal plate of area S and thickness Y ok.

So, that you know that experiment you know demonstrate the experiment that we are going to see here to understand how to get the Fick's law of diffusion that we already know it ok. So, at $t < 0$ that is before starting the experiment what we have? We have a fused silica is there.

So, the horizontal surfaces both top and you know bottom horizontal surfaces of this fused silica plate are in contact with insoluble air. Because the horizontal plate has been kept which is made of fused silica and then both the surfaces are in contact with the air. And then air is insoluble in this fused silica so, that it is not going to interfere in the diffusion process of a helium penetrating through this fused silica because helium is soluble in silica, but air is not soluble.

So, initially we have silica; fused silica horizontal plate is there. So, and then helium substance is there. So, notations wise helium we are giving A and then silica we are giving B right; thickness of this slab is Y, axis coordinate system we are taking like this horizontal is x axis and then vertical is y axis. So, $y = 0$ is bottom plate and then $y = Y$ is nothing but the top surface of the plate right.

So, at the top surface we are taking boundary condition that helium is not present ok. That is the mass fraction of helium is 0 at the top surface. This pictorial representation is at $t < 0$ where helium has not been introduced. So, insoluble air is present both bottom and top horizontal surfaces of this plate ok. So, this is the system that we are having.

So now, what we do? At $t = 0$ we are going to introduce helium at the bottom right whose mass fraction we are taking $w_A = w_{A0}$; and this w_{A0} is nothing but the solubility of helium in fused silica. So, that is the maximum of you know helium that can you know penetrate or soluble in the fused silica at given temperature and pressure conditions right.

So, this air is replaced by the helium at $t = 0$. So, then because of the molecular mechanism or molecular transport virtue what will happen? This helium will penetrate into the surface gradually and then a kind of concentration profile would be developed. And then that concentration profile is function of both y and t for t, right.

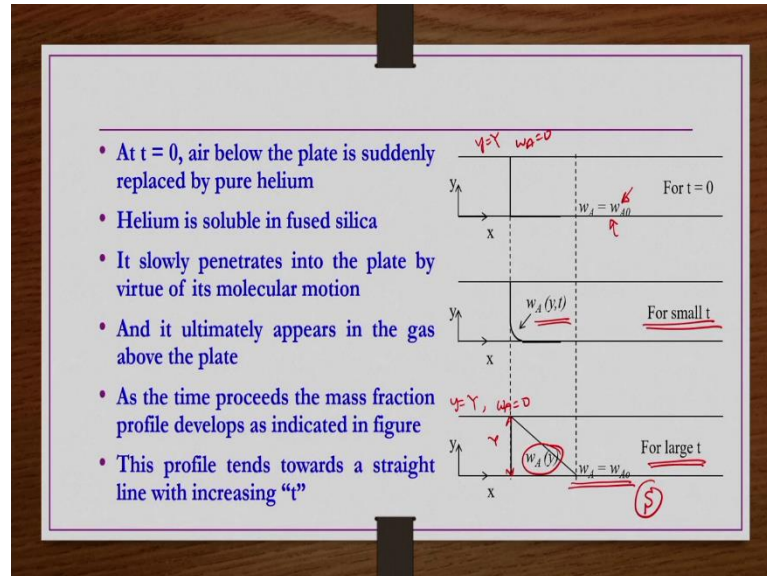
So, then obviously, what we have? We can have a kind of a profile something like this. So, this is w_A function of y and t right. But what happens when time increases gradually for steady state or large t this concentration profile whatever is there, it becomes independent of the time.

And then this profile is linear this profile is linear for large t and at largest for the such large values of time when steady state is established; steady state for the process of solubility of this component helium into the fused silica through the diffusion you know that attains a linear profile ok. That attains a linear profile.

So, that flux whatever is there, that we can relate it to relate it to the concentration gradient of helium within this slab; within this slab. So, that is what is the basic experiment that we are going to have demonstration experiment; and then from here we get the required so, called you know equation for the flux and then that flux we are going to relate to the concentration gradient from there we get the Fick's law of diffusion which we already

know ok. So, in this system helium is species A and then silica is species B, their mass fractions are w_A and w_B respectively.

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So, whatever we have discussed in the previous slide have been shown pictorially. So, at $t = 0$ helium has been introduced at the bottom of the plate fused silica horizon plate. So, the very first layer within the fused silica whatever is there that very first layer now helium is there at $t = 0$ that concentration in terms of mass fraction we are writing w_{A0} .

At $y = Y$, the concentration of helium is 0; the concentration we are representing in terms of mass fractions for the time being right. As the time progress this helium penetrates into the plate and then a concentration profile develops which is a function of both space and time. Now here we are taking only in y direction for the simplicity one direction ok.

So, that is for the t we can have such kind of concentration profile right. But as the time progress if you wait for the large time and then steady state is established what we can find this concentration profile is only function of y because it is steady state established. And then this profile is linear with a $w_A = w_{A0}$ at the bottom surface and then the $w_A = 0$ at the top surface where $y = Y$, right.

So, because this thickness of this plate is Y , right. Area through which the penetration is taking place is S ok. So, all this information is provided here as a text to the students.

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- At $t < 0$, mass fraction of helium, w_A , is zero everywhere
- At $t > 0$, at the lower surface, i.e., at $y = 0$, mass fraction of helium is equal to w_{A0} just inside the solid
- w_{A0} is solubility of helium in silica expressed as mass fraction
- At steady state, it is found that mass flow w_{Ay} of helium in +ve y-direction can be described to a very good approximation by

$$\frac{w_{Ay}}{S} = \rho D_{AB} \left(\frac{w_{A0} - 0}{Y} \right) \quad (1)$$

- i.e., mass flow rate of helium per unit area (or mass flux) is proportional to the mass fraction difference divide by the plate thickness
- Here ρ is the density of silica-helium system and the proportionality factor D_{AB} is diffusivity of helium in silica

So, finally, at steady state it is found that mass flow w_{Ay} of helium in positive y direction can be described to a very good approximation by $\frac{w_{Ay}}{S}$ this is nothing but the flux and then it is proportional to the concentration gradient that is given by $\frac{w_{A0} - 0}{Y}$. Why 0 here? Because $w_A = 0$ at $y = Y$ ok and then at $y = 0$ $w_A = w_{A0}$. So, the concentration gradient is given by this expression, right.

So now, here we have taken only in one direction for the simplicity. So, whatever y is there that is the positive y direction or the direction in which the species is diffusing is shown. And then A is nothing but the component and which component is being diffused that is shown here right.

So, that is mass flow rate of helium per unit area or mass flux is proportional to the mass fraction difference divided by the plate thickness right. We are calling it as mass flux not molar flux because everything we have taken in mass units; including this w_A all we have taken mass fractions not the mole fractions ok.

So, and then this ρ is the density of the systems both A and B system right and then proportionality factor whatever D_{AB} is there it is diffusivity of helium in silica. That is diffusivity of A in B.

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- Now rewriting eq. (1) for a differential element within the slab:
- $$j_{Ay} = \frac{w_{Ay}}{S} = -\rho D_{AB} \frac{dw_A}{dy} \quad (2)$$
- It is 1-D form of Fick's first law
 - First index in j_{Ay} indicates chemical species being diffused
 - Second index indicates direction in which diffusive transport taking place
- Valid for any binary solid, liquid or gas solutions provided that j_{Ay} is defined as mass flux relative to mixture velocity v_y : $v_y = w_A v_{Ay} + w_B v_{By}$ (3)
- i.e., v_y is an average in which v_{Ay} and v_{By} are weighted according to mass fractions (i.e., it is mass average velocity)

Now the same equation if you write for a differential element within this slab. So, then how we can write? You can write $-\rho D_{AB} \frac{dw_A}{dy}$ why this minus is coming? Because we know this mass transfer occurring from higher concentration region to the lower concentration region and then as the y increases the concentration is decreasing. So, that is the reason negative concentration gradient is there. So, we have to have a minus here right.

So, whatever this w_{Ay} divided by the area through which diffusion is taking place S is nothing but the mass flux that we have already seen. So, these mass flux we can indicate by j_{Ay} right. So, these notations we are following as per the book transport phenomenon by Bird, Stewart and Lightfoot where j 's are indicating for the mass units J 's or N 's that we are going to see they are for the molar units ok.

So, this equation is nothing but the 1-D form of Fick's first law right. So, first index in this j_{Ay} indicates the species that is being diffused that is component A here and then second index, that is y here indicates the direction in which the diffusive transport taking place ok.

Then it is valid for binary solid or binary liquid or gas solutions provided that j_{Ay} is defined as mass flux relative to the mixture velocity. And then mixture velocity is nothing but given by the mass weighted average velocity of all the molecules A and B; v_{Ay} is nothing

but the molecular velocities of component A and then v_{By} is the molecular velocity of component B in y direction. And then these are not the individual velocities.

So, let us say component A is moving in different you know in y direction in different locations different value. So, all the you know molecules are different y locations whatever the velocity of this molecule A is there that has been averaged similarly for the B also right. And then these are the local velocities. So, these velocities are measured using Pitot tube or Doppler velocity velocimetry etcetera right.

So, v is average in which v_{Ay} and then v_{By} are weighted according to mass fractions that is the mass average velocity.

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- In eq. (3), species velocity \bar{v}_{Ay} is not instantaneous molecular velocity of a molecule of A
- Rather it is arithmetic average of velocities of all molecules of tiny volume element
- Same is true for v_{By}
- Mass flux j_{Ay} is defined as: $j_{Ay} = \rho w_A (\bar{v}_{Ay} - v_y) \rightarrow (4)$
 - i.e., mass flux is defined relative to mixture velocity v_y
- Mass flux of B is defined analogously as: $j_{By} = \rho w_B (\bar{v}_{By} - v_y)$

Then in equation 3 species velocity v_{Ay} is not instantaneous molecular velocity of molecule A as mentioned, rather it is arithmetic average of velocities of all molecules of tiny volume element. Within the tiny element whatever we are doing this analysis, whatever the A component you know moving in y direction, all the velocities have been taken as a kind of consideration and then their arithmetic average is reported as v_{Ay} same is true for v_{By} as well.

So, mass flux now if you wanted to report in terms of velocity difference as a gradient, then you can report $j_{Ay} = \rho w_A (v_{Ay} - v_y)$ right. So, this $(v_{Ay} - v_y)$ is also known as the

diffusion velocities right; it is also known as the diffusion velocities. Similarly for component B we can write $j_{By} = \rho w_B (v_{By} - v_y)$ right.

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• If molecular weights of A and B differ, there is a locally shifting of centre of mass in the direction (y-) of diffusion as two species inter-diffuse
 • And the mass fluxes, j_{Ay} and j_{By} are so defined accordingly
 • i.e., fluxes, j_{Ay} and j_{By} are measured w.r.t. motion of centre of mass
 • For a binary system:

$$j_{Ay} + j_{By} = \rho w_A (v_{Ay} - v_y) + \rho w_B (v_{By} - v_y)$$

$$\Rightarrow j_{Ay} + j_{By} = \rho (w_A v_{Ay} - w_A v_y + w_B v_{By} - w_B v_y)$$

$$\Rightarrow j_{Ay} + j_{By} = \rho (v_y - v_y (w_A + w_B)) = 0 \Rightarrow j_{Ay} = -j_{By}$$

Handwritten notes in red ink on the right side of the slide:

- $\sum j_{Ay} = 0$
- $j_{Ay} + j_{By} = 0$

So, now if molecular weights of A and B are different from each other then obviously, what will happen? There will be locally shifting of center of mass in the direction of diffusion as two species are inter diffusing. Obviously, here in this case in the y direction the center of mass of the species moves in y direction and then because of that one there will be a kind of you know flux would be developed. And then accordingly those fluxes j_{Ay} and j_{By} are defined; that is j_{Ay} and j_{By} are measured with respect to the motion of the center of mass.

What is the motion on the center of the mass in this case? That is whatever the diffusion velocities are you know difference between the velocities is there that is mathematically represented; this motion of center of the mass ok. So, for binary system, if you add them together that is $j_{Ay} + j_{By}$. So, this is j_{Ay} this is j_{By} . Now we are taking ρ common from both the components; from both the terms of the right hand side then this is what we have.

So, this $w_A v_{Ay}$ and then $w_B v_{By}$ is nothing but v in the previous slide we have seen that is the mass average velocity. From the remaining two components if you take v_y common, $w_A + w_B$ would be there and then $w_A + w_B$ is nothing but 1, because these are mass fractions. And then summation of the mass fraction should be 1 and this is a binary system. So, only two components are there. So now, we have this is 0.

So, that what does it mean? $\sum j_\alpha$ should be 0 and then α is you know number of the components and all that ok. So that means, if you have in the y direction let us say if you are taking. So that means, if you have α number of components if you obtain the flux of all the components in the y direction and then add them together you are going to get 0. If you have only binary components, so then $j_{Ay} + j_{By} = 0$ the same thing we can write it as $j_{Ay} = -j_{By}$.

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• Finally, the vector form of Fick's First Law is

$$j_A = -\rho D_{AB} \nabla w_A \rightarrow (5)$$

• And similarly for flux B

$$j_B = -\rho D_{BA} \nabla w_B \rightarrow (6)$$

• Since for a binary system $j_A = -j_B$

$$-\rho D_{AB} \nabla w_A = +\rho D_{BA} \nabla w_B$$

$$\Rightarrow \boxed{D_{AB} = D_{BA}} \text{ Since for a binary system } \nabla w_A = -\nabla w_B$$

*

So, in the vector form now we are going to write Fick's first law. So, what we have seen? $j_{Ay} = -\rho D_{AB}$ and then concentration gradient. So, that concentration gradient we are writing in the vector form. So, ∇w_A we are writing. So, $j_A = -\rho D_{AB} \nabla w_A$ right.

So, similarly for B if you write $j_B = -\rho D_{BA} \nabla w_B$. Now here component B is diffusing in A in this equation number 6 whereas, equation number 5 A is diffusing in B. So, are they different or not that we are going to see now, right.

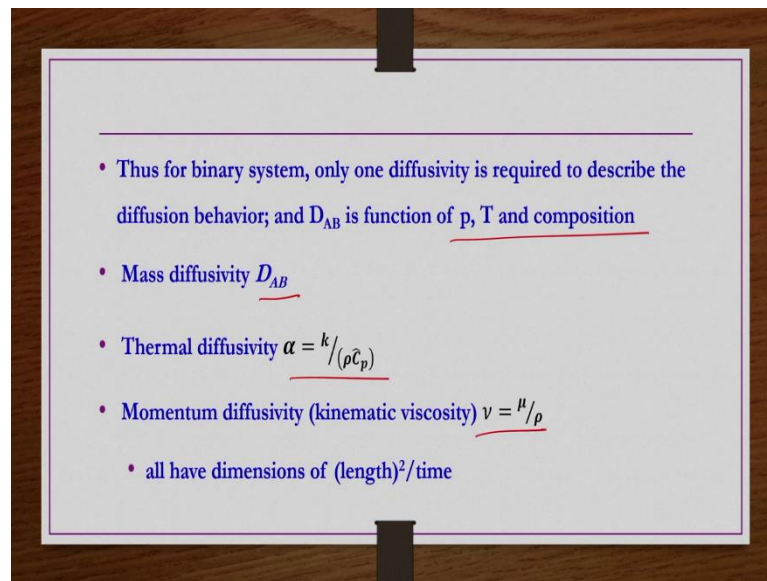
So, for the binary system just now we have seen the summation of these two that is a summation of the mass flux should be 0 that is when you add these two what will happen. Or we take a one flux is equals to the minus of the other flux because binary system we are taking. So, $j_A = -\rho D_{AB} \nabla w_A = -j_B$ is nothing but $+\rho D_{BA} \nabla w_B$, right.

So, ρ is the density of the system. So, that is going to be same. So, both of them are cancelled out. And then ∇w_A is nothing but $-\nabla w_B$ because it is a binary system only right.

So that means, $D_{AB} = D_{BA}$. So that means, for binary system whether D_{AB} or D_{BA} it is only one diffusivity is required to define the diffusion of the system ok.

Only thing that flux would be negative of flux of A would be the negative of the flux of B that is it. But the diffusivity only one diffusivity is required to define the diffusion in a binary system.

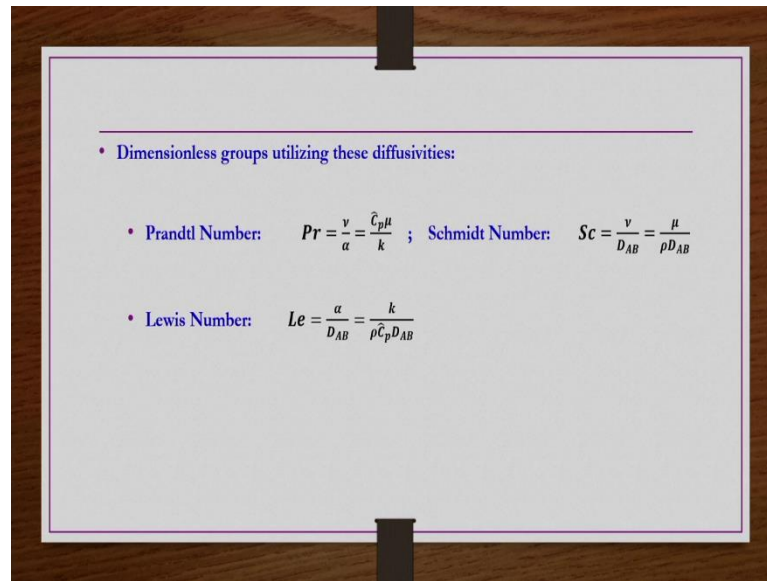
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Thus for a binary system only one diffusivity is required to describe the diffusion behavior and then D_{AB} is function of temperature pressure and composition. So, what we have this mass diffusivity D_{AB} ? Earlier we have thermal diffusivity α that is $k / \rho \hat{c}_p$ and then before that we have the momentum diffusivity or kinematic viscosity $\nu = \mu / \rho$. So, all of them are having the units you know length square per time right.

So, they indicate you know the molecular transport behavior in different processes, heat transfer, mass transfer, and momentum transfer like that ok. So, they have a similarity; they have a similarity.

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So, what we do? We get dimensionless groups utilizing these diffusivity; then what we get? Prandtl number $Pr = \hat{c}_p \mu / k$ that is v/α and Schmidt number that is $Sc = v/D_{AB}$ that is nothing but $\mu/\rho D_{AB}$, and then Lewis number that is α/D_{AB} or possible. Then that means, $k/\rho \hat{c}_p D_{AB}$ that is what Lewis number.

So, now what we understand from these numbers? Let us say if they transport; if the transport is occurring whether the momentum transport or heat transport or the mass transport whatever it is occurring. If it is occurring only because of the molecular mechanism, if it is occurring because of the molecular mechanism which transport process is dominating? Momentum transfer is the dominating or mass transfer is dominating or the heat transfer is dominating that we can understand.

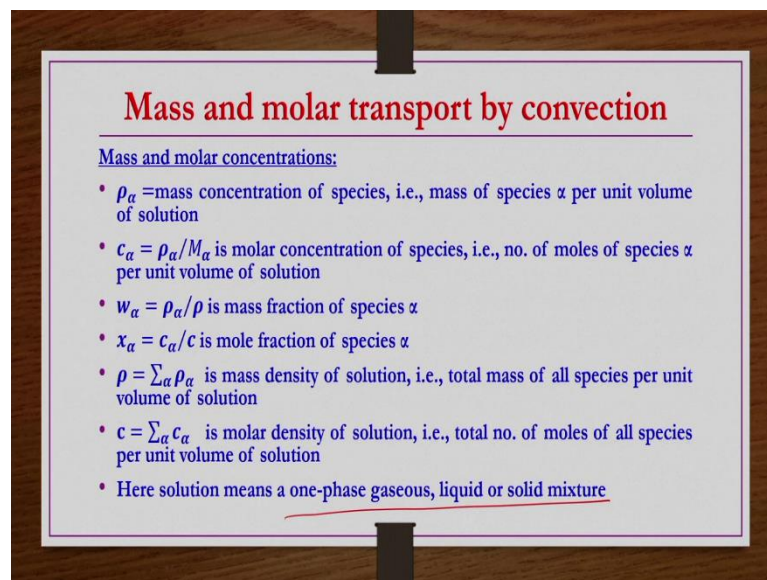
And then accordingly we can simplify the problem. If in a given problem all these transport processes are occurring simultaneously. That is the use of this dimensionless numbers in general.

So, till now what we have seen? We have seen you know mass transport by the molecular transport mechanism. So, now what we are going to see? We are going to see the mass transfer by the convection; that is mass transport by the convection and then same that

mass transfer whatever he said that we also represent in terms of the molar units. So, that is mass and molar transport by the convection that is what we are going to see now.

That is simply when the mass transfer is taking place only by diffusion. So, what is the flux out; what is the expression for the flux for component A and B if it is a binary system that is what we have seen. So, but now this mass transfer is occurring by the bulk motion or convection, so then what is the expression for this flux that is what we need to understand, right. So, we know that $\rho_\alpha v$ are $c_\alpha v$, but you know we are going to derive them. However, before deriving these things we need to have some understanding about the nomenclature.

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Mass and molar transport by convection

Mass and molar concentrations:

- ρ_α = mass concentration of species, i.e., mass of species α per unit volume of solution
- $c_\alpha = \rho_\alpha / M_\alpha$ is molar concentration of species, i.e., no. of moles of species α per unit volume of solution
- $w_\alpha = \rho_\alpha / \rho$ is mass fraction of species α
- $x_\alpha = c_\alpha / c$ is mole fraction of species α
- $\rho = \sum \rho_\alpha$ is mass density of solution, i.e., total mass of all species per unit volume of solution
- $c = \sum c_\alpha$ is molar density of solution, i.e., total no. of moles of all species per unit volume of solution
- Here solution means a one-phase gaseous, liquid or solid mixture

So, ρ_α is nothing but the mass concentration of species that is mass of species α per unit volume of a solution and c_α is nothing but the molar concentration of species α . That is nothing but number of moles of species α per unit volume of solution. And w_α is nothing but ρ_α / ρ that is mass fraction of species α . And then x_α is nothing but mole fraction of species α that is c_α / c and then ρ is nothing but $\sum \rho_\alpha$. Similarly c is nothing but $\sum c_\alpha$.

Here solution means one-phase gaseous liquid or solid mixture whichever we are taking. Only thing that they have to be homogeneous, then only these equations are in general valid.

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• Other relations:

$$c_\alpha = \rho_\alpha / M_\alpha \quad \text{hence,} \quad \rho_\alpha = c_\alpha M_\alpha$$

$$\sum_{\alpha=1}^N x_\alpha = 1; \quad \sum_{\alpha=1}^N w_\alpha = 1$$

$$\sum_{\alpha=1}^N x_\alpha M_\alpha = M; \quad \sum_{\alpha=1}^N \frac{w_\alpha}{M_\alpha} = \frac{1}{M}$$

$$x_\alpha = \frac{w_\alpha / M_\alpha}{\sum_{\beta=1}^N w_\beta / M_\beta}; \quad w_\alpha = \frac{x_\alpha M_\alpha}{\sum_{\beta=1}^N x_\beta M_\beta}$$

• Here M_α is molecular weight of species α *

M is molar mean molecular weight of solution

Other relations amongst this c_α ρ_α etcetera are provided here which are all well known to us, ok. M_α is nothing but the molecular weight of species α here whereas, M is the molar mean molecular weight of solution ok. It is not the molecular weight of one component, but the molar mean molecular weight of the solution whatever number of components are there. So, that should be considered.

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Mass average and molar average velocity:

- In diffusive mixture, various chemical species are moving at different velocities
- v_α , "velocity of species α ", is the average of all velocities of molecules of species α within a small volume
- For a mixture of N species, the local mass average velocity v is defined as,

$$v = \frac{\sum_{\alpha=1}^N \rho_\alpha v_\alpha}{\sum_{\alpha=1}^N \rho_\alpha} = \frac{\sum_{\alpha=1}^N \rho_\alpha v_\alpha}{\rho} = \sum_{\alpha=1}^N w_\alpha v_\alpha$$

- ρv is local rate at which mass passes through a unit cross section placed perpendicular to mass average velocity v
- It is local velocity that can be measured by Pitot tube or laser Doppler velocimetry

So, mass average and then molar average velocity we defined now, because we know this we are discussing mass transfer by the convection. So, when it is convection, so then

velocity would be there. So, then velocity which velocity should we consider? Mass average velocity or molar average velocity both of them can be utilized. So, individually we see what are they.

So, in diffusive mixture various chemical species are moving at different velocities. Then if v_α is the velocity of species α which is nothing but average of all velocities of molecules of species α within a small volume that we have seen. And then for a mixture of N species the local mass average velocity v is nothing but $\frac{\sum \rho_\alpha v_\alpha}{\sum \rho_\alpha}$.

And then $\sum \rho_\alpha$ we have seen it is nothing but ρ that is the density of the mixture. So, and then ρ_α/ρ is nothing but w_α that is nothing but the mass fraction of species α . So, v is nothing but $\sum w_\alpha v_\alpha$. This is the mass average velocity; local mass average velocity got it right.

Then ρv is local rate at which mass passes through a unit cross section placed perpendicular to mass average velocity v ok. Now it is local velocity so, that can be obtained by a Pitot tube or laser Doppler velocimetry.

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• Local molar average velocity v^* is: $v^* = \frac{\sum_{\alpha=1}^N c_\alpha v_\alpha}{\sum_{\alpha=1}^N c_\alpha} = \frac{\sum_{\alpha=1}^N c_\alpha v_\alpha}{c} = \sum_{\alpha=1}^N x_\alpha v_\alpha$

• $c v^*$ is local rate at which moles pass through a unit cross section placed perpendicular to molar velocity v^*

• In Summary:

v_α = velocity of species α w.r.t. fixed co-ordinates

$v = \sum_{\alpha=1}^N w_\alpha v_\alpha$ = mass average velocity

$v^* = \text{molar average velocity} = \sum_{\alpha=1}^N x_\alpha v_\alpha$

$v_\alpha - v$ = diffusion velocity of α w.r.t. v

$v_\alpha - v^* = \text{diffusion velocity of } \alpha \text{ w.r.t. } v^*$

$v - v^* = \sum_{\alpha=1}^N w_\alpha (v_\alpha - v^*)$ and $v^* - v = \sum_{\alpha=1}^N x_\alpha (v_\alpha - v)$

Similarly, molar or local molar average velocity if you wanted to define v^* . So, again coming to the notation wherever we have this $*$, $*$ or we have a capital letters like J N etcetera then those things should be related to the molar quantities ok. That has that is the

notation that we are that is followed by the transport phenomena book by Bird, Stewart and Lightfoot we are following the same thing.

So, local molar average velocity v^* is nothing but $\frac{\sum c_\alpha v_\alpha}{\sum c_\alpha}$ and then $\sum c_\alpha$ is nothing but c , and then c_α/c is nothing but x_α . That means, v^* is nothing but $\sum x_\alpha v_\alpha$ that right. And then $c v$ would be local rate at which moles pass through a unit cross section placed perpendicular to molar velocity v^* .

So, in summary v_α is the velocity of species α with respect to fixed coordinates and then v is mass average velocity, v^* is molar average velocity, $v_\alpha - v$ is nothing but diffusion velocity of α with respect to v . Whereas, $v_\alpha - v^*$ is nothing but diffusion velocity of α with respect to v^* ; local molar average velocity v^* . And then these are $v - v^*$ or $v^* - v$ whatever are there, they are in general known as the diffusion velocities. And so, now what we are going to see now?

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• Molecular mass and molar fluxes:

• Molecular mass flux of α is flow of mass of α through an unit area per unit time

$\star j_\alpha = \rho_\alpha (v_\alpha - v)$ (or $j_\alpha = \rho w_\alpha (v_\alpha - v)$)

• Similarly molecular molar flux of species A is no. of moles of A flowing through unit area per unit time $J_A^* = c_A (v_A - v^*)$ \star

• Now similarly Fick's First law of diffusion

- in mass units: $j_A = \rho_A (v_A - v) = -\rho D_{AB} \nabla w_A$ ✓
- in molar units: $J_A^* = c_A (v_A - v^*) = -c D_{AB} \nabla x_A$ ✓

Molecular mass and molar fluxes. Molecular mass flux of α is a flow of mass α through an unit area per unit time. So that means, $j_\alpha = \rho_\alpha (v_\alpha - v)$ that we have already seen.

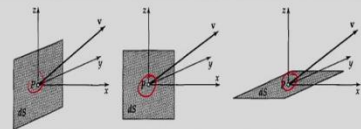
Similarly, molecular molar flux of species A is number of moles of A flowing through unit area per unit time. So, then this J_A^* right. So, this is in mass units basically and this is in molar units that is the difference. $J_A^* = c_A (v_A - v^*)$ right. J, j is wherever J or j are coming then they are with respect to the molar units right.

Now Fick's first law of diffusion if you write. So, in terms of mass units we have this thing, in terms of molar units we have this thing, right. Here in the mass units ∇w_A we are having, in the molar unit we are having ∇x_A right. In mass units you know diffusion velocity is with respect to v , local mass average velocity. In molar units diffusion velocity is nothing but with respect to v^* that is local molar average velocity.

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Convective mass and molar fluxes

- Mass may also be transported by bulk motion of the fluid in addition to transport by molecular motion
- Consider three mutually perpendicular planes of area ' ds ' at a point ' P ' where fluid mass average velocity is ' v '



- Volume rate of flow across the plane perpendicular to the surface element ds perpendicular to x-axis is $v_x ds$
- Mass rate at which mass of species ' A ' is being swept across the same surface element is $\rho_A v_x ds$

So, now expression for convective mass and molar fluxes. The flux is by convection, but we are going to write it in both mass and molar units. That is the reason it is convective mass flux and then convective molar flux. Mass may also be transported by the bulk motion of the fluid in addition to the transport by molecular motion. That we understand.

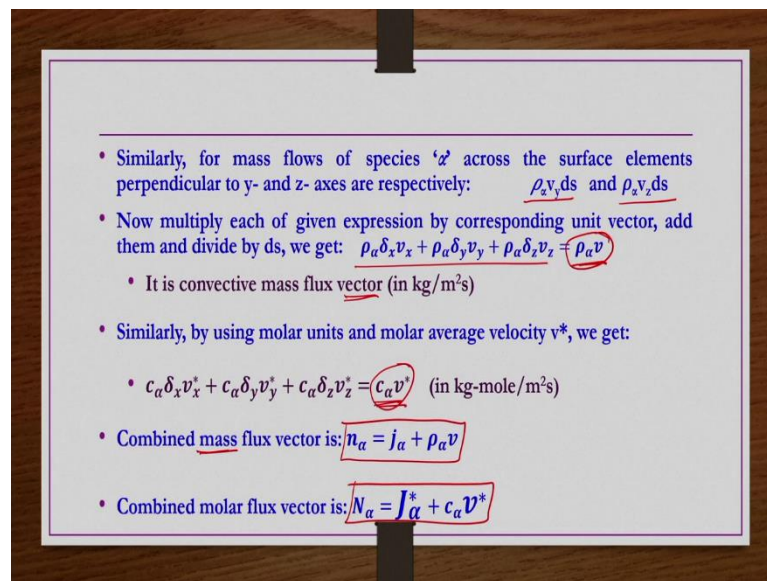
Now consider three mutually perpendicular planes of area ' ds ' at a point P where fluid mass average velocity is v and then pictorially is represented by this. The surface ds is there at this point P you know we are taking the fluid mass average velocity v at all three planes. Basically these planes are presented you know in one picture the perpendicular plane is perpendicular to the x direction, another picture plane is perpendicular to the z direction, another picture plane is perpendicular to the y direction like that only. That is a simple difference.

So, volume rate of flow across the plane perpendicular to the surface element ds perpendicular to the x axis would be nothing but $v_x ds$ simple because the mass average

velocity at the point P is nothing but v_x . And then the area of the plane perpendicular to that x axis x direction is nothing but ds .

So now, at this point when it is perpendicular to the x axis if you wanted to know the mass rate, then this one you have to multiply by ρ_a that is you get $\rho_a v_x ds$. Corresponding things when perpendicular to y and z directions are there.

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So, then we have $\rho_a v_y ds$ and then $\rho_a v_z ds$. Now these three quantities what we do? We multiply by their unit vectors in x y z directions normal unit vectors that is $\delta_x \delta_y \delta_z$ right. Then we divide by ds then we add them together then we get this is what that is $\rho_a \delta_x v_x + \rho_a \delta_y v_y + \rho_a \delta_z v_z$. So, this we can write it as $\rho_a v$ and this is nothing but the mass flux because of the convection. So, it is the convective mass flux vector generalized one, in kg per meter square second.

Similarly, we can write using molar units and then molar average velocity v^* then we get $c_a \delta_x v_x^* + c_a \delta_y v_y^* + c_a \delta_z v_z^*$ which is nothing but $c_a v^*$, right. So, now, what we have? We have the expression for you know mass flux because of the convection as well as the molar flux because of the convection. That is the flux because of the convection whatever is there that we got in terms of the mass units as well as the in terms of the molar units.

Previously, the same thing we got when the mass transfer is only by diffusion, then flux because of the mass; then flux in mass units and flux in molar units we have already seen.

So now, these fluxes are in general added now. If you wanted to know the combined complete flux then you have to add them together. So, then when you add them together they are known as the combined flux; combined mass flux is in small letters that is $n_\alpha = j_\alpha + \rho_\alpha v$.

The same thing if you write in molar units then capital letters that is $N_\alpha = J_\alpha^* + c_\alpha v$ and then v^* , v^* is local molar average velocity v is nothing but the local mass average velocity.

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Table 1: Notation for Mass and Molar Fluxes

Quantity	w.r.t. stationary axes	w.r.t. mass average velocity v	w.r.t. molar average velocity v^*
Velocity of species α	v_α	$v_\alpha - v$	$v_\alpha - v^*$
Mass flux of species α	$n_\alpha = \rho_\alpha v_\alpha$	$j_\alpha = \rho_\alpha (v_\alpha - v)$	$j_\alpha^* = \rho_\alpha (v_\alpha - v^*)$
Molar flux of species α	$N_\alpha = c_\alpha v_\alpha$	$J_\alpha = c_\alpha (v_\alpha - v)$	$J_\alpha^* = c_\alpha (v_\alpha - v^*)$
Sums of mass fluxes	$\sum_{\alpha=1}^N n_\alpha = \rho v$	$\sum_{\alpha=1}^N j_\alpha = 0$	$\sum_{\alpha=1}^N j_\alpha^* = \rho(v - v^*)$
Sums of molar fluxes	$\sum_{\alpha=1}^N N_\alpha = cv$	$\sum_{\alpha=1}^N J_\alpha = c(v - v)$	$\sum_{\alpha=1}^N J_\alpha^* = 0$
Relation between mass and molar fluxes	$n_\alpha = M_\alpha N_\alpha$	$j_\alpha = M_\alpha J_\alpha$	$j_\alpha^* = M_\alpha J_\alpha^*$
Interrelations among mass fluxes	$n_\alpha = j_\alpha + \rho_\alpha v$	$j_\alpha = n_\alpha - w_\alpha \sum_{\beta=1}^N n_\beta$	$j_\alpha^* = n_\alpha - x_\alpha \sum_{\beta=1}^N \frac{M_\alpha}{M_\beta} n_\beta$
Interrelations among molar fluxes	$N_\alpha = J_\alpha + c_\alpha v$	$J_\alpha = N_\alpha - w_\alpha \sum_{\beta=1}^N \frac{M_\beta}{M_\alpha} N_\beta$	$J_\alpha^* = N_\alpha - x_\alpha \sum_{\beta=1}^N \frac{N_\beta}{N_\alpha} N_\beta$

So, notation for mass and molar fluxes are given here with respect to stationary axis, with respect to the mass average velocity v , with respect to the molar average velocity v^* as given. So, if the velocity of species α is considered. So, with respect to stationary axis it is v_α , with respect to the mass average velocity it is nothing but $v_\alpha - v$, with respect to the molar average velocity it is nothing but $v_\alpha - v^*$.

So, mass flux of species α since mass flux it is $n_\alpha = \rho_\alpha v_\alpha$, with respect to the mass average velocity that is $v_\alpha - v$ terms. So, then $j_\alpha = \rho_\alpha (v_\alpha - v)$. And then we are writing it mass flux, so this last column is with respect to the molar average velocities it is a hybrid flux; hybrid flux because j_α is there and $*$ is there j stands for the mass units and then $*$ stands for the molar unit.

So, both of them are involved here. So, that is the reason it is known as the hybrid flux. How it is both of them are involved? Because this v^* is nothing but local molar average velocity whereas, the ρ_α is nothing with the mass concentration of the species α .

Similarly, molar flux of species α if you write with respect to the stationary axis $N_\alpha = c_\alpha v_\alpha$. And then with respect to the molar average velocity it is $J_\alpha^* = c_\alpha (v_\alpha - v^*)$. We are writing molar fluxes, but the middle column is with respect to the mass average velocities. So, that is the reason heat is represented in red font.

So, again it is hybrid flux because J_α is nothing but the J_α is nothing but flux in molar units, but it is the diffusion velocity is whatever is there that is given with respect to the mass average velocity v not the molar average velocity v^* . So, molar flux in terms of the diffusive mass velocities are reported. So, it is again the hybrid flux like that you know other quantities we can evaluate. So, wherever this red font are there so they indicate hybrid flux ok.

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Table 2 : Equivalent forms of Fick's First law of Binary Diffusion

Flux	Gradient	Form of Fick's law
j_α	∇w_A	$j_A = -\rho D_{AB} \nabla w_A$
J_A^*	∇x_A	$J_A^* = -c D_{AB} \nabla x_A$
n_a	∇w_A	n_A $= w_A (n_A + n_B) - \rho D_{AB} \nabla w_A$ $= \rho_A v - \rho D_{AB} \nabla w_A$
N_a	∇x_A	$N_A = x_A (N_A + N_B) - c D_{AB} \nabla x_A$ $= c_A v^* - c D_{AB} \nabla x_A$
$\rho(v_A - v_B)$	∇w_A	$\rho(v_A - v_B) = -\frac{\rho D_{AB}}{w_A w_B} \nabla w_A$
$c(v_A - v_B)$	∇x_A	$c(v_A - v_B) = -\frac{c D_{AB}}{x_A x_B} \nabla x_A$

Similarly, different equivalent forms of Fick's first law for binary diffusion as shown here. So, flux mass flux if it is represented gradient is ∇w_A and then form of Fick's law is nothing but $j_A = -\rho D_{AB} \nabla w_A$ similarly, molar flux then J_A^* , then concentration gradient is ∇x_A , then form of the Fick's law is nothing but $J_A^* = -c D_{AB} \nabla x_A$.

Similarly, component A we can write here the combined flux we can write here in mass unit molar units as well as in terms of the diffusion velocities also we can write these expressions as given here ok.

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Most conveniently used form of Fick's law

- If w.r.t fixed space: $J_A = -\rho D_{AB} \nabla w_A$ or $J_A^* = -c D_{AB} \nabla x_A$
- If there exist motion of solution as well and flux w.r.t. average velocity of solution, then for species A:
- $N_A = J_A^* + c_A v^*$ but $J_A^* = -c D_{AB} \frac{\partial x_A}{\partial z}$ “(considering in z-direction only)” $\sum J_A = 0$
 $\sum J_A^* = 0$
- And $cv^* = \sum_{a=1}^N N_a$ for binary system $cv^* = N_{Az} + N_{Bz} \Rightarrow v^* = \frac{N_{Az} + N_{Bz}}{c}$
- $\therefore N_{Az} = -c D_{AB} \frac{\partial x_A}{\partial z} + \frac{c_A}{c} (N_{Az} + N_{Bz})$
- $\Rightarrow N_{Az} = -c D_{AB} \frac{\partial x_A}{\partial z} + x_A (N_{Az} + N_{Bz})$ *
- This is the most convenient form of Fick's law of diffusion if there exist motion of solution

Now, we are going to write most conveniently used form of Fick's law in solving majority of the mass transfer problems in this course. So, with respect to the fixed space what we have seen? Mass flux is this one in table 1 just now we have seen, and then molar flux is this one.

Then if there exists motion of solution as well and in flux with respect to the average velocity of solution then for species A this is what we have seen combined flux right. In molar; in the in terms of the molar units combined flux is the flux because of the diffusion in molar units and then the flux because of the local molar average velocity is this one both of them are added together. And then whereas, J_a^* is nothing but this one, this also we know and then we are taking only one direction for simplicity that is in z direction.

Now, this equation we can use only we know the v^* and then v^* are the local molar average velocity that are in general not available. Bulk average velocities etcetera available for a given system are measurable. For most of the system you cannot use always Pitot tube or laser Doppler velocimetry to find out these average local average velocities that is not possible. So, then we need to have an expression.

So, what we do? Let us say if you have a binary component. If you have a binary component then if you have N_A N_B right both of them you add together. So, then what we understand? $\sum j_\alpha$ is 0 or $\sum J_\alpha^*$ is also 0. That is the summation of the flux because of the diffusion is there that is 0 for all the component if you take the flux of all the components.

So, then when you do these two then what you get; $c v^*$ is nothing but $\sum N_\alpha$ because $\sum c_\alpha v^*$ is nothing but $c v^*$ that also we have seen. So, this is what you get. So, $\sum N_\alpha$ is nothing but $c v^*$; from here v^* you can have $\sum N_\alpha / c$. So, for the binary components $\sum N_\alpha$ is nothing but $N_{Az} + N_{Bz}$ we are taking only in the z direction for simplicity.

So, v^* we have $(N_{Az} + N_{Bz}) / c$. So, this we can substitute here in place of v^* , then we have N_{Az} is equals to in case of $J_a^* - c D_{AB} \frac{\partial x_A}{\partial z} + \frac{c_A}{c} (N_{Az} + N_{Bz})$ because this c_A and then whatever remaining multiplied by this thing is there that is nothing but your v^* ; this is nothing but v^* .

So, $\frac{c_A}{c}$ we can as x_A . So, this is the combined flux for a binary system. And this is the most convenient form of Fick's law that has been used you know for solving majority of the mass transfer problems associated with the; with diffusion right and bulk motion both.

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Similarly, in terms of mass units:

$$n_A = -\rho D_{AB} \frac{\partial w_A}{\partial z} + \rho_A v$$

But $\rho v = \sum_{\alpha=1}^N n_\alpha = (n_A + n_B)$ for binary system

$$\Rightarrow v = \left(\frac{n_A + n_B}{\rho} \right)$$

$$\therefore n_A = -\rho D_{AB} \frac{\partial w_A}{\partial z} + \frac{\rho_A}{\rho} (n_A + n_B)$$

$$n_A = -\rho D_{AB} \frac{\partial w_A}{\partial z} + w_A (n_A + n_B) \quad *$$

Before solving eq. (1), generally N_{Bz} is eliminated by using known N_{Bz} / N_{Az} ratio

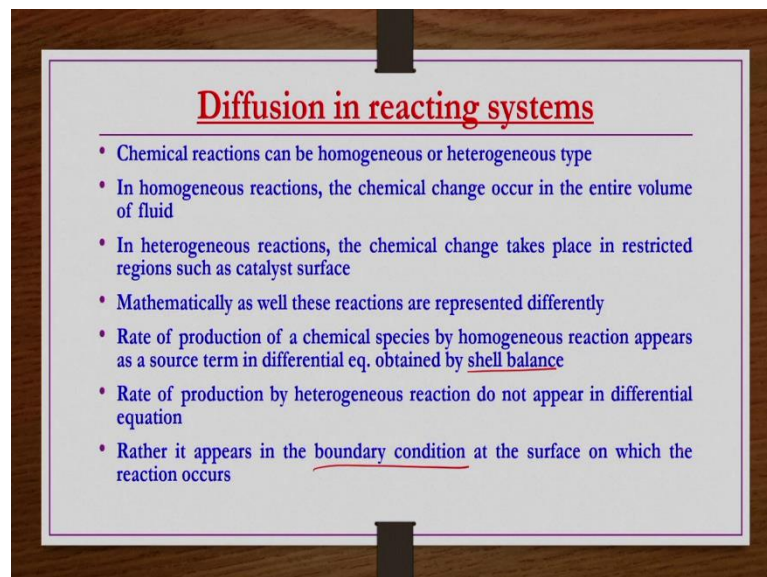
So, now same thing if you wanted to write in terms of the mass units. So, $n_A = j_A + \rho_A v$ and then j_A is nothing but $-\rho D_{AB} \frac{\partial w_A}{\partial z}$ we are taking here again only in the z direction for simplicity.

Now, here also if you have a binary system and then if you add the flux by diffusion for all component that should be 0. That means, $\sum n_\alpha = \sum \rho_\alpha v$ that is this one. $\sum \rho_\alpha v$ is nothing but ρv that we know and then $\sum n_\alpha$ is nothing but $n_A + n_B$ for binary system.

So, from here v you get $(n_A + n_B)/\rho$. So, that you can substitute here. So, that this equation can be usable in n B usable form. So, that you get. So, here in place of v you have $(n_A + n_B)/\rho$. So, ρ_A/ρ is nothing but w_A . So, this is the most convenient form of Fick's law of diffusion when there is a solution motion is also bulk motion is also existing. So, this is the expression for the combined flux, right.

So, now in these equations whether you write in molar units or mass units. Generally one of the component flux that is N_{Bz} or N_{Az} may be eliminated if we know the relation between N_{Az} and N_{Bz} ok. Or one of them in general stagnant I mean 0 if the stagnant one of the phases stagnant like that. So, that we see.

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Diffusion in reacting systems

- Chemical reactions can be homogeneous or heterogeneous type
- In homogeneous reactions, the chemical change occur in the entire volume of fluid
- In heterogeneous reactions, the chemical change takes place in restricted regions such as catalyst surface
- Mathematically as well these reactions are represented differently
- Rate of production of a chemical species by homogeneous reaction appears as a source term in differential eq. obtained by shell balance
- Rate of production by heterogeneous reaction do not appear in differential equation
- Rather it appears in the boundary condition at the surface on which the reaction occurs

So, now what if diffusion in reacting system? So, if there is a mass transfer + there is a reaction also taking place. So, then reactions can be categorized in different ways, but now with respect to the problems that we are dealing with the mass transfer combined with

reaction. So, then reaction can be categorized as two types of reactions homogeneous reactions and heterogeneous reaction.

Homogeneous reaction takes place in the entire volume of the system whereas, the heterogeneous reaction in general takes on a specified location like surface of the catalyst etcetera right. So, if it is homogeneous reactions in since the reaction is taking place in the entire volume, so that mathematical representation should come into the mass transfer equation accordingly right.

If it is taking only at the particular location you know surface of the catalyst etcetera, so then that information mathematically should come into the problem as a boundary condition because it is occurring at a specified location. So, how to bring them into the picture; that is what we are going to see here.

So, chemical reactions can be homogeneous or heterogeneous. In homogeneous reaction the chemical change occur in the entire volume of the fluid, in heterogeneous reactions the chemical change takes place in restricted regions such as catalyst surface. Mathematically as well these reactions are represented differently because one is taking place in the entire volume, another one is taking place only at specified locations ok.

So, rate of production of chemical species by homogeneous reaction appears as a source term in differential equation obtained by the shell balance that is also we are going to see. Whereas the rate of production by heterogeneous reaction do not appear in differential equation, rather it appears in the boundary condition at the surface on which the reaction occurs, ok.

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• For homogeneous reactions: $R_A = k_n''' c_A^n$

where R_A : molar rate of production A (mol./cm³.s)
 c_A : concentration of A (mol./cm³)
 n : order of reaction
for first order reaction, rate constant k_n''' has s⁻¹ unit

• For heterogeneous reactions: $N_{Az}|_{surface} = k_n'' c_A^n|_{surface}$

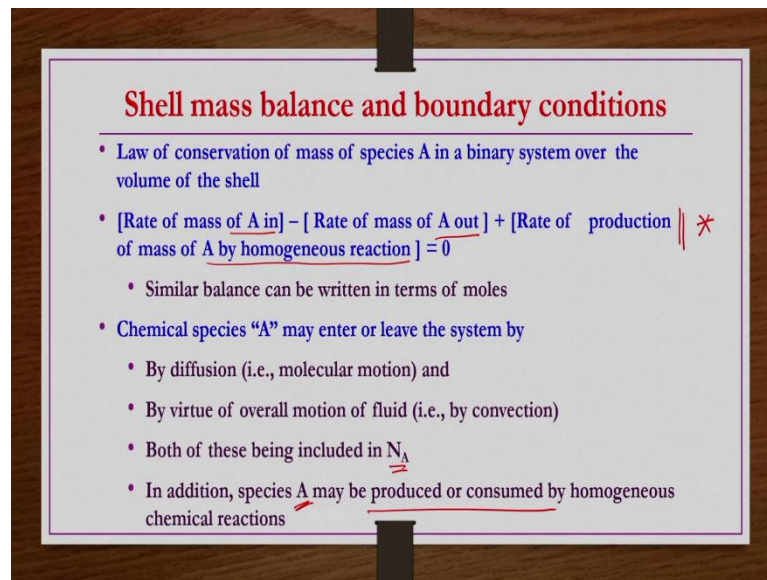
where N_{Az} (moles/cm².s) and k_n'' is cm/s for first order reaction
'''- indicates volume source and ''-indicates surface source

So, let us say for homogeneous reactions rate of production we can represented; we can represented by this expression $R_A = k_n''' c_A^n$. Where R_A is the molar rate of production of A, c_A is concentration of A, n is the order of reaction. If first order reaction then rate constant k_n''' has second inverse of units ok.

For heterogeneous reactions let us say flux is known at the surface that is N_{Az} surface is $k_n'' c_A^n$ at the surface. This reaction whatever the c_A^n surface that should also be found at the surface at which reaction is taking place because its a heterogeneous reaction, right.

So, N_{Az} is the molar flux, k_n'' or here k_n'' is for first order reaction and given as centimeter per second. So, here double prime, here triple prime they are just notations only. Triple prime indicates volume source and double prime indicates surface source. That is triple prime is for the reaction taking place in entire volume, double prime is for the reaction which is occurring only at specified surfaces.

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Shell mass balance and boundary conditions

- Law of conservation of mass of species A in a binary system over the volume of the shell
- $[\text{Rate of mass of A in}] - [\text{Rate of mass of A out}] + [\text{Rate of production of mass of A by homogeneous reaction}] = 0$ *
- Similar balance can be written in terms of moles
- Chemical species "A" may enter or leave the system by
 - By diffusion (i.e., molecular motion) and
 - By virtue of overall motion of fluid (i.e., by convection)
 - Both of these being included in N_A
- In addition, species A may be produced or consumed by homogeneous chemical reactions

Now, shell balance and then boundary conditions in general that are useful to solve the mass transfer problems associated with the diffusion for as well as the bulk motion and chemical reaction that is what we are going to see. Because, now we see the basics and then after that we can take different types of problems associated as per you know problem.

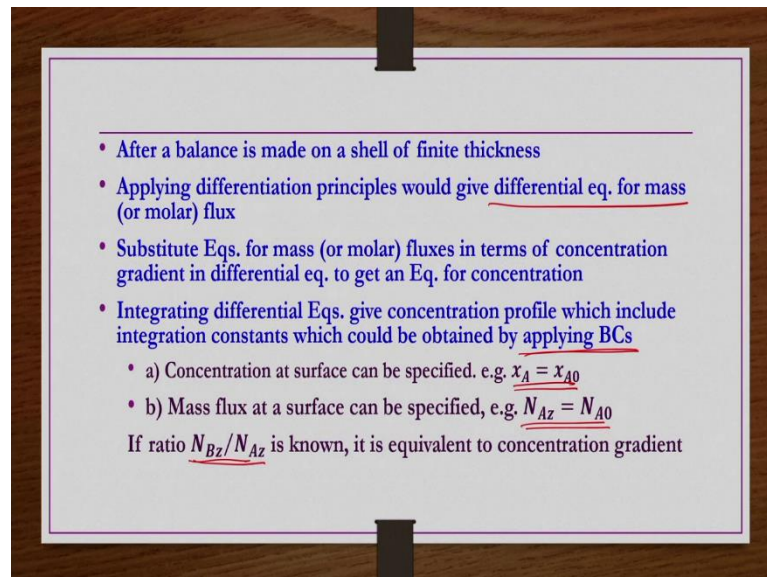
Because now we see you know balance equation writing boundary conditions in general for you know individual processes with and without reaction. So, that when we solve the problems as per the problem we can take the equations and then solve the problems without any difficulty.

So, law of conservation of mass of species A in a binary system over the volume of the shell if you wanted to write: Rate of mass of A in minus rate of mass of A out + rate of production of mass of A by homogeneous reaction. If it is homogeneous reaction then it should come as a source term that is what we are doing here and in all that should be equals to 0, right.

So, this is the balance equation. So, we are not going to do the differential equation derivation as we have done the momentum transfer equations or heat transfer equations, but every time we are going to follow this simple approach, because in the case of mass transfer writing such kind of balance for a given specified problem is much easier ok.

Similar balance can be written in terms of moles as well. And then chemical species A may enter or leave the system, but by both diffusion convection and then both of these are being included in combined flux N_A . And then in additions species A may be produced or consumed by homogeneous chemical reactions that are also possible, right.

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After a balance is made on a shell of finite thickness what we do? We apply differentiation principles and would get differential equation for mass flux or molar flux, right. Then substitute equations for mass flux or molar fluxes in terms of concentration gradient in differential equations to get an equation for the concentration. We when we solve these problems we can easily understand.

Then integrating differential equations will give concentration profile which include integration constants which can be obtained by the applying the boundary conditions. Because very similar way like what we have done in momentum transfer or heat transfer kind of problems also ok.

Now what are the boundary conditions in general possible in the mass transfer problem that is what we are going to see; because they are very much essential, right. And they are not conventional they are not very generalized or conventional boundary conditions like no-slip boundary conditions or constant temperature or constant flux heat flux equations etcetera those things we have seen. So, we have to be careful while applying the boundary conditions in mass transfer problems.

One is the concentration at surface can be specified that is the simplest boundary condition. Another one is the mass flux at a surface can be specified that is N_{Az} may be some constant N_{A0} something like that may be specified or the ratio is known N_{Bz}/N_{Az} is known then it is equivalent to the concentration gradient.

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• c) If diffusion is occurring in a solid, it may happen that at the surface substance A is lost to a surrounding stream according to relation:

$$N_{A0} = k_c(c_{A0} - c_{Ab})$$

Where, N_{A0} is molar flux at the surface ; c_{A0} is surface concentration
 c_{Ab} is concentration in the bulk fluid stream
 k_c is the mass transfer coefficient

• d) Rate of reaction at the surface can be specified; e.g. If A disappears at a surface by first order chemical reaction then, $N_{A0} = k_1''c_{A0}$ ← heterogeneous reaction
 i.e., rate of disappearance at a surface is proportional to the surface concentration
 Here proportionality constant k_1'' is first order chemical reaction rate constant

Then if diffusion is occurring in a solid, it may happen that the surface substance; it may happen that at the surface substance A is lost to the surrounding stream according to this relation: $N_{A0} = k_c (c_{A0} - c_{Ab})$. Where N_{A0} is molar flux at the surface it is a fixed value it is not changing right, it is not changing it is not N_{Az} it is N_{A0} fixed one right; c_{A0} is the surface concentration. And then c_{Ab} is nothing but the bulk concentration or concentration in the bulk fluid stream, k_c is nothing but the mass transfer coefficient.

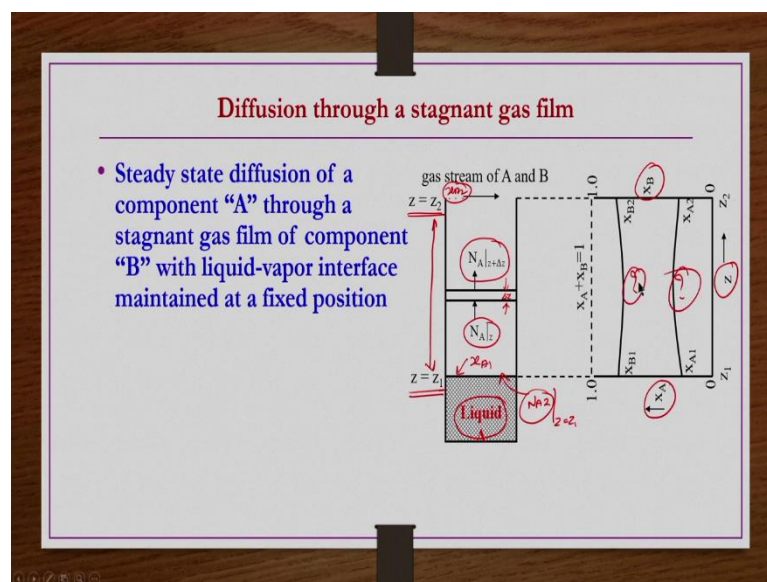
Other boundary condition is the rate of reaction at the surface can be specified. That is if A disappears at a surface by first order chemical reaction, then $N_{A0} = k_1''c_{A0}$ this is associated with the heterogeneous reaction.

So, that is rate of disappearance at surface is proportional to the surface concentration, if it is a first order chemical reaction. If it is second order chemical reaction then power 2 would be there ok. So, here proportionality constant k_1'' ; k_1'' is the first order chemical reaction rate constant. Mostly we take first order reactions in the problems.

So, those are the basics that we have seen. On the basics of flux by diffusion flux by convection and then flux and mass units, flux in molar units in either of the diffusion and bulk motion cases we have seen. We have seen the combined fluxes and then we have seen how to write the balance equations for the mass transfer, and then what are the boundary conditions required to solve the species concentration differential equations etcetera those things we have seen.

Now what we do? Before going into the complicated problems of mass transfer combined with the heat transfer or reaction etcetera we take a simple diffusion through non-stagnant gas film problem which is very well known and very basic problem in the mass transfer.

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So, diffusion through a stagnant gas film that we are considering here. Steady state diffusion of a component A through a stagnant gas film of component B with liquid-vapor interface maintained at a fixed position is taken. So, what we have? We have a column in which we have a liquid A and then interface of this liquid is located as $z = z_1$.

And now there is a gas stream above in which you know this liquid is diffusing its evaporating and then diffusing into that gas stream which is located above. So; obviously, this location $z = z_1$ decreases, but what we take for simplicity? We take a fixed location.

And then top of the column we are taking as $z = z_2$. The concentration at this location $z = z_1$ we are writing x_{A1} and then concentration at $z = z_2$ x_{A2} . This x_{A2} is the fixed

concentration we are maintaining in general in order to have a kind of simple measurements; easy measurements.

Now, in this between these two locations; now between these two locations if you wanted to find out the concentration profile of component A and or component B how to do that is what the problem. So, that is first concentration profile you have to find out and then what is the flux; what is N_{Az} at $z = z_1$ that also we have to find out. That is a problem.

So, let us say first we have to develop an expression for the flux. So, within this column in diffuse a column in which the diffusion is taking place or only the diffusion region not inside the liquid within the diffusion region. So, this is the empty region whatever is there from $z_1 = z_2$ in that region only diffusion is taking place between A and B; A is diffusing into B, B is non-diffusing stagnant gas film ok.

So now, so within this region we take a film of thickness Δz and then we write a balance. So, flux at $z = z$ some location z is N_{Az} and then flux going out at location $z = z + \Delta z$ is N_A at $z + \Delta z$. So, this concentration x_A versus z if you represent. So, then we can have a line curve something like this. The same thing x_B versus z also if you represent you may have something curves like this. So, what are these expressions; those things we are going to find out now right.

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- Consider a system in which liquid A is evaporating into stagnant gas "B"
- Assume that constant interface position is maintained at $z = z_1$
- At liquid – gas interface, the gas phase concentration of A (expressed as mole fraction) is x_{A1}
- This x_{A1} is taken to be the gas phase concentration of A corresponds to the equilibrium with the liquid at the interface
- i.e., x_{A1} is vapor pressure of A divided by total pressure (P_A^{vap} / P) provided that A & B form ideal gas mixture and that solubility of gas B in liquid is negligible
- A stream of gas mixture A-B of concentration x_{A1} flows steadily past the top of the tube, to maintain the mole fraction of A at $z = z_2$ as x_{A2}
- Entire system is kept at constant T and P; and gases A and B are assumed to be ideal

So, consider a system in which liquid A is evaporating into stagnant gas B. Assume that constant interface position is maintained at $z = z_1$. At liquid gas interface the gas phase concentration of A expressed as mole fraction is x_{A1} , this x_{A1} is taken to be the gas phase concentration of A corresponds to equilibrium with the liquid at the interface that is x_{A1} is the vapor pressure of A divided by the total pressure provided that A and B form ideal gas mixture and that solubility of gas B in liquid is negligible. So that means, N_{Bz} is 0.

A stream of gas mixture A-B of concentration x_{A2} flow steadily past the top of the tube to maintain the mole fraction of A at $z = z_2$ as x_{A2} . Now entire system is kept at constant temperature and pressure and gases A and B are assumed to be ideal, right.

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- There will be net flow of gas upward from gas – liquid interface; and gas velocity at cylinder wall will be smaller than that in the center of tube
- However, to simplify this problem, we neglect variations in velocity across tube cross section; i.e., v_z is constant
- When this evaporating system attains steady state, there is a net motion of A away from interface and the species B is stationary, i.e., $N_{Bz} = 0$
- Thus combined flux in molar units should be used and simplified to get required concentration profile: $N_{Az} = -cD_{AB} (dx_A/dz) + x_A(N_{Az} + N_{Bz})$
- $\Rightarrow N_{Az} = \frac{-cD_{AB} dx_A}{1-x_A} dz$ * $2 \text{ v } 2$

So, there will be net flow of gas upward from gas liquid interface and gas velocity at cylinder wall will be smaller than that in the center of the tube, because flow through pipes or tubes what we have seen you know there is a velocity profile developed across the cross section even if the L/D is very large.

We do not have a constant velocity in general. So, we have the maximum velocity at the center and then 0 velocity at the wall. That is what we have already seen in the momentum transfer part of the course, but what we are doing? We are taking it for simplicity we are taking it as a constant velocity, right. And then that constant velocity we are calling v_z , right.

So now, when this evaporating systems attains steady state there is net motion of A away from interface and the species B is stationary. So, $N_{Bz} = 0$. Then this combined mass flux units this equation we have already taken. Here in this case what you do? N_{Bz} you take 0 and then you take this N_A ; $x_A N_{Az}$ to the left hand side when you take N_{Az} common you have N_{Az} multiplied by $1 - x_A$.

So, in the (Refer Time: 54:15) in the subsequent step that whatever $1 - x_A$ also if you bring it to the right hand side then we have $N_{Az} = -\frac{cD_{AB}}{1-x_A} \frac{dx_A}{dz}$. Now this equation actually what we need to find out? We have to find out x_A versus z . If you solve this equation you can do it, you can get it, but we can solve this equation only we have this N_{Az} information otherwise we cannot do it, right.

(Refer Slide Time: 54:49)

• Now steady state mass balance for Δz thickness of column

$$SN_{Az}|_z - SN_{Az}|_{z+\Delta z} = 0$$

• where S is cross-section area of column; now divide by $S\Delta z$ and apply limit $\Delta z \rightarrow 0$,

$$\Rightarrow \frac{-dN_{Az}}{dz} = 0 \Rightarrow \frac{d}{dz} \left(\frac{cD_{AB}}{1-x_A} \frac{dx_A}{dz} \right) = 0$$

• For ideal gas mixture, EoS is $P = cRT$, i.e., at constant T & $P \rightarrow c$ is constant and for gases D_{AB} is nearly independent of composition

• $\Rightarrow \frac{d}{dz} \left(\frac{1}{1-x_A} \frac{dx_A}{dz} \right) = 0 \Rightarrow \frac{1}{1-x_A} \frac{dx_A}{dz} = C_1 \Rightarrow -\ln(1-x_A) = C_1 z + C_2$

Eq 9

So, that we can get by the balance. And now steady state mass balance for Δz thickness of column we do SN_{Az} at $z - SN_{Az}$ at $z + \Delta z = 0$, S is nothing but the area through which; area of the column or the very area of the thickness of the column through which diffusion is taking place. And then luckily and then in our system the area is not changing across the column height ok.

So, we can take S constant value. So, S is the cross section area of column. Now divide this equation by $S \Delta z$ and then apply the limiting condition Δz tends to 0; then what you get? $-\frac{dN_{Az}}{dz} = 0$ and then N_{Az} we already got $-\frac{cD_{AB}}{1-x_A} \frac{dx_A}{dz}$, right. Temperature pressures are

maintained constant and then it is mentioned that the system is obeying the ideal gas mixture.

So, then what we can take? We can take this concentration c as constant as well as D_{AB} can also be taken as a constant. Then we have $\frac{d}{dz} \frac{1}{1-x_A} \frac{dx_A}{dz} = 0$. First time integration you do $\frac{1}{1-x_A} \frac{dx_A}{dz} = C_1$ again integration if you do $\frac{\ln(1-x_A)}{-1}$. So, that is $-\ln(1-x_A) = C_1 z + C_2$ you get. Now, this C_1 C_2 if you know, then you can know the what is this x_A profile as function of z . So, we need two boundary conditions.

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The image shows a whiteboard with handwritten mathematical derivations for the concentration profile x_A as a function of position z . The derivations are as follows:

- Boundary condition 1: $z = z_1 \Rightarrow x_A = x_{A1} \Rightarrow -\ln(1-x_{A1}) = C_1 z_1 + C_2$
- Boundary condition 2: $z = z_2 \Rightarrow x_A = x_{A2} \Rightarrow -\ln(1-x_{A2}) = C_1 z_2 + C_2$
- Solving for C_1 : $C_1 = \frac{1}{(z_1 - z_2)} \ln \left[\frac{1-x_{A2}}{1-x_{A1}} \right]$
- Solving for C_2 : $C_2 = -\ln(1-x_{A1}) - \frac{z_1}{(z_1 - z_2)} \ln \left[\frac{1-x_{A2}}{1-x_{A1}} \right]$
- Substituting constants into the general equation: $-\ln(1-x_A) = C_1 z + C_2$
- Final expression for x_A : $x_A = 1 - \exp \left\{ \frac{z}{(z_1 - z_2)} \ln \left[\frac{1-x_{A2}}{1-x_{A1}} \right] - \ln(1-x_{A1}) - \frac{z_1}{(z_1 - z_2)} \ln \left[\frac{1-x_{A2}}{1-x_{A1}} \right] \right\}$

So, we already have two boundary condition at $z = z_1$ $x_A = x_{A1}$. So, this equation you get now $z = z_2$ $x_A = x_{A2}$. So, then this equation you get. Now if you subtract this equation second equation from the first equation you get $C_1 = \frac{1}{(z_1 - z_2)} \ln \left[\frac{1-x_{A2}}{1-x_{A1}} \right]$.

So, this if you substitute in the first equation here, you get $C_2 = -\ln(1-x_{A1}) - \frac{z_1}{(z_1 - z_2)} \ln \left[\frac{1-x_{A2}}{1-x_{A1}} \right]$. So now, we have C_1 C_2 . So now, this we can substitute in this equation to get the concentration profile like this. For simplicity what we do? Now we take this term to the left hand side and then we combine these two \ln terms in the right hand side.

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$\Rightarrow -\ln \left[\frac{1-x_A}{1-x_{A1}} \right] = \frac{z-z_1}{(z_1-z_2)} \ln \left[\frac{1-x_{A2}}{1-x_{A1}} \right] \Rightarrow \left(\frac{1-x_A}{1-x_{A1}} \right) = \left(\frac{1-x_{A2}}{1-x_{A1}} \right)^{\frac{(z-z_1)}{(z_1-z_2)}}$

- Profile for gas B can be obtained by using $x_B = 1 - x_A$ in above Eq.
- Average values of concentration and fluxes in the region between z_1 and z_2

$\Rightarrow \frac{x_{B,avg}}{x_{B1}} = \frac{\int_{z_1}^{z_2} \left(\frac{x_B}{x_{B1}} \right) dz}{\int_{z_1}^{z_2} dz} = \frac{\int_0^1 \left(\frac{x_{B2}}{x_{B1}} \right)^\xi d\xi}{\int_0^1 d\xi}$

where $\xi = \frac{z-z_1}{z_2-z_1} \Rightarrow d\xi = \frac{dz}{(z_2-z_1)}$

So, that we have $-\ln \left[\frac{1-x_A}{1-x_{A1}} \right] = \frac{z-z_1}{(z_1-z_2)} \ln \left[\frac{1-x_{A2}}{1-x_{A1}} \right]$. So, the same thing we can write like this equation. So, this is the concentration profile that we suppose to obtain between locations z_1 and z_2 .

Profile for gas B can be obtained by simply writing $1 - x_A = x_B$, $1 - x_{A1} = x_{B1}$, $1 - x_{A2} = x_{B2}$. Like that we can write in this equation we can get concentration profile in terms of B. So, average values of concentration and fluxes in the region between z_1 and z_2 if you wanted to find out we do in terms of B. So now, this equation if you write for B what you can write? $\frac{x_B}{x_{B1}} = \left(\frac{x_{B2}}{x_{B1}} \right)^{\frac{z-z_1}{z_2-z_1}}$ this is what we have right.

So, average of this one if you wanted to have, $\frac{x_{B,avg}}{x_{B1}} = \frac{\int_{z_1}^{z_2} \left(\frac{x_B}{x_{B1}} \right) dz}{\int_{z_1}^{z_2} dz}$. And then $\left(\frac{x_B}{x_{B1}} \right)$ is nothing but $\frac{\int_0^1 \left(\frac{x_{B2}}{x_{B1}} \right)^\xi d\xi}{\int_0^1 d\xi}$ because now we are writing $\frac{z-z_1}{z_2-z_1}$ as ξ ok.

So, that we have $d\xi = \frac{dz}{z_2-z_1}$. So, this $z_2 - z_1$ would be coming both in the numerator and denominator of this expression. So, that they can be cancelled out. So, only $d\xi$ is remaining here.

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$$\begin{aligned} \bullet \Rightarrow \frac{x_{Bavg}}{x_{B1}} &= \frac{\int_{z_1}^{z_2} \left(\frac{x_B}{x_{B1}}\right) dz}{\int_{z_1}^{z_2} dz} = \frac{\int_0^1 \left(\frac{x_{B2}}{x_{B1}}\right)^\xi d\xi}{\int_0^1 d\xi} = \frac{\left[\frac{\left(\frac{x_{B2}}{x_{B1}}\right)^\xi}{\ln\left(\frac{x_{B2}}{x_{B1}}\right)}\right]_0^1}{1} = \frac{\left(\frac{x_{B2}}{x_{B1}}\right)^1 - \left(\frac{x_{B2}}{x_{B1}}\right)^0}{\ln\left(\frac{x_{B2}}{x_{B1}}\right)} \\ \bullet \Rightarrow x_{Bavg} &= \frac{x_{B2} - x_{B1}}{\ln\left(\frac{x_{B2}}{x_{B1}}\right)} = (x_B)_{\ln} \text{ where } \xi = \frac{z - z_1}{z_2 - z_1} \\ \bullet &\text{ It is to nothing but logarithmic mean } (x_B)_{\ln} \text{ of } x_{B1} \text{ and } x_{B2} \end{aligned}$$

So, this you integrate then. So, this equation up to this part is written again. So, this part if

you integrate you get $\left[\frac{\left(\frac{x_{B2}}{x_{B1}}\right)^\xi}{\ln\left(\frac{x_{B2}}{x_{B1}}\right)} \right]_0^1$ and then whole divided by ξ is there, but that ξ limiting

conditions 0 to 1. So, $1 - 0$; 1 is there. So, that we are not writing only numerator part we are writing. So, this is one; the limits when you substitute when $\xi = 1$. So, these $\frac{x_{B2}}{x_{B1}}$ would be there when $\xi = 0$. So, something power 0 is 1. So, -1 and then same is applied here also ok.

So, that is x_{Bavg} is nothing but $\frac{x_{B2} - x_{B1}}{x_{B1}}$, but there is a x_{B1} in the numerator in the left hand side. So, that we bring it to the right hand side. So, that whatever divided by x_{B1} is there that one and then this multiplied by x_{B1} is cancelled out, so that we have only $\frac{x_{B2} - x_{B1}}{\ln\left(\frac{x_{B2}}{x_{B1}}\right)}$. So, that is $x_B \ln$. And then ξ is nothing but this one. Logarithmic mean of x_{B1} and x_{B2} .

(Refer Slide Time: 60:50)

- In order to obtain rate of mass transfer, we need derivative of concentration
- $\left(\frac{1-x_A}{1-x_{A1}}\right) = \left(\frac{1-x_{A2}}{1-x_{A1}}\right)^{\left(\frac{z-z_1}{z_2-z_1}\right)} \Rightarrow \ln\left(\frac{x_B}{x_{B1}}\right) = \left(\frac{z-z_1}{z_2-z_1}\right) \ln\left(\frac{x_{B2}}{x_{B1}}\right)$
- $\Rightarrow \left(\frac{x_{B1}}{x_B}\right) \left(\frac{1}{x_{B1}}\right) \frac{dx_B}{dz} = \left(\frac{1}{z_2-z_1}\right) \ln\left(\frac{x_{B2}}{x_{B1}}\right) \Rightarrow \frac{dx_B}{dz} = \left(\frac{x_B}{z_2-z_1}\right) \ln\left(\frac{x_{B2}}{x_{B1}}\right)$
- $\Rightarrow \frac{dx_B}{dz} \Big|_{z=z_1} = \left(\frac{x_{B1}}{z_2-z_1}\right) \ln\left(\frac{x_{B2}}{x_{B1}}\right)$

So, in order to obtain the rate of mass transfer, we need to have the derivatives of the concentration profile. So, then what we get? We get $\frac{dx_B}{dz}$. So, that would be easier. So, x_A profile this is what we have, the same thing in x_B if you write this is what we have. In \ln we are writing because we wanted to do the differentiation now.

So, now if you get $\frac{dx_B}{dz}$ if you wanted to do both sides you have to differentiate with respect to the z . So, what we have left hand side? $\left(\frac{1}{x_{B1}}\right) \frac{dx_B}{dz}$. So, $\left(\frac{1}{x_{B1}}\right) \frac{x_B}{x_{B1}}$ we are writing $\frac{x_{B1}}{x_B}$ and then multiplied by $\left(\frac{1}{x_{B1}}\right) \frac{dx_B}{dz}$ this is what we have.

So, these x_{B1} these x_{B1} is cancelled out. The right hand side this $\ln\left(\frac{x_{B2}}{x_{B1}}\right)$ are constant and also $\frac{1}{z_2-z_1}$ is also constant. And then this whatever $z - z_1$ is there, so that is nothing but you know differentiation we get, differentiation of $z - z_1$ is nothing but 1 ok. So that means, $\frac{dx_B}{dz} = \frac{x_B}{z_2-z_1} \ln\left(\frac{x_{B2}}{x_{B1}}\right)$ right.

So, $\frac{dx_B}{dz}$ we wanted to know the flux at $z = z_1$ is nothing then; that means, in this equation wherever this x_B is there that x_B should be replaced by the x_{B1} , because at $z = z_1$ $x_B = x_{B1}$ $x_A = x_{A1}$.

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The image shows a handwritten derivation on a piece of paper. It starts with a bullet point: "Now rate of mass transfer at the interface (i.e., rate of evaporation at $z = z_1$)". This is followed by an equation: $\Rightarrow N_{Az}|_{z=z_1} = -\frac{cD_{AB}}{1-x_{A1}} \frac{dx_A}{dz} \Big|_{z=z_1} = \frac{cD_{AB}}{x_{B1}} \frac{dx_B}{dz} \Big|_{z=z_1}$. A red note to the right says $x_A + x_B = 1$ and $\frac{dx_A}{dz} + \frac{dx_B}{dz} = 0$. The next step is $\Rightarrow N_{Az}|_{z=z_1} = \frac{cD_{AB}}{z_2-z_1} \ln \left(\frac{x_{B2}}{x_{B1}} \right)$. Then, a bullet point says "Now using $x_{B,avg}$ in above equation, we get". The final equation is $\Rightarrow N_{Az}|_{z=z_1} = \frac{cD_{AB}}{(z_2-z_1)(x_B)_{ln}} (x_{B2} - x_{B1}) = \frac{cD_{AB}}{(z_2-z_1)(x_B)_{ln}} (x_{A1} - x_{A2})$. Red arrows point from the x_{B2} and x_{B1} terms in the first part of the final equation to the x_{A1} and x_{A2} terms in the second part.

So, now rate of mass transfer at the interface that is rate of evaporation at $z = z_1$ if you wanted to find out that is N_{Az} or N_{Az} at $z = z_1 = -\frac{cD_{AB}}{1-x_A}$, but now we are evaluating it at $z = z_1$. So, this x_A should be replaced by the x_{A1} multiplied by $\frac{dx_A}{dz}$. And then this $-\frac{dx_A}{dz}$ is nothing but $+\frac{dx_B}{dz}$ because it is a binary system only where $x_A + x_B = 1$.

So that means, $\frac{dx_A}{dz} + \frac{dx_B}{dz} = 0$ or dx or $-\frac{dx_A}{dz} = +\frac{dx_B}{dz}$ at $z = z_1$ we are doing. So, and then just now we obtain this $\frac{dx_B}{dz}$ is nothing but $x_{B1} \ln \left(\frac{x_{B2}}{x_{B1}} \right)$. So, that x_{B1} from the $\frac{dx_B}{dz}$ and then here whatever the $\frac{1}{x_{B1}}$ is there cancelled out. So, then we have only $\frac{cD_{AB}}{(z_2-z_1)} \ln \left(\frac{x_{B2}}{x_{B1}} \right)$ this is what we have.

So, now using $x_{B,avg}$ we can use in the above equation because we already know what is $(x_B)_{ln}$. So, in place of $\ln \left(\frac{x_{B2}}{x_{B1}} \right)$ we can write it as; we can write it we can write you know $\left(\frac{x_{B2}-x_{B1}}{(x_B)_{ln}} \right)$. So, that is what we have written here. Now this $x_{B2} - x_{B1}$ what we can write $x_{A1} - x_{A2}$. Why we have written in terms of $x_{A1} - x_{A2}$ in the final form? Because the concentrations x_{A1} and x_{A2} are given in the problem.

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Example problem

- Diffusivity of gas pair O_2-CCl_4 is being determined by observing the steady state evaporation of CCl_4 into a tube containing oxygen
- Distance between CCl_4 liquid level and top of tube is $z_2-z_1 = 17.1$ cm
- Total pressure on system is 755 mmHg, and temperature is $0^\circ C$
- Vapor pressure of CCl_4 at that temperature is 33 mmHg
- Cross sectional area of diffusion tube is 0.82 cm^2
- It is found that 0.0208 cm^3 of CCl_4 evaporate in a 10 hour period after steady state has achieved.
- What is the diffusivity of the gas pair O_2-CCl_4 ?

Now, we wind up today's class with a simple example problem using the previous expression that we have taken diffusion through non-stagnant gas film. So, diffusivity of gas pair O_2-CCl_4 is being determined by observing the steady state evaporation of CCl_4 into a tube containing oxygen. Distance between liquid level and top of the tube is 17.1 centimeter that is $(z_2 - z_1)$ is given.

Total pressure on system is given, temperature is given vapor, pressure of CCl_4 is given. Cross section area of diffusion tube is given that is 0.82 centimeter square. It is found that 0.0208 centimeter cube of CCl_4 is evaporating. So that means, from here we can get what is N_{Az} at $z = z_1$. We have to do some simplifications; in 10 hours period time after steady state has achieved. What is the diffusivity of the gas pair O_2-CCl_4 ? That is the problem.

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Let A as CCl_4 and B as O_2
Molar flux of A is

$$N_A = \frac{(0.0208 \text{ cm}^3) \times 1.59 \frac{\text{g}}{\text{cc}}}{(154 \frac{\text{g}}{\text{gmol}} \times 0.82 \text{ cm}^2 \times 3.6 \times 10^4 \text{ s})} = 7.26 \times 10^{-9} \text{ gmol/cm}^2 \text{ s}$$

We have $D_{AB} = \frac{(N_A|_{z=z_1})(z_2 - z_1)}{\ln(x_{B2}/x_{B1})} \Rightarrow D_{AB} = \frac{(N_A|_{z=z_1})(z_2 - z_1)RT}{P \ln(P_{B2}/P_{B1})}$

$$D_{AB} = \frac{7.26 \times 10^{-9} \times 17.1 \times 82.06 \times 273}{(755/760) \times 2.303 \log(755/722)} = 0.0636 \text{ cm}^2/\text{s}$$

- This is a crude method of measuring diffusivity.
- It suffers from defects such as cooling of liquid by evaporation, concentration of non-volatile impurities at interface, climbing of liquid up the walls of tube and curvature of meniscus, etc.

So, let us take a notation A for CCl_4 and notation B for O_2 . Then molar flux of A is given that is a N_A is given like you know 0.0208 centimeter cube per 10 hours. 10 hours is 3.6×10^4 seconds and then flux we need in moles per meter square or moles gram moles for centimeter square second.

So, then now here this centimeter cube in centimeter cube the flux is given per flux is given in centimeter cube per time unit per 10 hour. So, that we are converting into the required gram mole per centimeter; gram mole per centimeter square second. So now, then this one we multiply by the density gram per cc that is 1.59 for CCl_4 , right. That we can get.

And then dividing by then these quantities numerator what we get? We will be having in gram units. So, that we divide by molecular weight of CCl_4 that is 154. And then this you get in gram mole per second right and then the area through which diffusion is taking place that is also given. So, if you divide that quantity by the area you get gram mole per centimeter square second. So, that is the flux is given indirectly it is given. So, we convert it in required units.

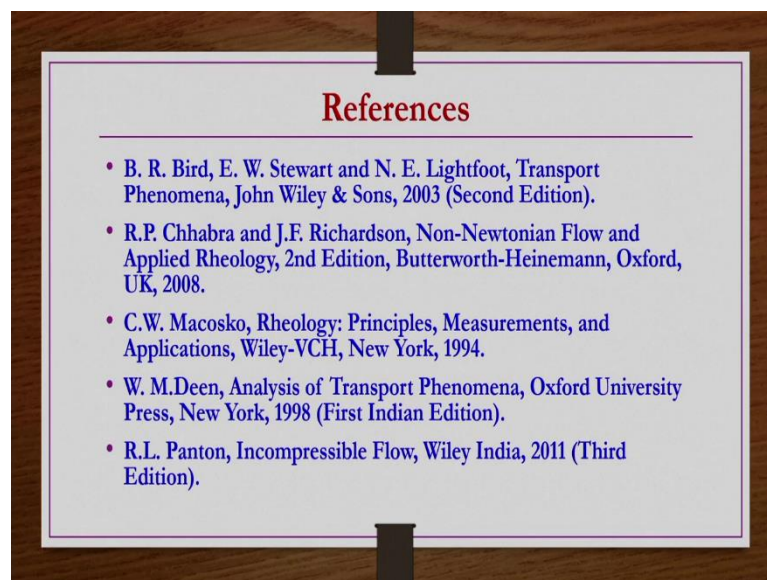
And then D_{AB} from the equation that we have derived is nothing but N_A at $z = z_1 \frac{(z_2 - z_1)}{\ln\left(\frac{x_{B2}}{x_{B1}}\right)}$

this is what we got right. N_A at $z = z_1$ is nothing but this quantity, $(z_2 - z_1)$ is given 17.1 centimeters something like that c we can write as $\frac{P}{RT} \ln$ and then the ideal behaviour (Refer Time: 67:49). So, then x_{B2} we can write in terms of P_{B2} and then P_{B1} . So, like this.

So, $\frac{x_{B2}}{x_{B1}}$ is nothing but $\frac{P_{B2}}{P_{B1}}$. So, 7.26 into 10^{-9} is N_{Az} as $z = z_1$, $z_2 - z_1$ is 17.1 r is 82.6 t is 0 degrees centigrade 273 kelvin, p is nothing but 755 mm Hg. So, 755 by 760 multiplied by 2.303 log I am taking. And then 755 divided by 722, so that is coming out to be 0.0636 centimeter square per second.

So, this tubes whatever the geometry that we have taken in general that is also used to measure the diffusivity in a very crude way; that is a very crude way of doing. Of course, it is a crude way because it is having several you know drawbacks defects. And such as cooling of liquid by evaporation is not considered, concentration of non-volatile impurities at the interface is not considered, climbing of liquid up the walls of tube and curvature of meniscus etcetera have not been considered.

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References for this lecture are provided here.

Thank you.