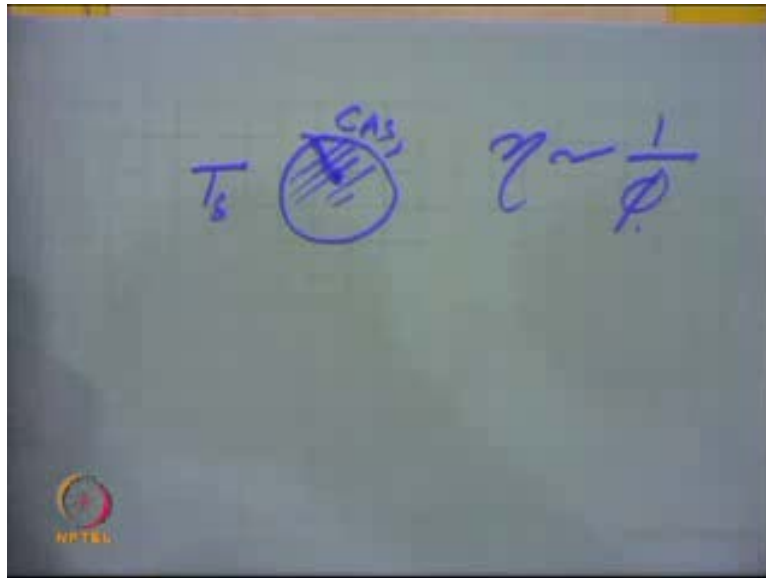


Heterogeneous Catalysis and Catalytic Processes
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Lecture – 30

Good morning, in the last lecture I was talking about effectiveness factor in a pellet; spherical pellet case, we were discussing. And, I told you the definition of effectiveness factor, which is defined as actual overall rate of reaction, divide by rate that would result, if entire interior surface; were exposed to external surface of the pellet conditions.

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So, that is the first basic thing which I discussed in a catalyst; that there is a diffusion and because of diffusion, there is concentration gradient. So, the average rate is based on average concentration from this CAS value to some final value; which will change down the length and, we calculated the effectiveness factor. So, that is some average rate; which is based on the whole surface and where there is a gradient. And, the maximum rate when it is non isothermal case; then, temperature is uniform throughout the pellet. And, that time your effectiveness factor η , we discussed by the equation for a Spherical pellet or in general by this expression.

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Internal Effectiveness Factor

$\eta = \frac{\text{Actual overall rate of reaction}}{\text{Rate of reaction that would result if entire interior surface were exposed to the external pellet surface conditions } C_{As}, T_s}$

$$\eta = \frac{-r_A}{-r_{As}} = \frac{-\dot{r}_A}{-\dot{r}_{As}} = \frac{-\dot{r}_A}{-\dot{r}_{As}}$$
$$\eta = \frac{3}{\phi_1^2} (\phi_1 \coth \phi_1 - 1)$$


So, eta is proportional to something like, one upon phi; when you have A Strong diffusion control and, we just discuss the consequences of diffusional resistance. Sometimes, when we define this CAS and there is a non isothermal; that is a temperature profile T_s and T then, because of the exothermic reaction; there may be a generation of heat. Then, it will higher temperature at the center, compared to temperature at the surface for exothermic reaction. So, one can find out the maximum temperature difference from wall to the center. So, when the reaction is exothermic this will be maximum T_s temperature is maximum at the center of the pellet and lower at the outer surface; when it is endothermic then reverse case will be there.

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$$\frac{d}{dr} \left[\frac{\lambda}{D_e(-\Delta H_r)} + C_A \right] + C_1 = 0$$

$$\Rightarrow \left\{ \begin{aligned} C_A + \frac{\lambda T}{D_e(-\Delta H_r)} &= \frac{C_1}{r} + C_2 \\ r=R, C_A &= C_{A_s}, T=T_s \end{aligned} \right. \Rightarrow \begin{aligned} C_1 &= 0 \\ \lambda &= 0 \\ C_2 &= \text{finite} \\ \frac{dT}{dr} &= 0 \end{aligned}$$

$$C_A + \frac{\lambda T}{D_e(-\Delta H_r)} = C_{A_s} + \frac{\lambda T_s}{D_e(-\Delta H_r)}$$

$$T = \frac{D_e(-\Delta H_r)(C_{A_s} - C_A)}{\lambda} + T_s$$

$$T = T_{max}, \text{ at } C_A = 0$$

$$T_{max} = T_s + \frac{(-\Delta H_r) D_e C_{A_s}}{\lambda}$$

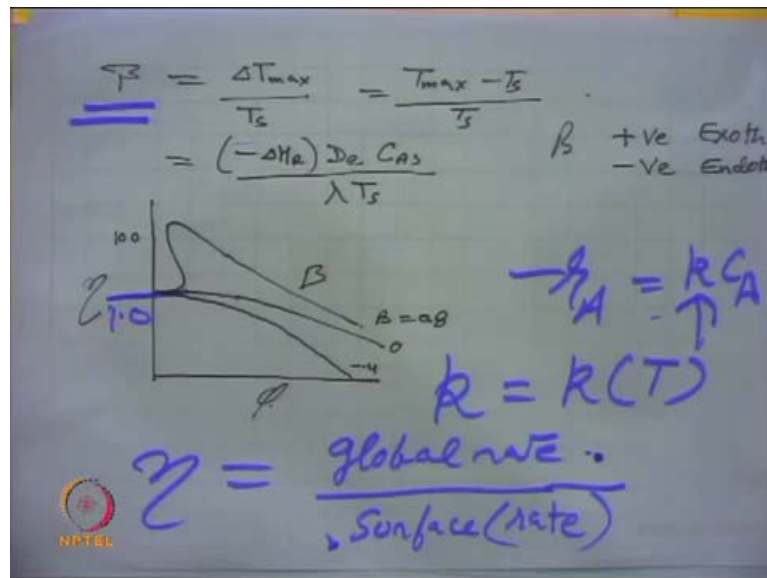
So, we discussed a kind of heat transfer equation or heat balance equation based on that q at r times $4 \pi R^2$ plus q at $r + \Delta r$; so, this equation has been discussed last time. So, just to recall that, we discussed that based on the heat balance; so, heat in for a spherical shell $4 \pi r^2 \lambda \frac{dT}{dr}$ and same thing evaluated at $r + \Delta r$ and minus heat disappeared because of chemical reaction; so, minus ΔH_r . So, ΔH_r minus means, positive for the exothermic reaction; times whatever the volume of the shell; so, $4 \pi r^2 \Delta r$ and then, we solve this differential equation by writing the boundary condition, which was something like this. So, that equation we solved for temperature and concentration together; so, from the mass balance equation the minus r value was substituted; and finally, we had the equation in the form of temperature and concentration.

So, C_A profile is already known; so, once you have that expression, I am not going in detail of this; because you have to do; that just look at the solution of this equation. I have already discussed this; the boundary conditions are here r is equal to R ; C_A is C_{A_s} ; that is the concentration at the surface. And, concentration profile is now already known $\cos C_A$ by $C_{A_s} \cos \frac{r}{R}$ divide by $\cos \frac{R}{R}$ what we discussed in earlier lectures. Temperature, boundary condition at T is equal to T_s ; that is T is equal to T_s at r is equal to R . And, at the center; there is the maximum temperature so, $\frac{dT}{dr}$ is 0; when the exothermic reaction or there is a kind of symmetry which you must have read in transfer phenomena.

So, by just by using these two so, one can write the expression in this form that is C 1 and C 2 can be written in form of T S and C S, C A S concentration. So, here, if you look at this temperature profile equation is related to your concentration variation because of the chemical reaction heat is generating; so, there will be a kind of concentration difference. So, C S is the concentration at the surface and C A will be the concentration profile and delta H R is the heat of reaction; for exothermic it is positive and negative for endothermic. Lambda is the thermal conductivity of the material or catalyst pellet, D E is the effective diffusion coefficient; which we have already discussed and T S is the surface temperature.

So, the parameter which can be defined here, because you know at the center that T A will be T max, when the concentration is minimum; that is, whatever the moles of A which leads to the center they reacted completely. So, all the moles reacted means, the temperature will be maximum. So, one can very easily solve this equation or find out from that T max is equal to T S plus delta minus of delta H R time D E C S divide by thermal conductivity lambda, it is simple.

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So, from these two, you can very easily write the expression for A parameter which is known as beta. It is a parameter, which talks about the exothermicity or the heat which is generated in the catalyst pellet and that is what; I told you this becomes important, when you have a highly exothermic reaction and you are doing a reaction something like

partial oxidation of methane. So, partial oxidation reactions are complete oxidation reaction; they are highly exothermic; so, hot spot formation may happen in the catalyst pellet. So, this is the maximum temperature; that is the parameter which is defined based on the maximum temperature difference divide by the surface temperature that is known as beta.

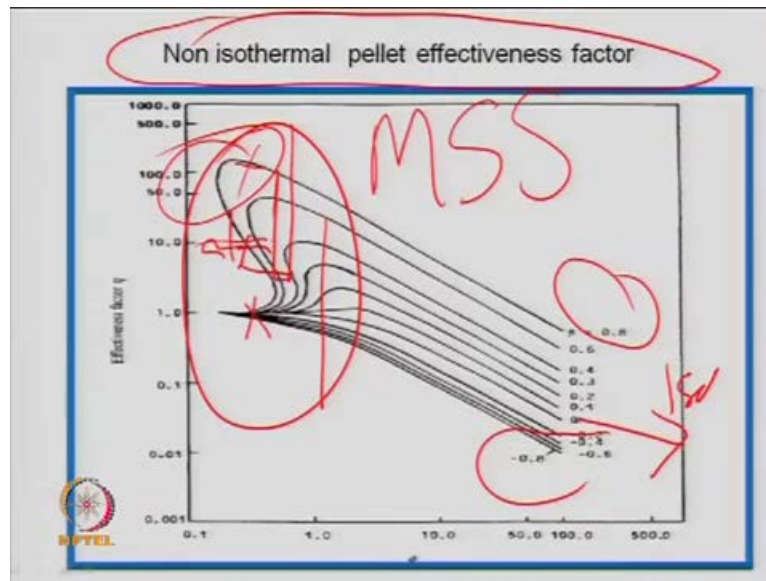
And, beta is a function and that effectiveness factor is a function of beta; basically, parameter on which your effectiveness factor will change because effectiveness factor is defined as global rate divide by intrinsic rate. So, when you write a rate which is something like $-r_A$ is equal to $k C_A$; so, rate is changing because of 2 terms; because of the temperature dependency this k is a function of temperature.

So, because of temperature dependency and it may happen; that this temperature raise highly exothermic reaction; so, temperature raise may be very high. So, in that your rate of reaction; in the center of the pellet will be very high; so, your effectiveness factor which is based on your global rate or actual rate what you say divide by the surface rate that is rate of reaction calculated at the surface.

So, here temperature is T_s ; here temperature may be higher at the center because of exothermic reaction. So, what will happen η can be greater than one; so, this is what for non isothermal case and exothermic reaction the effectiveness factor can be greater than one. And, this value which you have gotten from that is this beta parameter that can be determined from the heat of reaction and the conversion value.

So, 50 percent conversion, 60 percent conversion or 100 percent conversion; one can calculate the temperature or ΔH_R and then, this equation is resembling to this one; that is $-\Delta H_R \times D_e \times C_A \times S$ divide by $\lambda \times T_s$. Every term is known here, surface temperature is known, concentration at the surface is known, effectiveness diffusivity known and heat of reaction is known; so, this value can be determined. So, you can see here, that effective factor can go up to a value of 100 also, as high as 100; when it is isothermal case, it will always be less than 1.

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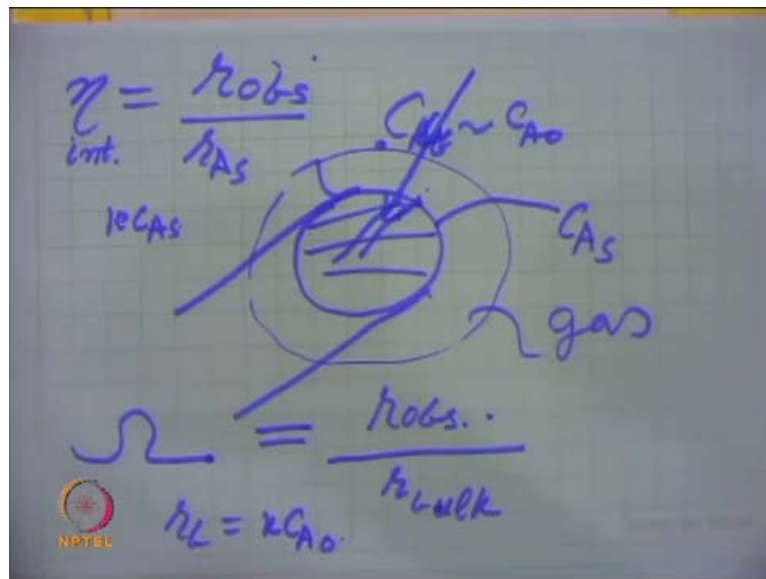
So, this is 1.0; so, what is the observation from this and the non isothermal case the pellet effectiveness factor can go as high as 100 and it will depend on ϕ as usual. Because you know your ϕ , Thiele modulus will depend on the several parameters like size of the pellet, will values of diffusion coefficient, values of rate constant. So, all these will change; so, depending upon the value of ϕ ; when the ϕ is large as usual that is when you are talking a strong diffusion resistance then, η is low, the strong diffusionation. But this is zone, where you see a kind of multiple steady states here, up to this section here. If you look at here, in all cases you have a kind of multiple steady state that is what is meaning of multiple; if you look at your Thiele modulus, less than 1. For less than 1, if I look at this value; here it is 1 point another point is here, another point is here, for the value of β 0.8.

So, β can have value depending up on this ΔT_{max} up on T_s ; it is positive for the exothermic reaction and negative for the endothermic reaction. So, these data are for endothermic reaction; and β is 0 is isothermal case. So, for isothermal case, this it effectiveness factor graph will always be less than 1; for endothermic reaction also, this will go on a lower side; that it will decrease. But for exothermic reaction, you have the problem of runaway conditions; so, this is kind of multiple steady state. What is known as M S S? Because this is a kind of transient solution unsteady state solution here, because at one value it shows that effectiveness factor is 1 and same value it shows 10

and then again, it is so, there is a Shift. So, it means, if you move to this side; eta is changing like this again, and if you go to this side again it changes.

So, this is a significant change in the value of effectiveness factor and that is known as a kind of multiple steady states, which is not desired instability; it is a kind of instability. So, one need to avoid these situations in the reactor or catalyst design; so, one thing is clear for exothermic reaction. The effectiveness factor can be greater than one; but for endothermic reaction and isothermal the effectiveness factor will always be less than one. Another term, which may be used or many times you must have seen is known as the kind of situation; when we defined the equation based on bulk concentration. When you do the homogenous kinetics; so, that time you just look at the concentration in the bulk. And, you can look at a kind of starrer; where the mass transfer is the important factor and that plays a role. But even, when you have a homogenous catalytic reaction also.

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So, here if you look at, the in the catalyst you have a pellet; which is surrounded by a film and $C_{A S}$ which we have defined is here, here it may be $C_{A 0}$ or $C_{A B}$ whatever you say. Sometime, you call it $C_{A 0}$ or bulk concentration $C_{A B}$ the notation may be either way can be used, either notation. So, sometimes, this effectiveness factor which I am talking is based on this pellet condition; this is your catalyst pellet which is surrounded by a film of gas, reactant gas. So, because when you know that there is a

mass transfer; so, if you are not controlled mass transfer, there will film that is solid is covered by a film of gas and that may have its resistance. And, when there is a resistance, there will be kind of concentration difference; and, that is the flux mass flux which you calculate that is nothing but K_G times $C_{A,G}$ minus $C_{A,S}$ or $C_{A,B}$ minus $C_{A,S}$.

Depending upon the mass transfer coefficient, you have to check that. And, I told you mass transfer coefficient is related to the velocity, gas velocity superficial gas velocity. So, you can minimize that, and that time $C_{A,B}$ becomes $C_{A,S}$; what we have discussed for the internal effectiveness factor. So, internal effectiveness factor is based on, only this surface and the inter near of the catalyst; so, that is the η you have defined r_{obs} divide by r_A dash; measured at the surface. And, that I say now η internal effectiveness factor. Internal effectiveness factor that is only related to the diffusion in A pores catalyst pellet; sometimes it is required that, it may be that your $C_{A,B}$ and $C_{A,S}$ are not equal. So, there is a kind of difference then, you need to define the rate based on the bulk condition, because you know only the inlet conditions.

So, rate if I define based on bulk condition; I will call it overall effectiveness factor. So, overall effectiveness factor ω defined by again the same definition; that is observed rate; because this is not going to change. Observed rate is what you have given the feet and at the exit, you measured the conversion or concentration; and then, you calculate the rate. So, observed rate this and this both are same. Here, I have already this value I am saying based on surface condition that is based on external surface; so, one can write it something like $k C_{A,S}$. If I write based on volumetric rate constant; so, k times $C_{A,S}$ but if I define this is your r measured at the bulk; that is the outer surface.

There you feel that, the products are coming back after diffusion; that what the step I discuss in the catalytic reaction that is first is the mass transform from external gas surface to the external surface of the catalyst that step. So, this is what the ω which is based on bulk condition; that is rate which is based on bulk gas condition or external condition. So, that will be, if you look at here it can be just like based on your k times $C_{A,0}$; no change in rate constant no change the only change is the $C_{A,0}$ and $C_{A,S}$. So, this is basically because $C_{A,S}$ is not known; when we have discussed the term, the rate is a combination of all these resistance.

But you know that, at steady state; the whatever the moles which comes from here, the same will go inside and they will react all these rates are equal. So, that is what I told you if nun step is rate controlling, you have to find out the contribution of each step because each step is creating its own resistance. So, at steady state; the net rate or moles of a transported from the bulk gas to the external surface of the catalyst, will be equal to moles which have been diffused inside that; what you are calculated from $d e d c a$ by $d r$ at r is equal to R . And, this and multiplied by the area πr^2 $4 \pi r^2$ for a Spherical pellet and that is equal to whatever you calculated in terms of the rate; based on chemical reaction.

But there is a lower, because of diffusion resistance; so, instead of writing diffusion resistance as resistance, we just introduced the term η ; which is nothing but talking a kind of resistance which is offered because of diffusion. So, this is what I mean to say some situations, we need to define the rate based on bulk concentration or bulk conditions. So, at that time, this is known as overall effectiveness factor. So, overall effectiveness factor means, rate, global rate, actual rate divide by rate measured at the bulk condition.

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Overall Effectiveness Factor

At Steady state, Moles transported from bulk fluid to the external surface of the Catalyst ($W_{Ar, Ap}$) = Net Rate of reaction with in and on the pellet.

$M_A = W_{Ar, Ap} = -r''_A (A_s + A_p)$, = (Molar Flux X Ext. Surface Area of pellet)

For a single spherical pellet of Radius R ,

$A_p = 4\pi R^2$, and $A_s = S_A \times \text{mass of pellet}$, ($A_s \gg A_p$)

$A_p = (\text{ext. SA/reactor volume}) (\text{reactor volume}) = a_c \Delta V$

$A_s = (\text{int. SA/mass of catalyst}) (\text{mass cat./vol. cat}) (\text{vol. cat./reactor vol.}) \cdot \text{Rect vol.} \Rightarrow A_s = S_A \rho_c (1 - \epsilon) \Delta V$ EV

So, if you look at here at steady state the moles transported; from bulk fluid to the external surface of the catalyst, this is your M_A total moles transported which will be equal to flux multiplied by the area of that pellet. So, for any radial diffusion if I am

talking which may be a diffusion only or which may be only a convection or a combination; partly it is diffusing, partly it is convecting, when we talk a Spherical pellet. So, $W A r$ in to A_p where A_p is now the external surface area. So, this is what the moles of a which is based on the flux multiplied by area; $4 \pi r^2 W A r$ at r whatever you have written the differential equation earlier.

And, now we are defining because we know what is the value of $W A r$ calculated; that is what the value here and multiplied by the area which is the external surface area of the catalyst. And, these same moles are reacting; diffusing and reacting so, that will be equal to the net rate of reaction in and inside the pellet; inside the pellet, and on surface of the pellet.

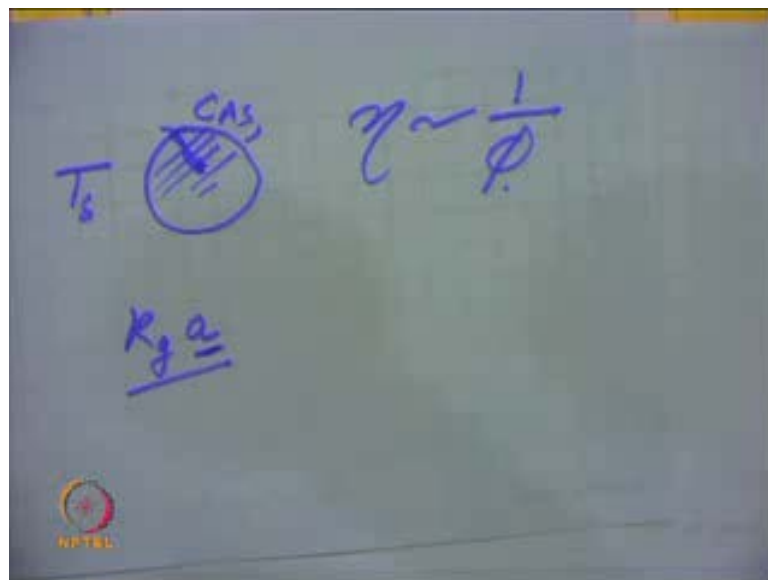
So, if you look at here this is the total molar flow rate; which is flux that is molar flow rate per unit area multiplied by area and that is equal to nothing but the rate of reaction per unit surface area. And, now I am saying rate based on internal surface area and based on external surface area total moles reacted. So r a double dash which is based on here per unit area of the catalyst; so, per unit area means internal area plus external area.

So, internal area is your $b e t$ area; which is here, this is your $b e t$ surface area, which is very high and this is your area which is $4 \pi r^2$. And, that is equal to this; the meaning of this is nothing, but molar flux multiplied by the surface area of the pellet. Because I told you at steady state, whatever moles which calculated or flux which goes at this surface; the spherical surface and that is flux calculated based on this area multiplied by the area of the; that is what you have defined A_p . But same also will go inside, no additional moles are coming, same moles will go and react inside. So, total moles which has been calculated like this and that can be defined by the rate also.

So, if you look at just for a Single spherical pellet; for a Single spherical pellet of radius R A_p is $4 \pi R^2$ is area surface area of the spherical pellet A_S . A_S is the surface area which is internal surface area and you define it based on $b e t$ surface area which is based on per unit mass of the catalyst. When you look at the $b e t$ surface area; generally, reported based on meter square per gram of catalyst; so, this surface area which is internal surface area multiplied by mass of catalyst. Now, this is the total area and you know, that this $b e t$ area is very high; that is 200 if you have just activated alumina the $b e t$ surface area is 200 meter square per gram of the catalyst.

So, external area is very high; compared to if you take 1.5 mm particle pellet; it is $4\pi R^2$ square of that. So, 1.5 mm I am talking; so, if you calculate, so, basically this surface area is very low compared to the internal surface area; so, that is why we neglect that in most of the calculation. So, this is what mentioned here that A_s which is internal surface area of the catalyst; per unit mass is very very high compared to the exterior surface of the catalyst. So, this is what definition has been mentioned A_p which is external surface area per unit reactor volume, multiplied by reactor volume. So, sometimes you write it based on surface area per unit volume of the catalyst or per unit volume of the reactor. So, that is a common most of the time you write; in the case of mass transfer equation if you look at, most of the time you write $k_g a$ into a that a because you do not you cannot measure k_g exactly; so, we calculate the k_g into a most of the time.

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What is this a ; this a is interfacial area or surface area per unit volume of the reactor or per unit volume of the liquid; so, either way it can be defined. So, that this a is something like which is related to the surface area which is the external surface area of the catalyst. So, this is some; in the case of the when you have a your reaction mass is also controlled then this has the importance. So, external surface area when I say a nano particle that is the meaning here; so, external surface area of the catalyst per unit volume or you have a mass transfer reaction you like a small globules or bubbles. The idea is again, to have the large surface area per unit volume; because mass transfer reaction the external surface

area is important. But when, you have a catalytic chemical reaction then internal surface area is important.

So, this is what here in terms of this surface area per unit reactor volume and multiplied by reactor volume. So, this surface area per unit reactor volume is reported as a_c and that can be defined per unit reactor volume it can be defined professor unit catalyst volume also. A_S is the internal surface area of that is again A_S the change the internal surface area; that is defined internal surface area per unit mass of catalyst, multiplied by mass of catalyst, divide by volume just to define the terms multiplied by volume of catalyst divide by reactor volume. So, ultimately, it is the surface area internal surface area. So, reported value is in terms of S_A because this is S_A Surface area per unit mass $b_e t$ surface area this is your S_A mass of catalyst per unit volume of catalyst. You know this is the known property of the catalyst ρ_c . Volume of catalyst per unit reactor volume; this is volume of the solid in the bed. Especially, this is for a packed bed; so, when a packed bed the; you are packing the catalyst; and the catalyst particles may be spherical or non spherical of some size. So, there will be voids between them; so, the mass catalyst density is based on the volume of catalyst.

So, this is what defined here, this volume of catalyst divide by reactor volume; that is your bed that is solid fraction in the bed. So, ϕ is the bed porosity; so $1 - \phi$ is the solid fraction; that is the catalyst in the bed and ΔV is your as usual into reactor volume. So, ultimately, this has the unit now surface area unit internal surface area which has been defined and all the when you define our rate of reaction; we use this terminology. So, this is surface area per unit mass; mass of catalyst per unit per unit volume of the catalyst. This is the fraction of the solid in the bed and this is the volume of reactor and this term ρ_c into $1 - \phi$; if you recall, that is your ρ_b bulk density of the catalyst.

That is, when you have place the catalyst in the bed; then, how much volume it has occupied to volume of catalyst in the bed and divide by the total volume; if you look at reactor volume. Because volume of catalyst in the bed means; now, it is the volume of catalyst plus whatever the bed porosity, ϵ_b . So, v_r if I say volume of reactor actually it is volume of the solid material plus ϵ_b times v_r ; where ϵ_b I say or ϕ_a it is same. Sometimes, you see it ϵ_b also bed porosity; so, bed porosity and this ϕ both are same term. So, basically what I mean to say, the volume actual of

catalyst w is mass of catalyst divide by density of catalyst that is the volume of catalyst. And, actual volume of the bed will be; if you know this ϕ multiplied by the; this is definition of ϕ , that is mass catalyst per unit volume of catalyst.

So, if you just take that, you can calculate the ϕ ; sometime, you can define it based on the volume of the reactor. So, if I know bed porosity of ϵ multiplied by the v_r it means total voids in the bed ΔV voids in the bed. So, that is what written here.

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$\rho_c (1 - \phi) = \rho_b = \text{bulk density of catalyst, } \phi = \text{bed porosity}$
 $\Rightarrow M_A = W_{Ar} A_p = -r''_A A_s,$
 $-r''_A$ = is overall rate of reaction with in and on the pellet per unit surface area.

The relationship for the rate of mass transport

$$M_A = W_{Ar} A_p = k_c (C_{A0} - C_{As}) A_p$$

If internal diffusion is also important,

$$-r''_A = \eta (-r''_A) = \eta K C_{As} \text{ (for First order reaction)}$$

(Eliminate C_{As})

So, you should know this term, because you have already defined them again and again. So, ρ_c into 1 minus ϕ is equal to ρ_b ; so, bulk density of the catalyst. So, bulk density of the catalyst is 1 ρ_b , pellet density is ρ_p and solid powder density is ρ_s . That is you have made the pellet from different; the particles of that solid. So, ρ_s is basically true density of the solid; if I have alumina powder so ρ_s is the density of the aluminum material. But when, you made the pellet from this aluminum material; so, that is ρ_p . So, ρ_s will be in high ρ_p will be lower; because now, this pellet itself contains the void and that is the porosity of a catalyst.

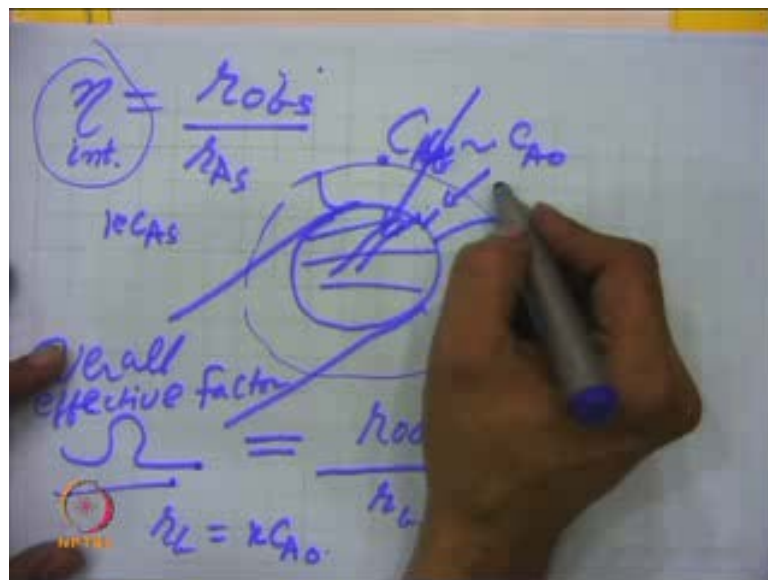
So, same relationship holds there also and then, this pellet or large number of pellets have been taken together and placed in a reactor; so, that is now bed porosity. So, M_A which is the total moles which have been transported is defined by flux, multiplied by a p that is based on external surface area. So, this is something like you can call in terms of mass transfer also; because these are the moles which have come from bulk to the

external surface of the catalyst. And, same moles are transporting inside; that is there are diffusing and then, they are reacting chemically.

So, that is written in terms of surface area which is; because I told you now, in an on the catalyst but this A_s is much more greater than A_p . So, you can write it approximately minus r_A rate of reaction based on surface area, multiplied by the total surface area. So, this is what defined here, the relationship for the rate of mass transported now; because the, it is from external to the surface of the solid catalyst. So, C_{A0} is concentration in the bulk and C_{As} is the concentration at the surface and this is happening because there is difference in concentration; great driving force is therefore, mass transfer. So, k_c is the mass transfer coefficient; sometimes, you see k_g also k_g ; gas phase mass transfer coefficient.

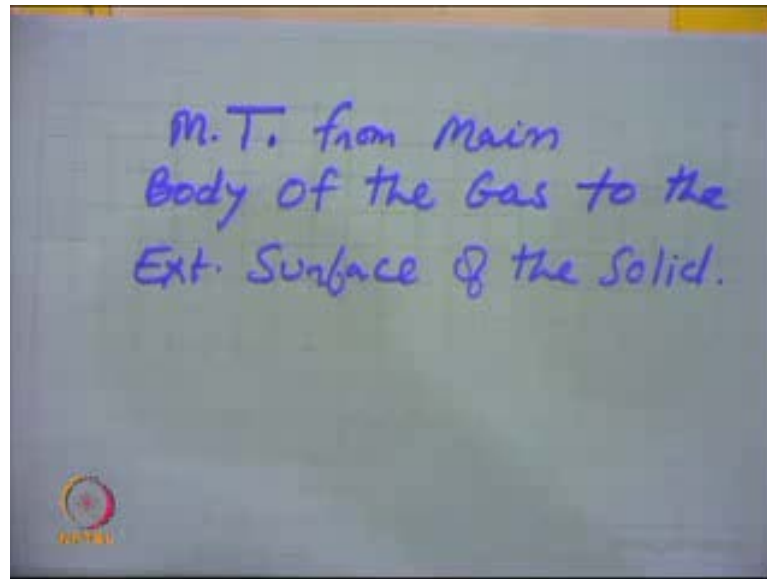
So, here it is denoted by $k_c (C_{A0} - C_{As})$ times the surface area which is the external surface area. If internal diffusion is also taking place then $r_{A''}$ you have already defined based on η times $r_{A''}$ measured based on surface condition r_{As} . This point is discussed earlier also; and here also what I said.

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See, the moles which have come from here to here; that is the first case because of mass transfer.

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So, mass transfer; so I discussed this thing mass transfer from main body of the gas to the external surface of the solid; that is your first step. Mass transfer from main body of the gas; so, this is your main body here all gas and it comes from here to the external surface of the solid because solid is covered by a film of the gas itself. If the concentration is high; this will more dominating. And, suppose there is a gas there is a liquid depending upon solubility there will a gradient or difference. So, this is your first term, which is written here $k_c (C_A - C_{A_s})$ times the concentration in the main body C_A minus concentration at the surface.

So, this is your flux basically; and multiplied by the area. So, this is your total moles which have been transported like this; and when, there is no resistance; so, why this is happening? Because your mass transfer coefficient is low or your conditions are not well controlled so there is a concentration difference. And, when this is then, this will create some kind of resistance. So whether you write it $k C$; so, k substituted C or k_g it has same means. So, first step and when this happens now the gas has reached to the surface and it will diffuse inside.

So, again you have to find out rate of diffusion; which you will calculate again from the fixed law of diffusion, $D \frac{dc}{dr}$ evaluated at r and multiplied by the $4 \pi R^2$. So, there is a gradient from this surface to the center of the pellet again diffusion into the solid catalyst; which you have already discussed and then, there is chemical reaction. So,

diffusion and chemical reaction step; have been combined together by into distinguish term which is effectiveness factor. Because you know, effectiveness factor now internal effectiveness factor I am talking global rate divided by intrinsic rate. So, what is global rate which has a contribution of diffusion resistance also.

So, that is why this eta has been introduced. So, the net rate of reaction on the pellet is nothing; but the internal diffusion that is term which is related to the internal effectiveness factor, which is related to the internal diffusion resistance eta times this thing kinetic rate. So, if there is no internal diffusion thing eta will be 1; so, that time only the kinetic. So, it means there is no concentration gradient inside the pellet; when the Thiele modulus value is low. So, this is eta times rate constant; which is surface reaction of volumetric rate constant and calculated times C A S whatever.

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The image shows a handwritten derivation on a slide. It starts with the mass balance equation: $M_A = W_{Ar} A_p = W_{Ar} a_c \Delta V = k_c (C_{A0} - C_{As}) a_c \Delta V$. It then states that M_A is also the net rate of reaction, which is $\eta (-r''_A) A_s = (\eta k_s C_{As}) (S_a \rho_b (1 - \theta) \Delta V)$. This is simplified to $(\eta k_s C_{As}) (S_a \rho_b \Delta V)$. Equating the two expressions for M_A gives $k_c (C_{A0} - C_{As}) a_c \Delta V = (\eta k_s C_{As}) (S_a \rho_b \Delta V)$. Solving for C_{As} yields the final expression: $C_{As} = (k_c a_c C_{A0}) / (k_c a_c + \eta k_s S_a \rho_b)$. The slide concludes with the text: "Expression for concentration at the pellet surface as a function of bulk gas concn." and includes the NPTEL logo.

So, one can very easily write down the expression $W A r$ into $A p$; I have already discussed $A p$ in terms of $a c$ into ΔV . So, flux now surface area up on unit volume into volume so external and so, this is written now $k c$ times $C A 0$ minus $C A S$ times $a c$ into ΔV which is your in terms of the $a c$ Surface area per unit volume. So, same thing has been written based on rate; so, eta times $r A$ double dash a and based on the internal surface area. So, eta times you are assuming a first order reaction; so, eta times $r A$ double dash is $k s$ times $C A S$ surface reaction rate constant times the concentration. Once, you have defining here concentration based on surface or rate based on surface

area; then, you need the term which have been defined already $S_a \times \rho_c$ into $1 - \phi$ times volume ΔV .

So, this is the area which we have defined earlier. So, this is surface area $b_e t$ area per unit mass; so, mass per unit volume for the catalyst this is again the bed porosity. So, this $1 - \phi$ representing the fraction of the solid and times the ΔV . So, ultimately, this is the rate which is again based on the same unit. So, now because this and this both are same; so, just we can equate these two. Because $C_A S$ is unknown here; bulk concentration is known based on your inlet condition and concentration at the surface $C_A S$; so, that is unknown but by using these two terms one can solve them. Because this rate should be equal to this and we are talking steady state operation.

So, if you do that; $C_A S$ is equal to simple k_c which is mass transfer coefficient times a C Surface area; external surface area of the catalyst per unit volume times C_A naught. Because now, we have reported the value in terms of C_A naught divide by $k_c a_c$ plus η times $k_s S_a \rho_b$. So, this whole term can be written in terms of the k also; this is nothing, but the rate constant based on volumetric unit also; that choice is yours. So, what I mean to say, if you just divide this equation by $k_c a_c$; this term then, you have simply its C_A naught divide by whatever $1 + \eta$ times k by k_c that is surface reaction rate constant divide by this k_c or chemical reaction rate constant divide by mass transfer coefficient.

So, basically, this term k by k_c into a both have identical unit; it is a dimensionless number basically and, this represents known as Damkohlar number. And, this gives you the indication about the chemical rate divide by the mass transfer rate; contribution of these two rates. So k by $k_c a_c$; that is a chemical reaction rate, divide by mass transfer rate; just like, the Thiele modulus we defined; the kinetic rate divide by diffusion rate, here it is chemical reaction rate, that is kinetic rate divide by the external mass transfer rate. Because you multiply here, by C_S divide by C_S and that are these are the terms which are related to your transfer coefficient concentration.


(Refer Slide Time: 35:34)

Therefore observed rate in terms of bulk concentration
(1st Order Reaction)

$$-r''_A = \eta (-r''_A) = \eta k_s C_{As} \quad (-r''_A = -r''_A S_a)$$

$$\Rightarrow -r''_A = \eta k_s (k_c a_c C_{A0}) / (k_c a_c + \eta k_s S_a \rho_b)$$

$\Omega =$ (Actual overall rate of reaction) divided by
(rate that would result if the entire surface were
exposed to the bulk conditions, C_{A0}, T_0).

$$\Rightarrow -r''_{A \text{ overall rate}} = \eta k_s C_{As} = \Omega (-r''_{A0}) = \Omega k_s C_{A0}$$


So, this is the expression which represents the concentration profile. So, one can very easily write now because the first order rate we have assumed; so, r''_A has been defined. So, in terms of η times k_s which is the rate constant based on surface area times this C_{As} , so rate of reaction. So, because C_{As} is now known; earlier, case this when there is no mass transfer resistance we have already said that this concentration is equal to C_{A0} . But when, there is a gradient term difference or mass transfer resistance has contributing; then, $-r''_A$ which is defined η times k_s times C_{As} ; substitute the value of C_{As} .

So, this includes now, the contribution of mass transfer resistance also. So, this is simply your $-r''_A$ which is η times k_s as usual C_{As} has been substituted now $k_c a_c$. So, mass transfer coefficient this is external this is external surface area per unit volume; this is C_{A0} divide by $k_c a_c$ plus η times k_s so this whole term is just nothing but a volumetric rate constant k_s if look at. So, this; that is what k by $k_c a_c$ if you divide so 1 plus k_s by $k_c a_c$; so that is nothing but your d_a . So, sometimes you write it this equation η ; this is this term that is, η times k_s divide by 1 plus η times d_a for a first order reaction.

(Refer Slide Time: 37:10)

$$\frac{k C_A^0}{k_c a} = \text{Damkohler No.}$$

Chemical Reaction Rate
mass tr. rate.

$$\frac{k C_A^{n-1}}{k_c a}$$

So, Damkohler number actually for nth order reaction it will be write k by k g a times C A S c a to the power n minus 1. Again, just like in the case of Thiele modulus if you define. Because for first order reaction here it is 0; so, for nth order reaction this comes k by k g C A S to the power n minus 1. So, one can do this kind of exercise just to check the values for first order of reactions.

(Refer Slide Time: 37:33)

Therefore observed rate in terms of bulk concentration
(1st Order Reaction)

$$-r''_A = \eta (-r'_A) = \eta k_s C_{As} \quad (-r'_A = -r''_A S_a)$$

$$\Rightarrow -r''_A = \eta k_s (k_c a_c C_{A0}) / (k_c a_c + \eta k_s S_a \rho_b)$$

$\Omega =$ (Actual overall rate of reaction) divided by
(rate that would result if the entire surface were
exposed to the bulk conditions, C_{A0}, T_0).

$$\Rightarrow -r''_{A \text{ overall rate}} = \eta k_s C_{As} = \Omega (-r''_{A0}) = \Omega k_s C_{A0}$$

$$\Rightarrow \Omega = \eta (k_c a_c) / (k_c a_c + \eta k_s S_a \rho_b)$$

$$\Rightarrow \Omega = \eta / (1 + (\eta k_s S_a \rho_b) / (k_c a_c))$$

So, once, this is known; this is your actual rate now when there is a mass transfer coefficient is also involved. You can see here, this is mass transfer coefficient and when

you say that mass transfer is not controlling I have already discussed I can write it in terms of resistances. So, $1/k_c$ is a contribution of mass transfer resistance; same thing, when you write diffusion then, there will be a diffusion resistance, same thing for kinetic. So, this term w is representing here, these are representing a kind of resistance which have been offered; but reciprocal of these say mass transfer coefficient kinetic constant. So, there will be nothing but in terms of the resistance offered. So, ω which is defined based on actual overall rate of reaction; divide by the rate that would result if entire surface were exposed to the bulk condition.

So, now we have already calculated that in fact. So, overall rate of reaction which is nothing but same global rate; this one, this is your actual rate that is $\eta k_s C_S$ same expression is here. Now, the whole term can be written in terms of ωr_{A0} ; where r_{A0} is rate measured at bulk concentration. So, rate measured not at surface condition; but at the bulk condition and bulk condition will be same as the surface condition, when the mass transfer external mass transfer does not control the rate. That is meaning of mass transfer coefficient is very high; how will you make that high use the high velocity high superficial gas velocity a small size of the particle. Because I told you, mass transfer coefficient is proportional to U/d_p to the power half this k_c or k_g whatever here is given by U/d_p to the power half in kinetic. So, this, if you have high superficial gas velocity; then, this will be high.

So, this that the; a kind of resistance one by k_c will be a mass transfer resistance that will be 0, negligible. Same thing, d_p is the diameter of the particle; so use the smaller pellets. For large size pellet it will be your dominating term; mass transfer resistance because the film thickness will increase. Basically, mass transfer coefficient is nothing but D_{AB}/δ ; if you remember your kinetician theory or film theory the mass transfer coefficient is given by D_{AB}/δ ; where δ is the film thickness. So, it means where what is the meaning of film thickness; the gas which is the solid is covered by a film of gas and you try to remove that film. So, when you have a batch reactor; you use a stirrer you increase the rpm and then, you can see that your rate of dissolution or that reaction increase; because you are removing the mass transfer. When that is has eliminated there won't be any change in rate.

So, this is what the $\eta k_s C_S$ either you define; and or you define based on bulk condition; so r_{A0} so, this can be written like this rate. So, I can have the

relationship now for ω or η I can find out ω because you know this thing. The rate is, global rate is not changing actual rate is same; whether you define it based on whatever I said; per unit mass, per unit surface area, per unit volume or you define global rate based on the bulk condition or you define based on the surface condition. The rate has moles which has been transported they will remain same; so, that is what has been done here. So, one can very easily write the expression for η or ω . So, ω is calculated based on this; so, just you can see here now this k_s and C_{A0} gets canceled. So, this is simply η divide by $1 + \eta k_s \rho_s a \rho_p$ I can I just recall again and again this is you can write k also which is a volumetric rate constant and, k by k_c times a . So k by $k_c a$; which I was talking a Damkohlar number here.

So, this expression is finally, reached to that ω ; overall effectiveness factor is η divide by $1 + \eta k_s \rho_s a$, Damkohlar number. So, that is the complete picture for a first order kinetic rate and ω is the overall effectiveness factor. ω will be η ; when there is no mass transfer. If external mass transfer resistance is not contributing; then, ω will become η you can check that. Because when this is this k_s by $k_c a$ is a term which is representing the kinetic rate divided by the mass transfer rate or 1 by mass transfer rate; so, I can call it a mass transfer resistance. If mass transfer resistance is not controlling or if $k_c a$ is very very high compared to k rate constant term; then, this $1 + \eta k_s \rho_s a$ can be approach to 1 or can be written as approximately 1 . So, in that case, ω becomes η . So, if mass transfer does not control the rate of reaction then, overall effectiveness factor will be equal to the internal effectiveness factor.

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Rate of reaction, $-r_A$

$\Omega =$ (Actual overall rate of reaction) divided by
(rate that would result if the entire surface
were exposed to the bulk conditions, C_{Ab}, T_s)

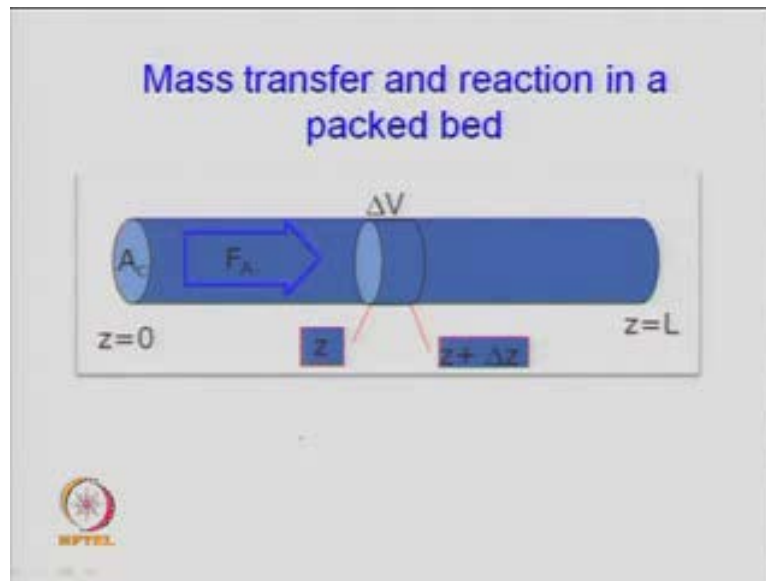
$$\Omega = \frac{\eta}{1 + \eta k_1 S_a \rho_b / k_c a_c} = \frac{\eta}{1 + \eta Da}$$

$$-r_A = \Omega(-r_{Ab}^*) = \Omega k_1 C_{Ab}$$

$$-r_A = -r_A \rho_b = -r_A S_a \rho_b = \Omega k_1 C_{Ab} S_a \rho_b$$

So, we have defined this, I am now; just to recall or summarize it the omega which is overall rate of reaction or overall effectiveness factor measured; based on the bulk condition and has been co related by this. That is, and this term is your what I said a overall that is chemical reaction rate constant and this is mass transfer rate constant. And, that; what the contribution of this is written in terms of eta over 1 plus eta times a Damkohlar number D a. Damkohlar number, which talks about the ratio of the mass transfer resistance divide by the chemical reaction resistance or chemical reaction rate divide by mass transfer rate. So, when this is not contributing; so, omega becomes eta. So, one can write the expression which I have already explained you again and again you should know this relationship. Rate of reaction based on volume is related to the mass unit; is equal to related to surface area and that one can write in terms of omega now.

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So, after talking so many things, about the external mass transfer and when, you have a reactor like a packed bed reactor there may be a limitation of or mass transfer control reaction also.

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$$F_A = U_G A$$
$$F_A = C_A U_0 = C_A A_c U \text{] convective flow}$$
$$W_A/2 = \left[(-D_{AB} \frac{dC_A}{dz}) + C_A U \right]$$

So, the packed bed reactor; now, the same type of equation which you write in general moles in; because now, it is related to when you are talking a mass transfer the gas superficial velocity. And, there can be a contribution of the external dispersion term; there can be a contribution of just the convective term that. So, you have to F_A which is

the molar flow rate is just most of the times, when you have highly inner gas velocity you write it something like $U A C_A$ times the area of cross section. ((Refer Time: 44:46) A into U is your volumetric volume; a this is C_A naught into V naught. So, basically, I should write it here F_A is your molar flow rate. Molar flow rate how do we define? That is based on concentration C_A times the volumetric feed rate V_0 this and volumetric flow rate. How do we define area of cross section of the tube, multiplied by the velocity; so, this is what the term has been written here.

So, this generally will come only when you have the dominance of the convective term. So, this is basically a convective flow; a convective flow when there is a diffusion or dispersion to dispersive term will also arise. And, that is and that times you are writing it in terms of the flux. So, I write it in the form of W_A ; $W_A Z$, $W_A R$; so, that is known as flux which will be a contribution of convective and dispersive. So, that time what will be the value it is minus D_{AB} what you write $d C_A$ by $d z$ if I write in the form of z . So, $d c_a$ by $d z$ multiplied by area of the cross section; so, I am not I am talking flux. So, I will not multiply here and plus the second term which is C_A into U which is your n_A plus n_B times the mole flow y a mole fraction. If you remember your transport phenomena; then, you write the all the time the flow is because of 2 terms or flux is because of two contribution; one is the convective flow and second one is the diffusive flow. So, diffusive flow will arrive because of the concentration gradient and convective will come because of the flow, velocity term.

Just write that you have put some a bottle of scent here and just run a fan; so, that is now a forced convection type problem. If you just do not your air is almost stagnant. So, it will just because of the diffusion concentration gradient. So, that is what we are talking here, in the case of a mass transfer control reaction.

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Mass Balance in a Packed bed (Mass Transfer control)


$$A_c W_{Az} - A_c W_{A, Z+\Delta Z} - (-r'_A) \rho_b A_c \Delta z = 0$$

$$\Rightarrow -dW_{Az}/dz - (-r'_A) \rho_b = 0$$

Flux, $W_{Az} = -D_{AB} dC_A/dz + y_A(W_{Az} + W_{Bz})$

(For convective flow, $W_{Az} = y_A(W_{Az} + W_{Bz}) = U C_{Ab}$)

U superficial velocity.

$$(-r'_A) = (-r'_A)_b \Omega = \Omega k_s S_a C_{Ab}$$


So, for a mass transfer control reaction in a packed bed; your equation which is already discussed so many times. So, quickly I am writing A_c into W_{Az} minus A_c into $W_{A, Z+\Delta Z}$ plus Δz minus disappearance because of chemical reaction. So, minus r'_A dash rho b times A_c times Δz ; that choice is yours how to define. So, the rate of reaction professor unit mass of the catalyst; this is mass of the catalyst basically so rho b I have written but it is actually rho c into $1 - \phi$. So, rho b when I write; mass of the catalyst per unit volume of the reactor and multiplied by A_c into Δz is the volume of the reactor that is differential section. So, this is equal to 0; because you are talking a steady state. So, input minus, output minus, disappearance because of chemical reaction is equal to 0.

So, we have just written; just taking the limit just Δz tends to 0. So, equation becomes minus d over $d z$ of W_{Az} minus r'_A dash, r'_A dash which is per unit mass times rho b is equal to 0. Because this A_c cancelled; so, simple equation you can do that. So, quickly I am talking now; flux which I have already discussed so W_{Az} is equal to minus D_{AB} , dC_A by $d z$ plus the mole fraction of the species A times W_{Az} plus W_{Bz} . That is the total flux which you write n_A also sometimes. So, N_{Az} flux that is a contribution total flux is contribution of the Az plus N_{Bz} ; suppose, you have a equimolar counter diffusion. So, N_{Bz} is equal to minus N_{Az} . Then, whole term will become 0. So, it is a vector basically; so, y_A is the mole fraction; so, N_{Az} plus N_{Bz} is total moles n .

So, n_A is simply nothing but N_A . So, this whole term is nothing but N_A or F_A which is because of the velocity term. F_A ; which you have already seen here. Now, C_A brought into that is C_A brought into V or C_A into V at any z position. So, if you look at here, for any convective flow I have already written this term here now. So, $W_A Z$ because convective term you are talking there is this contribution can be neglected. And, you have y_A times $W_A Z$ plus $W_B Z$ total flux; that can be written N_A is equal to nothing but this is N_A basically or w_A flux of A . And, that is nothing but U times C_A concentration of A which I have already defined here. So, flux in terms of the flux; so, this is basically C_A into V divided by area; so, that is C_A into U . So, U is the superficial gas velocity; so, you can calculate total volumetric flow rate and divide by the area of cross section so that is your superficial velocity. And, r_A dash we have already discussed based on overall effectiveness factor; so, one can write it.

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$$D_a \frac{d^2 C_A}{dz^2} - U \frac{dC_A}{dz} - \Omega \rho_b (k_s S_s) C_A = 0.0$$

Thus, For convective flow, Neglecting axial dispersion and Mass transfer controlled reaction,

$$-U \frac{dC_A}{dz} - (k_c a_c)(C_{A0} - C_A) = 0.0$$

$$\Rightarrow U \frac{dC_A}{dz} = -k_c C_A a_c$$

At $Z=0$, $C_A = C_{A0}$

$$C_A = C_{A0} \exp(-k_c a_c z / U)$$

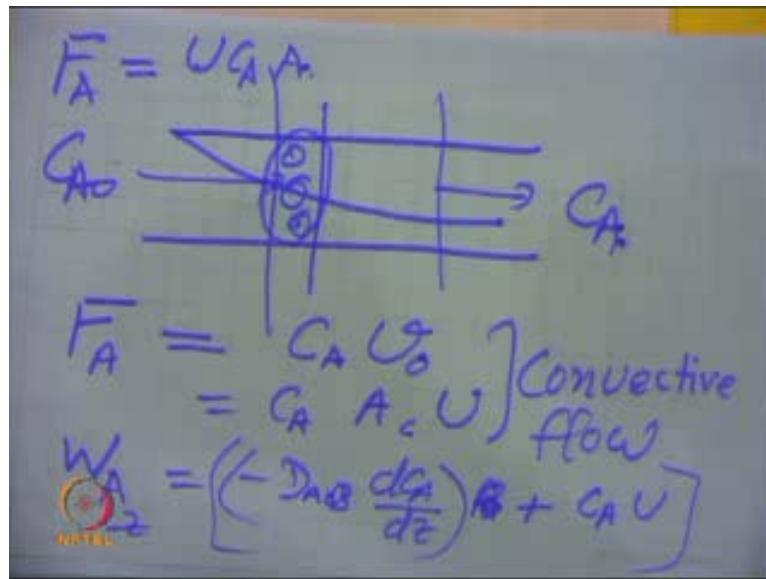
Or $-\ln(1-X) = (-k_c a_c z / U)$

So, when there is contribution of 2 term then, you have the axial dispersion term or diffusion also. So, $D_a \frac{d^2 C_A}{dz^2}$ which is written from this equation minus $D_a \frac{dC_A}{dz}$ at z minus $D_a \frac{dC_A}{dz}$ at $z + \Delta z$ and term is multiplied by cross sectional area $e C$. So, when Δz tends to 0; so, this becomes $D_a \frac{d^2 C_A}{dz^2}$ so that is the because of the axial dispersion or diffusion this is your $u C_A$ at z minus $U C_A$ at $z + \Delta z$. So, and divide by Δz ; so, this becomes simply U is a constant superficial gas velocity $d C_A$ by $d z$. And, third is your kinetic term which is

again based on omega now bulk concentration this can be written based on eta also. So, if you define based on omega; then, this is basically the concentration which is measured in the bulk.

But remember, I am talking a flux flow or a packed bed reactor. So, I am talking bulk means at a differential section of this bulk.

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But if, you have something here C_A naught exist conversion is there; so, C_A so down the length this is changing concentration is decreasing because reactants are reacting in a reactor. So, and at any section if you look at that that is what the concentration I am talking here. So, this is the C_A which is representing at any position between z and z plus delta z ; but down the length C_A is changing. So, when you design a packed bed reactor you need to find out what should be this length of a packed bed reactor; which will give a conversion which is related to this value of C_A . So, just now for simplification for convective flow only we have done it so minus $U d C_A$ by $d z$ and equation; we are saying that it is governed by mass transfer. So, packed bed mass transfer we are assuming that it is only a mass transfer contribution just like in a monolith. Now, a channel type of reactor on A plate type reactor which are non pores material so there it will be a mass transfer.

So, $k_c a_c$ is the mass transfer this is based on mass transfer coefficient; C_{A0} is the concentration in the main body. So, main body but at any point here it is changing. C_A

is again the concentration; so, how the concentration changes in the in a particular location z that what we are calculating here. So, between z is equal to 0 we know C_A is equal to C_{A0} . And, if you calculate at z is equal to certain length z then you have to find out the C_A . So, your equation now becomes, $U d C_A$ by $d z$ is equal to simply k_c times C_A times a_c which is k_c times C_A times a_c . Because I am saying that, the mass transfer is not only controlling the rate; so, what is the meaning of this; that what I discussed that for only mass transfer or this will be happening in a kind of a non pores solid material.

(Refer Slide Time: 53:38)



So, metallic plate; so the concentration gradient is only on the external surface. So reaction I am saying not covered because I have taken ω_1 so there is no diffusion in to the pore and kinetics is very very fast. That is the meaning of mass transfer controlled reaction. So, in the case of mass transfer controlled reaction the concentration here is maximum; that is C_{A0} if I am saying; basically, it is C_A now, which is at any given location of z and the concentration is the bulk concentration at that and here it is 0. Because the mass transfer is controlling; mass transfer controlling means, this difference is maximum concentration difference is maximum. So, as soon as the gas reaches here at the surface of a Solid material catalyst; it immediately reacts. So, kinetics is very fast; the problem is here transport limitation is here. So, that is the meaning of this; so, we have written it in terms of C_A . So, basically this C_A is reporting a bulk concentration as I

said that down the length of reactor this C_A is changing and this will be your $C_A(z)$ minus x when $C_A(0)$ is the concentration at z is equal to 0.

So, one can very easily integrate this equation now; it is a very simple equation. So, C_A is $C_A(0) \exp(-k_c z / U)$ and so of $k_c z / U$. So, one can use this equation to find out the length of the reactor for a given conversion. This is for mass transfer controlled reaction. So, C_A is $C_A(0) \exp(-X_A)$ all of you know that constant volume I am assuming so one minus x so this can be written in terms of C_A by $C_A(0) \exp(-X_A)$ is $1 - X_A$. So, $\ln(1 - X_A)$ is equal to simply $-k_c z / U$. So, for a given conversion suppose 90 percent conversion or a 100 percent conversion what value of length of reactor is required for a given flow condition. Because U is known to you; so, one can very easily find this.

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Ex: • Mole balance in flux form, where A_c is


$$-\frac{dW_{Az}}{dz} + r_A \rho_b = 0$$

where

$$W_{Az} = -D_{AB} \frac{dC_{Ab}}{dz} + C_{Ab}U \quad \text{and}$$

$U = \text{superficial velocity}$

hence

$$D_{AB} \frac{d^2 C_{Ab}}{dz^2} - U \frac{dC_{Ab}}{dz} + r_A \rho_b = 0$$


So, the expressions I have again written again in order to define you W_{Az} , D_{AB} , dC_{Ab}/dz and that is given $C_{Ab}U$ and one can write the expression. So just for your exercise you have to do this so just please do it as an exercise for practice.

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Overall Rate with in the pellet ($-r'_A = \Omega (r'_{Ab})$)


For first order reaction : $(-r'_{Ab}) = (r'_{Ab})Sa = k_s S_a \rho_b C_{Ab}$

$\Rightarrow (-r'_A) = \Omega (r'_{Ab}) = \Omega S_a \rho_b k_s C_{Ab}$

$$Da \frac{d^2 C_{Ab}}{dz^2} - U \left(\frac{dC_{Ab}}{dz} \right) - \Omega k_s \rho_b S_a C_{Ab} = 0$$

Neglecting Axial Dispersion $\left(\frac{dC_{Ab}}{dz} \right) = - \left(\frac{\Omega \rho_b k_s S_a}{U} \right) C_{Ab}$

$\Rightarrow C_{Ab} = C_{Ab0} \exp(- \Omega S_a \rho_b k_s Z/U)$



So, one can define it and one can write in terms of the expression which I have already discussed here. So, when omega is not 0 when there is a contribution of other resistances also the same expression will be written in terms of omega now. So, that time I assume that only mass transfer; but even if other terms are there just write omega into minus r A double dash and then calculate.

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Mass transfer and reaction in a packed bed – cont.

- Axial diffusion, $D_a \frac{d^2 C_{Ab}}{dz^2}$ can be neglected when


$$\left| \frac{U_0 d_p}{D_a} \right| \gg \left| \frac{-r'_A \rho_b d_p}{U_0 C_{Ab}} \right| \quad F_A \text{ is very large}$$

So $\frac{dC_{Ab}}{dz} = - \left(\frac{\Omega \rho_b k_s S_a}{U} \right) C_{Ab}$

- Finally, the conversion for 1st order reaction in PBR is

$$X = 1 - \frac{C_{Ab}}{C_{Ab0}} = 1 - e^{-(\rho_b k_s S_a \Omega L)/U}$$

Remember the forced convection in binary external diffusion, J_c is also neglected



So, there are certain checks for this. So, you can eliminate this diffusion because we assume that diffusion is neglect neglected but one can check it. So, there are several

criteria to define that. So $U_0 d_p$ divide by d_a is much more greater than this rate term. Then, your diffusion can be neglected; so, I have already discussed that if you have your velocity is high this l by d ratio length of the bed to the catalyst particle. If it is large then, your axial dispersion can be neglected. Same thing is defined in terms of this also based on diameter flow velocity; so, you should have high flow velocity you should have a diameter of the particle related to the diameter of the reactor d by d_p more than 10. Then, radial dispersion can be neglected; same thing for this diffusion coefficient. So, one can just control this and check that parameter.

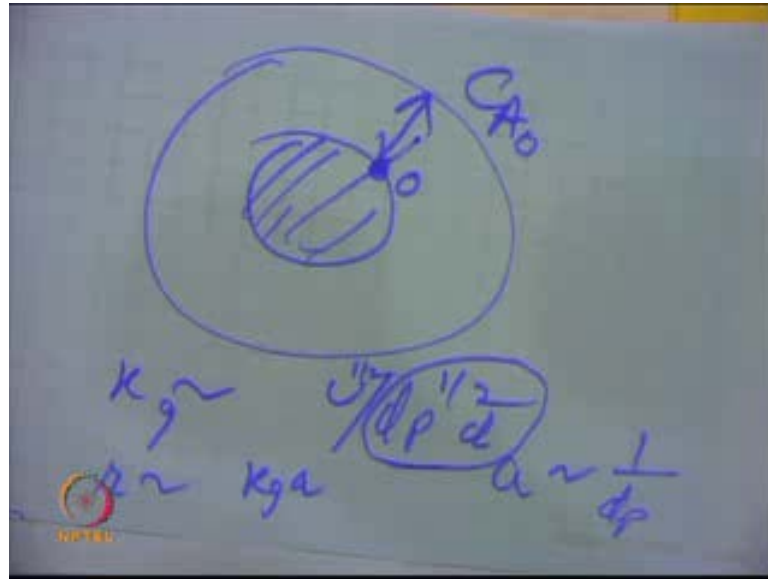
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Determination of limiting situation from reaction data

Type of Limitation	Variation of Reaction Rate with:		
	Velocity	Particle Size	Temperature
External diffusion	$U^{1/2}$	$(d_p)^{-3/2}$ <small>(Rate $\propto k_s C_A$)</small>	\approx Linear
Internal Diffusion	Independent	$(d_p)^{-1}$	Exponential
Surface Diffusion	Independent	Independent	Exponential

So, that I have already discussed; so, this is what important here in terms of the determination quickly I am closing it. So, that external diffusion rate control then velocity to the power half you have already seen that diameter to the power rate is proportional to U by d_p this k_g is proportional U by d_p to the power half if you remember that is what we have said.

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And, rate is proportional to k_g times a ; a is the external surface area. So, r is proportional to k_g times a where a is surface area per unit volume of the catalyst or per unit mass of the catalyst. So, this a is $1/d_p$ inversely proportional to the size of particle you know a Surface area per unit volume. Suppose, it is spherical particle $4\pi R^2$ square is the surface area volume of the particle $4/3\pi r^3$ cube. So, ultimately it is $1/r$. So, this is the meaning here; so, overall if you look at $k_g d_p$; so, here another d_p will come so rate will become d_p to the power $3/2$.

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Determination of limiting situation from reaction data

Type of Limitation	Variation of Reaction Rate with:		
	Velocity	Particle Size	Temperature
External diffusion	$U^{1/2}$	$(d_p)^{-3/2}$ <small>(Rate $\propto k_g a C_A$)</small>	\approx Linear
Internal Diffusion	Independent	$(d_p)^{-1}$	Exponential
Surface Diffusion	Independent	Independent	Exponential

So, that is what written here for particle size effect so rate will go by this. If you have just mass also coefficient it will be d_p to the power half. When internal diffusion controls rate is independent of the velocity; but it is inversely proportional to the particle size. Because in Thiele modulus we have defined. So, ϕ is r under root k by d and η is one upon ϕ ; so, it is inversely proportional to the size of the particle. So, smaller the particles your internal diffusion will be minimum; fine powder you take. When you do the kinetics study; you have to take a fine powder or smaller particle size. You have to check it and same thing for mass transfer do it at different linear velocity superficial gas velocity and check.

When the kinetic controls when it is independent of the velocity, it is independent of the particle size and with temperature it depends based on Arrhenius equation. So, more temperature dependent; so, when you have a very high temperature then, diffusion may be controlling resistance because diffusion is also changing like this. So, when you do the kinetic control diffusion, do not consider the reaction or conduct the reaction at extremely high temperature because t time this k is very high. So, that time it may be that the contribution or diffusion may be dominating which I have discussed in my last lecture. So, this concludes this transport effect or internal and external effectiveness factor. So, I stop here. Next time, I will cover deactivation of catalyst.

Thank you.