Heterogeneous Catalysis and Catalytic Processes
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Lecture - 38
Trickle Bed Reactors

Good afternoon. In my last lecture, I was speaking about multi-phase reactors and I was discussing the trickle-bed reactor. So, today also, I will continue that, some design aspects and fundamentals of the trickle-bed reactor and then… or fluidize bed reactor.

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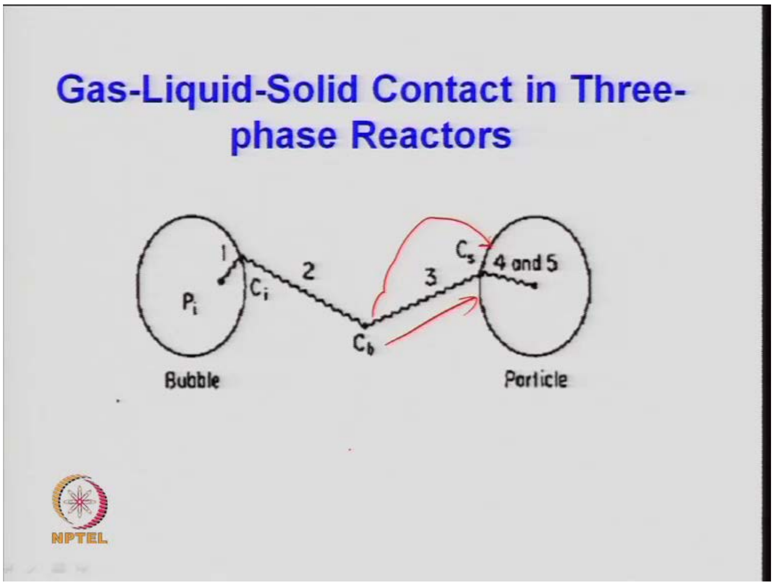

Gas-Liquid-Solid Contact in Three-phase Reactors

So, I was talking about a gas, liquid and solid. So, you can see here; there is a gas bubble. And, this can be a case of slurry bubble column reactor also. And, here I am talking just a trickle-bed reactor. But, it is for any gas liquid and solid reaction, this kind of system; whether it is slurry bubble column reactor or trickle-bed reactor or even in a fluidized bed reactor, as seen, may little bit different. But, in total, there will be a kind of resistances offered.

So, this is a gas bubble and then there is a concentration here at the interface; and, you have a bulk of liquids. So, this section is showing the bulk of liquid. So, from here there is a mass transfer from the external surface of the bubble to the center or the main body of the liquid. So, in between, there can be a gas film resistance as I discussed last time and the liquid film resistance. So, k A l in the liquid side; and, the same thing – k A g is the mass transfer coefficient for the gas side.

And, from this main body of the liquid, there is a transport of the gas A from the liquid, that is, the main body of the liquid to the external surface of the solid; which will again be governed by the concentration difference; that is, here of this concentration of gas A and concentration of gas A at the surface, which is again a mass transport step. Once this happens, then the fourth and fifth step – these are related to the diffusion into the pore of a catalyst and followed by chemical reaction.

So, in chemical reaction again, we will have the surface reaction to first adsorption of gas; then, surface reaction and then desorption of the product. So, that is inside the surface of a catalyst. So, the catalyst is porous. So, this is one resistance in terms of the mass transfer and this interfacial area, which is depending on the size of the solid particle. What is the surface area of this catalyst per unit mass of the catalyst or per unit volume of the catalyst? When you look at here the mass transport, it will depend on the interfacial film, that is, the liquid film, which has formed. So, one side it is gas; other side is a liquid; and, this is a film; and, thickness of that film will be important. And, how to minimize that thickness is nothing but a kind of reduction in these resistances as I discussed in my last lecture.

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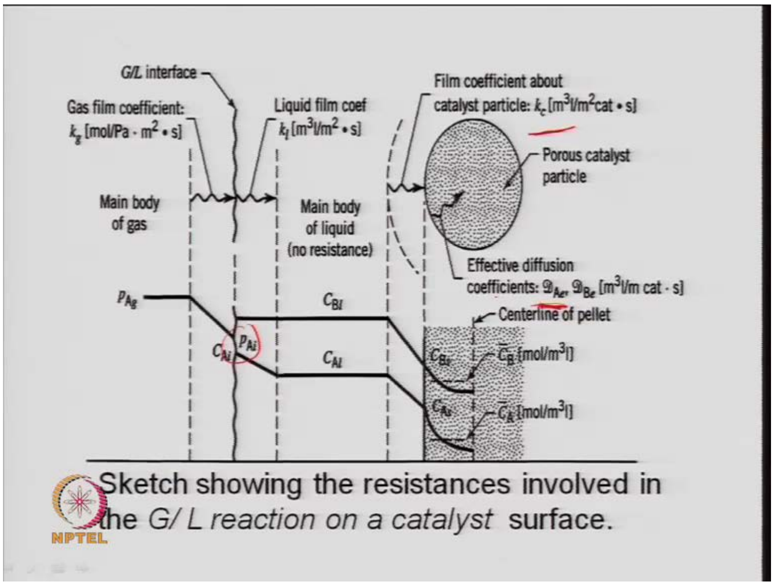

Sketch showing the resistances involved in the *G/ L reaction on a catalyst* surface.

We also discussed this picture. So, I said that, this is main body of the gas, where the pressure is P A g and then it reaches to… So, this is a kind of gas film; and, it reaches to the surface of the liquid. And, this has some kind of resistances – so, k A g or k g times whatever the concentration here and C A minus C A i. And, same thing here by equilibrium. So, C A i and P A i can be related by Henry law constant. So, P A i is equal to H A times C A i something. And then, this from here it is coming to the main body of the liquid. So, gas diffuses into the main body of the liquid or there is a mass transfer. So, again it will depend on the concentration C A i and concentration in the main body, which is written here C A l. So, this is the main body of the liquid. So, k A l times interfacial area times C A i minus C A l.

When it reach to the main body of the liquid; so, here the concentration is uniform. And then, you have a diffusion from main body to the external surface of the solid, because this is surrounded; this catalyst particle is surrounded by a film of the liquid. And, this mass transferred will depend on this mass transfer co-efficient, which is film co-efficient about the catalyst particle; and also, it will depend on the surface area of the solid per unit mass or per unit volume of the catalyst.

So, that is again the transport or mass transfer and then followed by the diffusion into the pores, which will depend on the effective diffusion coefficient of A and effective diffusion coefficient of B. So, depending upon the type of solid, it may be bulk diffusion, Knudsen diffusion. So, these steps may also control the overall rate of reaction. So, the concentration profile you can see C A s from surface of the solid; it drops like this. And, that will depend on the effectiveness factor, that is, the pellet effectiveness factor. C B is again the concentration of B, which will depend on the diffusion coefficients or the property of the liquid and the pore characteristic. So, that has been discussed earlier.

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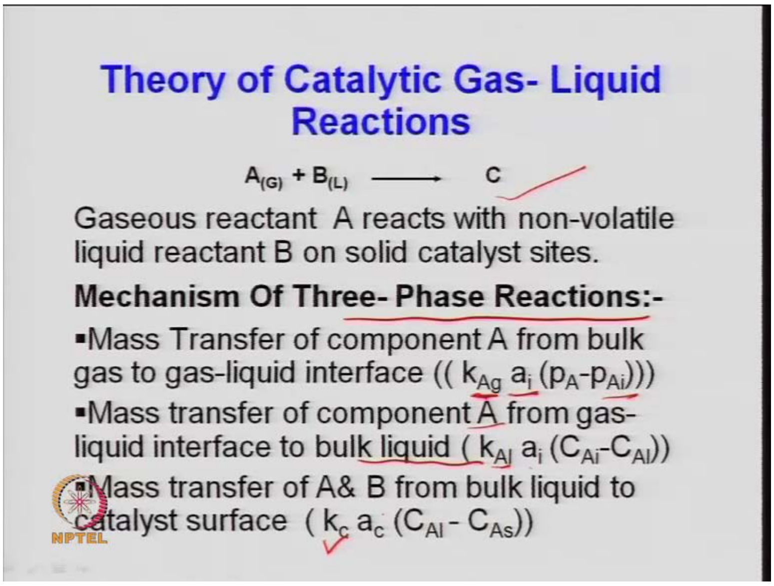

Theory of Catalytic Gas- Liquid Reactions

$A_{(G)} + B_{(L)} \longrightarrow C$

Gaseous reactant A reacts with non-volatile liquid reactant B on solid catalyst sites.

Mechanism Of Three- Phase Reactions:-

- Mass Transfer of component A from bulk gas to gas-liquid interface ((k_{Ag} a_i (p_A-p_{Ai})))
- Mass transfer of component A from gas-liquid interface to bulk liquid (k_{Al} a_i $(C_{Ai}-C_{Al})$)
- Mass transfer of A& B from bulk liquid to catalyst surface (k_c a_c $(C_{Al} - C_{As})$)

So, just I would like to recall the steps, which is for the heterogeneous gas solid reaction; we have already discussed; we derived the rate equations; and, we assumed certain steps at the rate controlling; that is approach. Similar approach is used in all the reactors, whether the only thing that, the mass transfer resistance, gas side, liquid side. So, the coefficients are to be calculated from the hydrodynamic steady or from the correlations. So, gas A reacts with liquid, which is B and transform into a product; let us say the simply stoichiometric reaction, which we assumed here.

So, the gases reactant A reacts with a B, which is not transferring into the gas side. So, it is a nonvolatile kind of liquid under the condition of the reaction. And, already the liquid is inside the pore of the catalyst, that is, the catalyst pores are already saturated with the liquid. So, if you look at the mechanism in these kind of reactions in a multi-phase reaction system; so, first step, which I discussed is the mass transfer of component A from the bulk gas to the gas liquid interface. So, this is….

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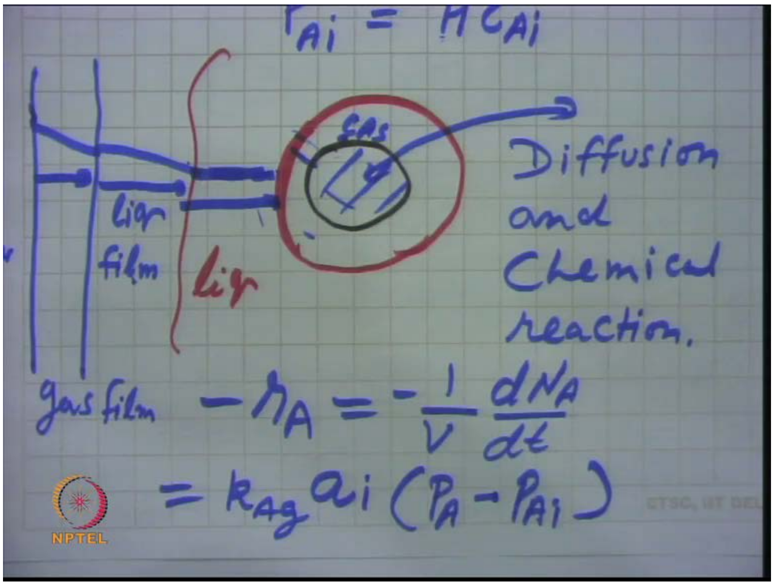

$$p_{Ai} = H C_{Ai}$$

$$-r_A = -\frac{1}{V}\frac{dN_A}{dt}$$

$$= k_{Ag} a_i (p_A - p_{Ai})$$

Sketch wise, if I just show you again; so, this is a solid catalyst, where you have a film of the liquid like this – a uniform size; and then, you have a bulk liquid. So, this is the bulk liquid and then you have a film of the liquid. So, I will say a kind of interface here. And so, this is the liquid film. So, liquid film here; and then, there is a film of the gas. So, gas comes from here to here like this. And then, this is a bulk gas. So, this is a bulk gas this side; so, gas. So, this is a gas film; this is a liquid film; and, from here it reaches to the bulk liquid. So, this is the same concentration throughout. But, when it reaches to this surface; so, again there is surrounded… The solid particles are surrounded by the liquid film. So, there will be a gradient. So, again there is a transport.

And then, in the porous structure, you have diffusion and chemical reaction here inside this. So, diffusion and chemical reaction. So, this is what the first step the mass transfer; which is a gas species from bulk gas to the gas liquid interface. So, from main body of the gas, it will come to the surface of the bulk, that is, the liquid film; that is, it is a film of the liquid: one side is the gas; other side is the liquid. So, that is the first step. So, it will depend on the mass transfer coefficient of this gas ((Refer Slide Time: 08:58)) It is a mass transfer coefficient – the area of the interface.

So, in the gas-liquid reaction as you know, the interfacial area is very important; same thing here, because it is a kind of the solubility of the gas into the liquid. So, it will depend governed by the Henry law and other experimental conditions. So, it is basically the interfacial area of the film; so, times the pressure that is P A or C A; so, partial pressure of gas A and minus the partial pressure of gas A at the interface. So, with this, these two points, which you are talking here; so, P A and P A i.

So, this is the first step, which is k A g times A i times P A minus P A I, which is the transfer or rate of reaction, which can be written in terms of minus 1 upon V d N A by dt, because all the time, we are writing minus r A is equal to minus 1 upon V d N A by dt. So, this is per unit volume of the liquid – bulk liquid. So, the choice can be based on the volume of the liquid, which is, if it is slurry bubble column reactor, it can be defined per unit mass of the catalyst like in a trickle-bed reactor or volume of the catalyst. And, this is what the most transported. And, if I write it; so, this same thing is whatever you write here k A g times the interfacial area; it may be per unit volume of the same unit – liquid times the pressure difference P A in the bulk minus P A i, which is at the interface.

And, because a steady state, all these rates are equal. So, whatever the molecules transports from here to here, the same molecule will come to this film and same will go here in this; diffused to that and react chemically. So, this is the rate of reaction. The only thing is that, depending upon the resistances offered by each, you have summation of all these resistances, because these are acting in series. So, one needs to minimize these resistances depending upon the severity or depending upon the system, that is, trickle-bed reactor system or slurry bubble column reactor. So, you have to select a system whether the gas film resistance is very high or liquid film resistance is very high or the diffusion and chemical reaction in a pore of a catalyst is very high.

Does the diffusion and chemical reaction control the rate? Obviously, you would like to have a smaller particles. If the liquid side resistance or gas side resistance is dominating, then obviously, one would like to have a bubble column reactor or a slurry bubble column reactor – large volume of liquid or large interfacial area. So, a good kind of a sparger design, where you should have a small gas bubbles diffused to that depending upon the solubility of the gas.

So, all these design will be important; a kind of a sparger, good kind of a sparger, good kind of agitating system, the catalyst particle size. So, everything is important, because you need to minimize all these resistances. So, this is first step. In the second step again, as I said from here to here; so, second step is mass transfer of gas A from the interface –

gas-liquid interface to the bulk liquid. So, you have a gas film; you have a liquid film. So, liquid from here; it reaches to the bulk liquid. So, that is the second step. So, k A l, which is the mass transfer coefficient in that liquid film.

A i is again interfacial areas – same interfacial area. C A i is now concentration of gas A at the interface, which can be related to P A i by P A i is equal to H A times C A i. So, one can write the Henry law – P A i is equal to H – Henry law constant times C A i. So, that will decide the… Depending upon the solubility of the gas, the concentration of gas in the liquid will be different. And, you have to look at accordingly a good kind of design or selection of a good kind of contacting pattern. So, once this happens, the gas reaches to this bulk; then, there is a transfer of A. So, mainly, it is B is already there. So, I am talking that, transfer of A from the bulk liquid to the external surface of the solid. So, this is a solid covered by a film of liquid. So, there is a transport. So, this is the third step.

And, this will depend… What is the mass transfer? It will depend on the size of the solid. So, simply this k c – a mass transfer coefficient, which is here at the surface of the solid; a c is now based on surface area of the catalyst per unit volume of the catalyst, or surface area of the catalyst per unit mass of the catalyst. So, either units can be used; and accordingly, the total rate can be calculated. So, here if you define based on this, it is per unit volume of the liquid.

So, C A i which is again here – the concentration at the interface minus C A s; where, C A s is the concentration of A at the surface of the solid. So, C A s is here at this point; the concentration is C A s. So, if the solid is non-porous, this will react here on it. But, if it is a porous material; so, now, this will diffuse from here to internal surface. So, again there will be a kind of concentration gradient. So, this is what the step. I already said that, B – we are assuming is already there; if it is not there, then B will also diffuse.

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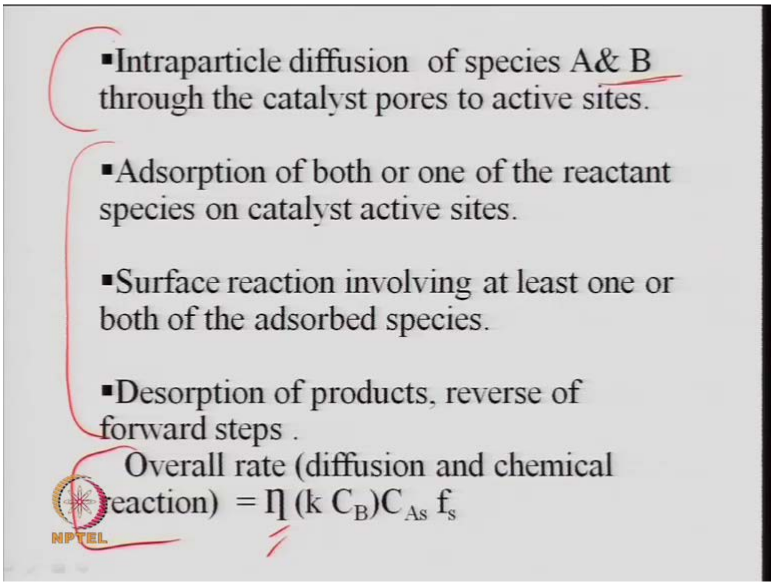

- Intraparticle diffusion of species A& B through the catalyst pores to active sites.
- Adsorption of both or one of the reactant species on catalyst active sites.
- Surface reaction involving at least one or both of the adsorbed species.
- Desorption of products, reverse of forward steps .

Overall rate (diffusion and chemical eaction) $= \eta\,(k\,C_B)C_{As}\,f_s$

So, intraparticle diffusion of reactant species, that is, mainly here A through the catalyst pore to the active site. So, again one needs to find out the pellet effectiveness factor. So, pellet effectiveness factor will be based on whatever the Thiele modulus. Thiele modulus will depend on the size of the catalyst particle. So, all these factors, what we have learnt before – these will be utilized here also, because the effectiveness factor is very important and we need to control that; that is, we need to basically maximize that or approach should towards the one if there are ((Refer Slide Time: 15:41)) diffusion resistances.

So, try to minimize that. Adsorption of both or one reactant on the surface of the catalyst; so, these three steps your adsorption surface reaction and desorption are related to the kinetic step. So, that is basically once the reactant reaches to the internal surface of a pore; now, it will be a chemical reaction at the surface. So, chemical reaction at the surface means we have already discussed that, the reactant species suppose A gas; it adsorbs on the active side and make something like AX, which is the adsorption step.

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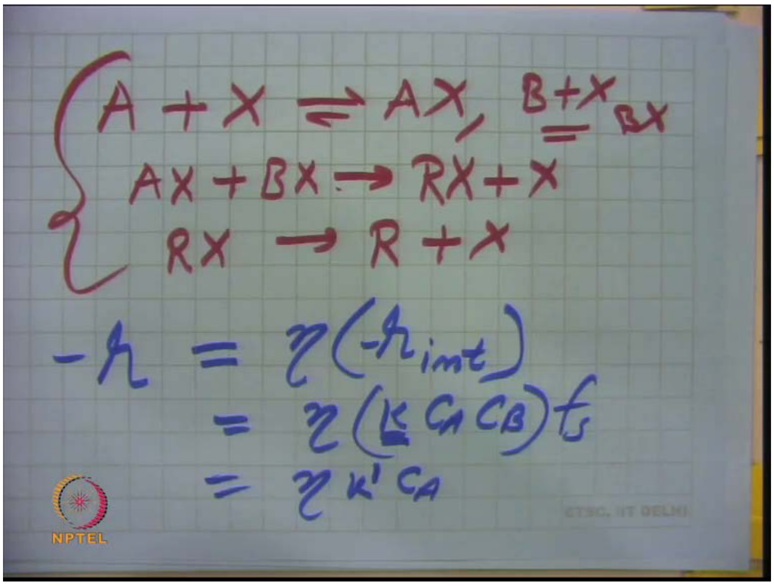

$$\begin{cases} A + X \rightleftharpoons AX, \quad B + X \rightleftharpoons BX \\ AX + BX \rightarrow RX + X \\ RX \rightarrow R + X \end{cases}$$

$$-r = \eta(-r_{int})$$
$$= \eta(k C_A C_B) f_s$$
$$= \eta k' C_A$$

And, same thing that the AX, which is already adsorbed, now, will react with liquid B and transform it into a product. So, that is a kind of surface reaction. So, either A is adsorbing or B is also adsorbing. So, both possibilities are there. So, these also adsorbing; you need to write B plus X is equal to BX like this. A plus B – these are the reactants. And then, product is forming. So, the product is forming; then, you have just like something like if I say R is the product, and then it may be adsorbed species and plus 1 vacant side. And then, this RX will desorb and will give you a product R and another vacant side.

So, this is what we discussed before in the kinetics of the catalytic reaction – heterogeneous catalytic. So, these steps will take place. And finally, you have a product. So, all these: one – diffusion and the chemical reaction – they can be clubbed together. And, one can write these diffusion effects in terms of effectiveness factor. So, eta is the pellet effectiveness factors. So, what is written here; if I write this, the overall rate because of diffusion in chemical reaction is equal to whatever the eta times the rate for the main reaction, because this is contributing the diffusion. So, eta times – I will write it r intrinsic; that is, in the absence of diffusion resistance.

And, that r intrinsic can be determined from Langmuir model; but, we have written here or it can be determined based on the overall power-law model also. So, here if you assume that, it is simply eta times k times C A times C B; suppose first order with respect to A; and, first order with respect to B. And… So, this is the rate of reaction per unit volume of the catalyst or per unit mass of the solid. If you write it per unit mass of the solid, then it should be multiplied by a fraction of the solid present in this bed.

So, that is the additional term, which you see here, is only when we are calculating the rate of reaction, because it is based on the mass of the catalyst or volume of the… So, fraction of the catalyst or solid in the bed. Or, one can write in terms of the mass or concentration of the catalyst mass per unit volume of the catalyst especially when you have a bubble column reactor or slurry bubble column reactor, where catalyst concentration is also important. So, the mass of the catalyst will come here, because we are calculating a total rate of reaction or total moles, which have been transported. So, this is per unit volume choice; choice is used; that will decide based on the unit of the small k, which is written here. So, per unit volume or per unit mass fraction of the catalyst.

C A and C B; C A is the concentration of A. If I say that, C B is already present. So, I can write this eta times some constant k dash and C A. And, most of the time, in trickle-bed reactor, we assume that, it is a kind of first-order kinetics. So, whatever the defense; that can be taken care by the unit of k dash or in the value of k dash. So, if you look at all these steps; as I said here, at steady state, all these rates are equal, because whatever the moles, which have been transported like this from the surface like this, the same moles are transporting and diffusing and reacting chemically.

So, it means this value k A g P A minus P A i will also be equal to this value. Just you have to take care of the units; per unit volume – multiplied by the volume of liquid per unit mass – multiplied by the mass of the catalyst. So, the unit consistency needs to be checked. And then, all these rates are equal in this reaction. And, if this is the case, then very easily you can derive the expression, which is written here in this form. So, what you have to do simply, because these are indicating all these steps are in series. So, k A g times A i times P A minus P A i will be equal to k A l, which I defined earlier times C A minus C A i minus C A l. So, that is what the step I can write here again for you.

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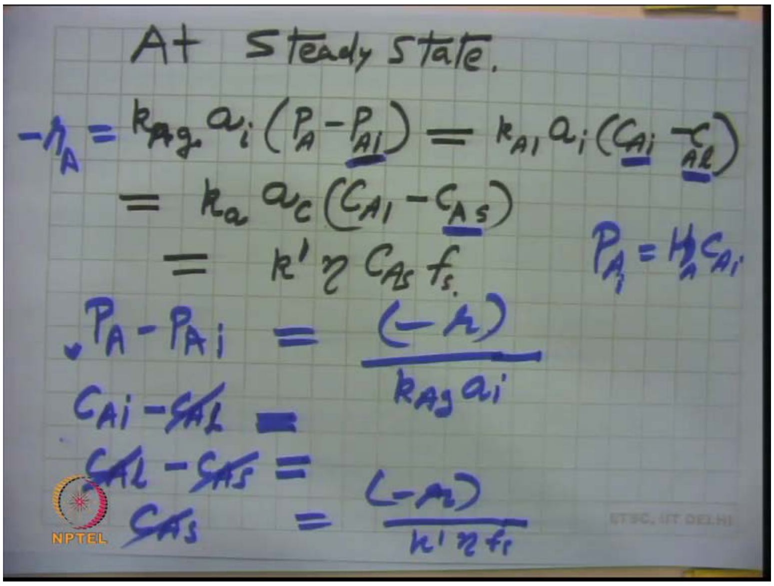

At steady state.

$$-r_A = k_{Ag} a_i (P_A - P_{Ai}) = k_{Al} a_i (C_{Ai} - C_{Al})$$

$$= k_a a_c (C_{Al} - C_{As})$$

$$= k' \eta C_{As} f_s.$$

$$P_{Ai} = H_A C_{Ai}$$

$$P_A - P_{Ai} = \frac{(-r_A)}{k_{Ag} a_i}$$

$$C_{Ai} - \cancel{C_{Al}} =$$

$$\cancel{C_{Al}} - \cancel{C_{As}} =$$

$$\cancel{C_{As}} = \frac{(-r_A)}{k' \eta f_s}$$

So, in that form; so, k A g, which is the mass transfer coefficient on the gas side times a i, which is interfacial area times P A minus P A i. This is the first step; will be equal to k A l times a i – again interfacial area times C A i minus C A l; which is the transfer from interface to the liquid face; so, will also be equal to… because these steps are in series. So, whatever the moles transferred because of this, these moles will go to the liquid and they will diffuse to the external surface of the solid. So, whatever k a – small a at the surface of the solid – times small surface area of the catalyst per unit volume or mass times C A l minus C A s – transport to the surface of the solid. And then, there is a diffusion and chemical reaction.

So, k dash times eta times C A s. Or, if you need, you can write this fraction of the solid. So, all these rates are equal at steady state. So, one can simplify this, because one can eliminate these intermediates. So, this P A i – all these – P A i, C A i, C A l and C A s are to be eliminated from the overall rate equation. So, basic idea is that, this is equal to this; this is equal to this; this is equal to this. So, you just make the equation – different set of equation and then eliminate. So, one can very easily write it like this.

So, P A minus P A i from the first expression; which is minus r A – if I write minus r A in any convenient unit, per unit volume or per unit mass can be written like this. So, what I mean to say; P A i – P A minus P A i is simply minus r A, which is the volume N A in one way – total most reactant if I calculate on any convenient unit. So, multiply by the volume or whatever and divide by – you will have here k A g times a I – something like this. Similarly, in the second case, you will have C A i minus C A l. In third case, you have C A l minus C A s. And, in fourth case, you have C A s is equal to again minus r divide by k dash times eta times f s – something like this. So, you can write this step; you can write this step yourself.

So, what I mean to say if I… C A i and P A i are related by Henry law. So, I can write this either P A i in terms of C A or I can write this C A i in terms of P A. And then, divide it. So, the Henry law constant will also come in the denominator in all cases. So, basic idea is that, if I add all these, these terms will be canceled. So, add 1, 2, 3, 4 – all four equations. So, you have what left? P A here. So, P A is equal to… This r is common. And, the term… The rest of the term will go in the bracket; which is representing nothing but combined resistance. So, one can very easily write the P A is equal to H A, that is, at the interface. So, P A i – H A times C A i. So, C A i – simply can be written in the form of any convenient unit of Henry law constant.

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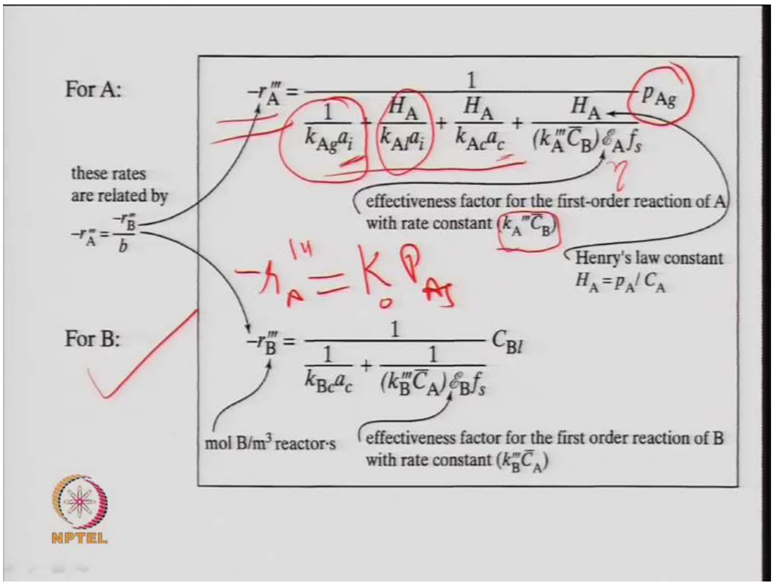

For A:

$$-r_A''' = \frac{1}{\frac{1}{k_{Ag}a_i} + \frac{H_A}{k_{Al}a_i} + \frac{H_A}{k_{Ac}a_c} + \frac{H_A}{(k_A'''\bar{C}_B)\mathscr{E}_A f_s}} p_{Ag}$$

η

effectiveness factor for the first-order reaction of A with rate constant $(k_A'''\bar{C}_B)$

Henry's law constant $H_A = p_A / C_A$

these rates are related by $-r_A''' = \frac{-r_B'''}{b}$

$-r_A''' = K_o P_{Ag}$

For B:

$$-r_B''' = \frac{1}{\frac{1}{k_{Bc}a_c} + \frac{1}{(k_B'''\bar{C}_A)\mathscr{E}_B f_s}} C_{Bl}$$

mol B/m³ reactor·s

effectiveness factor for the first order reaction of B with rate constant $(k_B'''\bar{C}_A)$

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And, if you do that and add this; so, here the rate of reaction per unit volume is mentioned for A – r A triple dash, which is simply now, PA g, which is PA gas phase concentration – a known value – at the inlet, a gas phase concentration – total pressure into mole fraction of that gas. So, this is known to you. And, the rest of the terms are representing… This is the resistance in the gas film; this is the resistance in the liquid film; this is a kind of resistance for mass transfer from the bulk liquid to the external surface of the solid; and, this is the resistance, which is offered because of diffusion and chemical reaction.

So, what do you see from this? If you add all these, you have this expression, which is minus r times 1 upon k A g a i. Here it is again 1 upon k a l a i times Henry law; which has gone to the numerator side. So, you can very easily write this expression and then you have the expression for the overall rate. So, now, which step is dominating? Will depend whether the mass transfer coefficient is very high; liquid side mass transfer coefficient is very high; surface of the solid, that is, mass transfer coefficient at the surface of the solid is very high; or, this chemical reaction constant is very high. So, it means by having the suitable temperature, by selecting a proper catalyst size, these two can be controlled. So, you have a good kind of catalyst particle size; diffusion is one – porosity of the particle; and, kinetics is there. So, temperature of the particle… So, resistances can be controlled.

Same thing on this side also; if you look at k A g and k A l – they depend again of the size of the bubble – gas bubble and a kind of stirrer design. So, basically, it is interfacial area per unit volume. So, small sized bubbles you need to have in the reactor if you have a bubble column reactor. So, that is the mass transfer coefficient. This will be a function based and can be calculated depending upon the hydrodynamic steady. So, one can do the hydrodynamic steady and one can find out the mass transfer coefficient. And accordingly, again the interfacial film thickness; which is as I said, just simple example – smaller the bubble.

So, if you have bubble column reactor, you design a good kind of sparger. Same thing – for the trickle-bed reactor, you need to design a good kind of distributor. So, that is k A g, k A l, which are related to the empirical formulas. Or, can be calculated depending upon the hydrodynamics. And, one can control these or one can maximize the coefficient or minimize these resistances, because these are nothing but the resistances offered by each step.

And, this step is the overall resistances. So, here this eta is represented by this. So, effectiveness factor for the first-order reaction with respect to a rate constant, which is taken a pseudo first-order rate. So, rate constant times the concentration of B. We have assumed that, B is in excess. And, H A is related to the Henry law constant as I said. So, P A is equal to H A times C A. And again, depending upon the solubility of the gas; so, as I said, if the gas is highly soluble, its Henry law constant is low. If a gas is sparingly soluble, that is very difficult to dissolve in the liquid; then, its Henry law constant will be very high. So, one can again design the system depending upon the solubility of the gas or give the high pressure, because at high pressure, the solubility will be high. And, there is always a relationship between the rates.

So, I told you that, r A upon A is equal to r B upon B. So, it will depend on the stoichiometric coefficient. So, one can very easily write that, if this much moles of A reacted, how many moles of B will react; one can very easily write down the expression for that also. So, so just one is sufficient, because in design equation, generally, we write the rate of reaction based on limiting component; and, one can very easily write down the reactor design equation, because this is the rate equation.

And, when you have a trickle-bed reactor, it will behave like a plug flow reactor. If you have a slurry bubble column reactor, you can resemble it to like a CSTR. So, you can have the overall volume of the reactor required or mass of the catalyst required for a given conversion. So, most of these liquid phase reaction – hydrogenation of the vegetable oils; and, they are generally carried out in the bubble column reactor. And, if there is a ((Refer Slide Time: 30:12)) catalyst in that; so, you have a slurry bubble column reactor.

So, you have a concentration of catalyst, which is important there; that is, how much mass, which you call catalyst loading there; mass of the catalyst per unit volume of the solution basically – volume of the reactor. So, that is very important. And, second thing is that, the size of this catalyst particle. That is again important, because these are offering a kind of resistance. So, smaller particle size will be preferred, because effectiveness factor will be higher when the particles are smaller in size. This is one thing. Same thing – if you have the gas, which is being bubbled – you should have small bubble size. And then, you need to have a good kind of sparger there.

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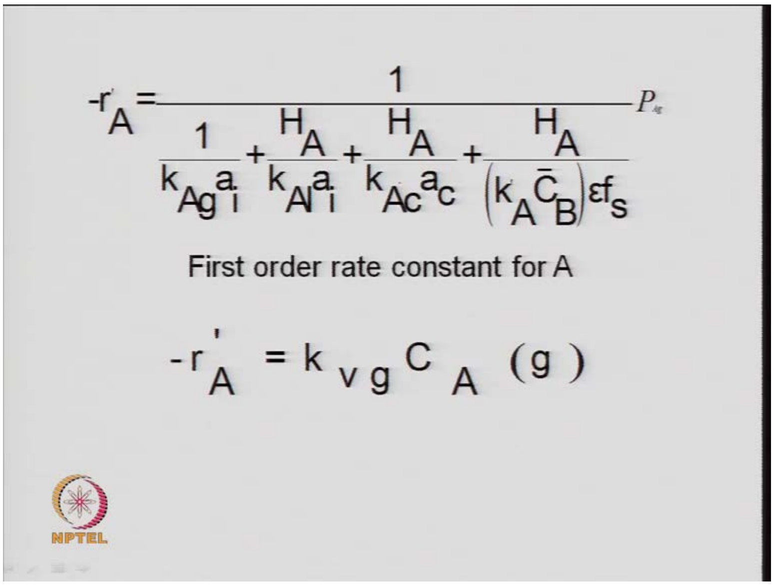

$$-r'_A = \frac{1}{\frac{1}{k_{Ag} a_i} + \frac{H_A}{k_{Al} a_i} + \frac{H_A}{k_{Ac} a_c} + \frac{H_A}{\left(k_A \bar{C}_B\right) \varepsilon f_s}} P_{Ag}$$

First order rate constant for A

$$-r'_A = k_{vg} C_A (g)$$

So, same expression is written here in terms of that. But, I have already talked if you write it in terms of per unit mass of the catalyst. So, only the overall rate constant. So, sometime, these all terms, which is written together here; we can write it in terms of the… because 1 upon 1 upon this plus this plus this plus this; this is representing the overall rate constant for the reaction. So, I can write it like this – minus r A triple dash is equal to capital K – some overall rate constant times whatever P A g – a kind of overall first-order rate; where, this is contributing to all resistances. So, if this is negligible, this is negligible; this is negligible; you are just like a kinetic rate; so, in terms of the concentrations.

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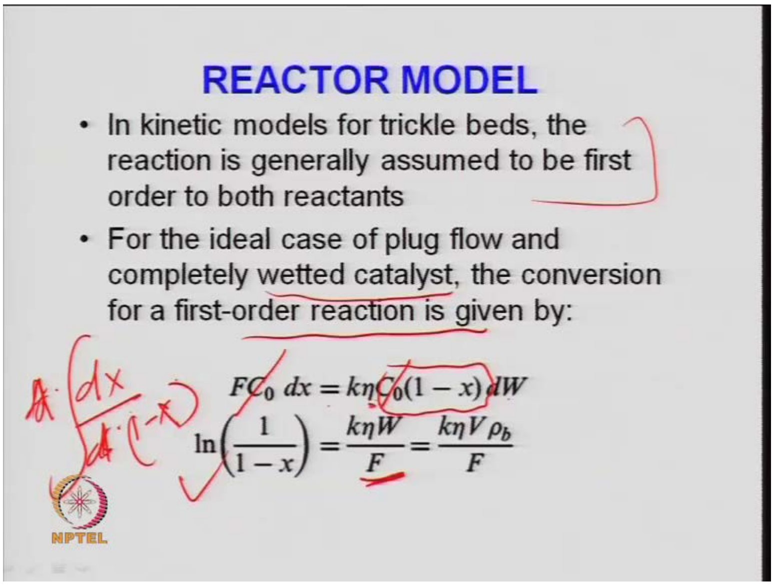

REACTOR MODEL

- In kinetic models for trickle beds, the reaction is generally assumed to be first order to both reactants
- For the ideal case of plug flow and completely wetted catalyst, the conversion for a first-order reaction is given by:

$$F C_0\, dx = k\eta C_0 (1-x)\, dW$$

$$\ln\left(\frac{1}{1-x}\right) = \frac{k\eta W}{F} = \frac{k\eta V \rho_b}{F}$$

So, when you do the reactor modeling; so, first thing is that, you have to look at the hydrodynamics of the reactor in the case of multi-phase reactor; very important. And, from that, you have to find out the resistance; then, you identify the overall rate of reaction. And, once the rate of reaction is known, then one can go for the sizing a reactor. So, this is what is done in the trickle-bed reactor also. So, a kinetic model for a trickle-bed reactor is generally assumed a first-order with respect to both reactants. So, generally, liquid is already there in the bed.

So, liquid is in excess. So, we make it a pseudo first-order rate. So, if the reactor is ideal and the catalysts is completely wetted, most of the time, the wetting efficiency here – it comes out to be one for the complete wetted surface. The conversion in a first-order reaction as usual you know that, F A naught dx is equal to minus r A dash dW. So, all of you know this design equation. So, a reactor design equation for a plug flow reactor.

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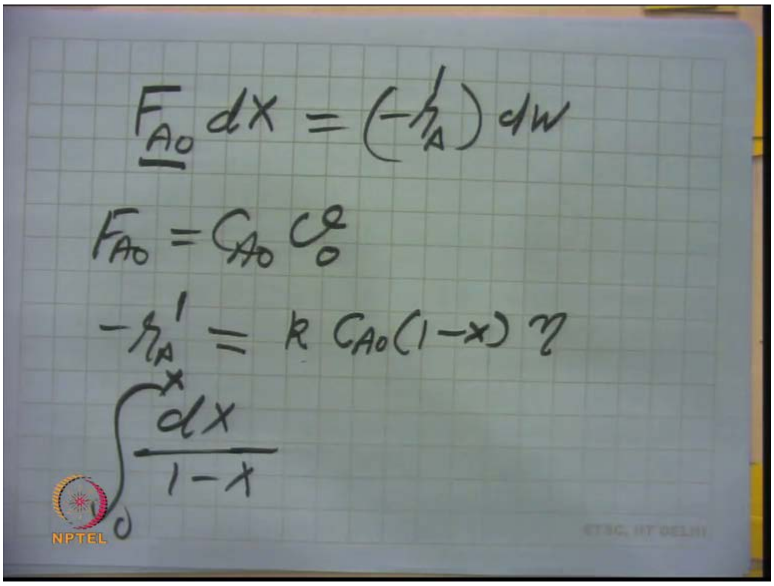

$$\underline{F_{A0}}\, dX = (-r_A)\, dW$$

$$F_{A0} = C_{A0}\, v_0$$

$$-r_A' = k\, C_{A0}(1-X)\, \eta$$

$$\int_0^X \frac{dX}{1-X}$$

So, F A naught if I write in terms of molar feed rate times dX for a differential element is equal to minus r A either you write it in terms of per unit mass or per unit volume; so, here it is written per unit mass times dW; where, dW is the mass of the catalyst in the bed. And, the mass of the catalyst in the bed can be written in terms of the density of the catalyst and times the volume of the catalyst. So, r A dash can be… This can be written in terms of r A triple dash into dV also. So, in the… Here we just reported it in terms of r A triple dash. But, always you can write the expression as I said, just by relating it with the density of the catalyst. So, this is the same expression, which is written here; where, F A naught is simply C A naught into v naught. So, C A… F A naught is molar feed rate. So, F A naught is related to the concentration of A and the volumetric feed rate. So, this is the volumetric feed rate. So, one can write in that form also.

And, this minus r A dash, which I was talking in terms of mass of the catalyst; so, there k will convert to something like a k dash, that is, based on the mass unit and if there is a diffusion limitation. So, intrinsic rate, which is k times C A. So, C A will be nothing but C A naught 1 minus X. So, basically, this thing, which is written here C naught is the C A naught – concentration of A at the inlet. And, this is here; it is written in terms of the volumetric feed rate; which is same expression here; and, k times rate constant times the effectiveness factor times the concentration, which is related to at any point. So, this is C A naught 1 minus X A. So, X is the fractional conversion. So, this data is simply in terms of the intrinsic kinetic.

So, since there may be a diffusion limitation; so, we have introduced eta into effectiveness factor; which is for isothermal case always less than 1. So, this is the effectiveness factor in the pellet. So, this is again a simple first-order rate. So, one can very easily integrate this by writing dx upon 1 minus x; and, this side, it is 0 to W dW – total mass of the catalyst required or volume of the catalyst required in the reactor.

So, this is simply dx divided by 1 minus x and integrate it from 0 to x. And, this side, it is 0 to W dW, because all other terms are constant at one temperature. So, if you integrate this dx upon 1 minus x, it will be simply log of 1 over 1 minus x. So, this is the integration of dx. So, whatever you have dx divided by 1 minus x. So, I will write it dx over 1 minus x – something like this; and, integrate it over that. So, something like this.

So, here if I write it dx over 1 minus x is this; and, limit is 0 to x. This is the term, which is here. And, integration of this is here; which is simply ln of 1 over 1 minus x. And, this rest of the terms have been taken to the other side. So, you have k; you have eta; integration 0 to W is W divided by F. So, C naught C naught gets canceled. So, these two terms, which is here written; F A naught is C A naught into v naught. But, here it is written only in terms of the volumetric flow rate. So, this gets canceled here. So, this equation C naught and C naught – both are common. So, this gets canceled here. So, finally, you have k, eta, and this is W now – divided by F. And, one can write it, because this W is nothing but the bulk density of the catalyst into volume of reactor. So, what is the…

The actual size of the reactor will depend on the bed porosity – void bed fraction. When I write it bulk density, it is nothing but the actual density of the catalyst plus whatever the void fraction term. So, basically, in terms of the volume, if I write the reactor; so, volume of reactor is not only the volume of catalyst plus the total void volume of the bed – bed volume in terms of the void fraction of the bed. So, that will increase the size of the reactor. So, this is actually the same expression, what you have seen here. And, one can write it in terms of the mass feed rate or the volumetric feed rate also.

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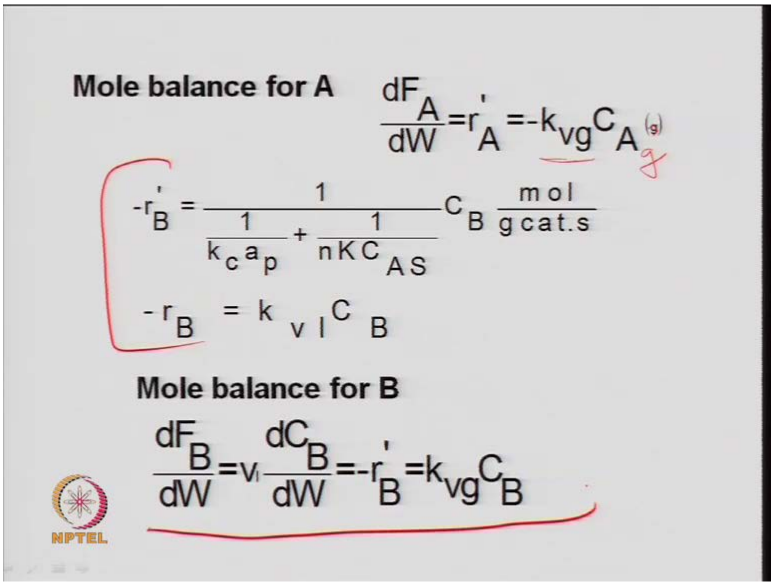

Mole balance for A $\frac{dF_A}{dW} = r'_A = -\underline{k_{vg}} C_{A_{(g)}}$ g

$$-r'_B = \frac{1}{\frac{1}{k_c a_p} + \frac{1}{nKC_{AS}}} C_B \; \frac{mol}{g\,cat.s}$$

$$-r_B = k_{vl} C_B$$

Mole balance for B

$$\frac{dF_B}{dW} = v_l \frac{dC_B}{dW} = -r'_B = k_{vg} C_B$$

So, the same expression I have been reported or has been reported here in terms of d F A by dW, which is equal to r A dash based on per unit mass of the catalyst. And, this we have defined in terms of the overall rate constant for the reaction times the concentration of A in the gas phase – bulk concentration whether you write in terms of the partial pressure or concentration, no problem; only this unit will change accordingly. So, we have written already in terms of r B relationship.

So, one can write in this form also, which is not required here, because this is simple design, which we have already done earlier. F A naught and F B naught are interrelated; simply, minus r A and minus r B are interrelated. And, that has been done here in this form when you write it in the form of B also, because you know what is d F A and what is d F B based on the stoichiometry. So, F A is F A naught 1 minus x A. And, if you write it in terms of the B, they are taken in the stoichiometry ratio; equal number of moles of B will react. So, one can write it in terms of that also. So, either ways… But, generally, it is advisable to use the limiting component. No limiting component, then one component can be written with the stoichiometry 1; and then, one can solve the expression.

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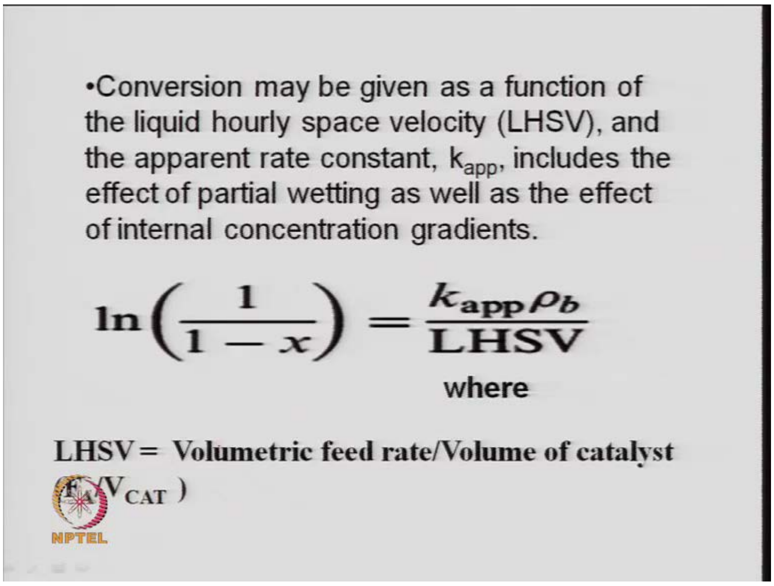

- Conversion may be given as a function of the liquid hourly space velocity (LHSV), and the apparent rate constant, k_{app}, includes the effect of partial wetting as well as the effect of internal concentration gradients.

$$\ln\left(\frac{1}{1-x}\right) = \frac{k_{app}\rho_b}{LHSV}$$

where

LHSV = Volumetric feed rate/Volume of catalyst (F_A/V_{CAT})

So, the expression has been shown what we have discussed earlier. I am not going in ((Refer Slide Time: 38:59)). So, sometimes we call it liquid hourly space velocity. So, liquid hourly space velocity is related to something – the volume of the catalyst in the bed, that is… and the volumetric feed rate. So, just like the space time, which we have defined or weight hourly space time sometimes – W by F A naught as I discussed earlier.

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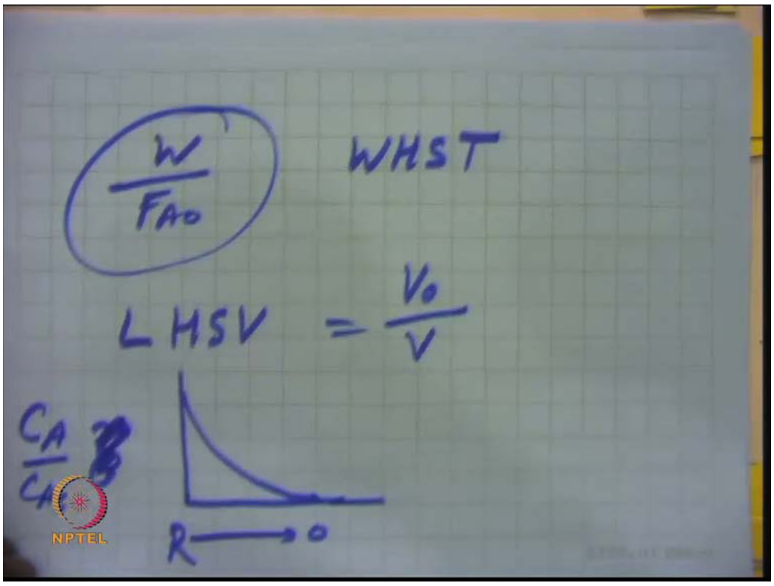

So, this term, which is here – W by F A naught; so, that we defined weight hourly space time. So, I can write it WHST. But, most of the time, in the case of trickle-bed reactor, it is defined based on the LHSV; that is, the feed, which is at the entering condition is the liquid. Or, sometime, we can define gas hourly space velocity also. So, liquid hourly space velocity means the reverse of this. And, only thing that, now, you are defining in terms of the volumetric feed rate of the liquid. So, volumetric feed rate of the liquid – if I write it by V naught divided by the volume of a reactor, which is… or mass of the catalysts in the bed. So, here it is defined in terms of the volumetric feed rate divided by the volume of catalyst.

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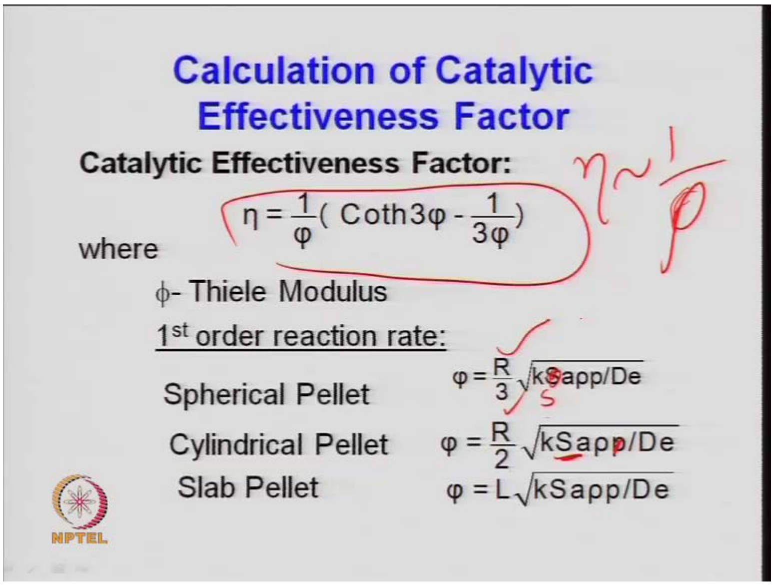

Calculation of Catalytic Effectiveness Factor

Catalytic Effectiveness Factor:

$$\eta = \frac{1}{\varphi}\left(\operatorname{Coth}3\varphi - \frac{1}{3\varphi}\right) \qquad \eta \sim \frac{1}{\phi}$$

where

ϕ- Thiele Modulus

1st order reaction rate:

Spherical Pellet $\varphi = \frac{R}{3}\sqrt{kSapp/De}$

Cylindrical Pellet $\varphi = \frac{R}{2}\sqrt{kSapp/De}$

Slab Pellet $\varphi = L\sqrt{kSapp/De}$

Effectiveness factor because the equation or expression has the effectiveness factor. So, that is also equally important when you want to look at the design aspect. So, theoretically, we would like to have effectiveness factor 1. So, no diffusion limitation at the surface of the catalyst or internal; when we look at the pore diffusion resistance, we would like to have maximum concentration, because the effectiveness factor will decrease the concentration to some value like this if the eta is very high; eta – if you look at here. Or, I will say that, rather writing eta, I will write C A by C A s. And, this is the distance from the… if I say R; and, here it is the center 0.

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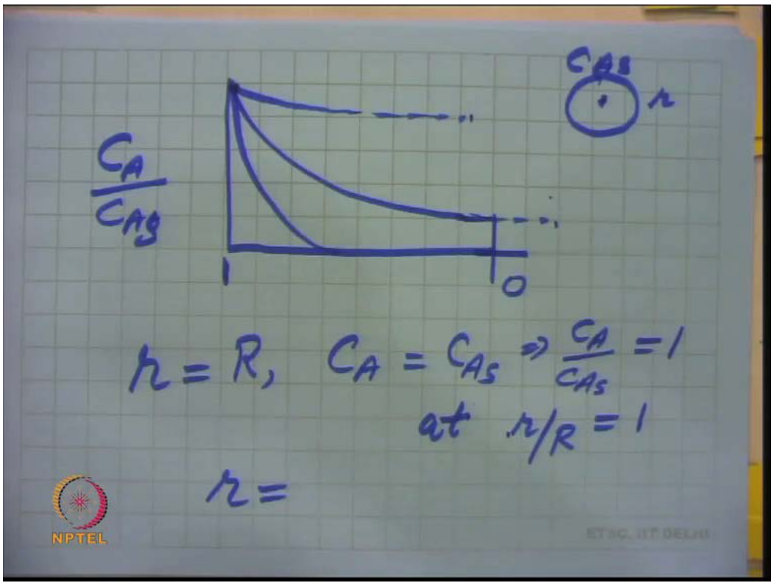

$r = R,\ C_A = C_{As} \Rightarrow \frac{C_A}{C_{As}} = 1$

at $r/R = 1$

$r =$

So, to be something like this, which we have discussed earlier in the pellet; that is, C A by C A s – the concentration at the surface right of the solid. So, the C A s is here; and, C A is talking at the center of the pellet. So, when you have… If I write it in the form of dimensionless form; so, I can write here r is equal to capital R; boundary condition if you write; at r is equal to capital R, C A is equal to C A s. So, C A by C A s will be 1. C A by C A s is equal to 1 at… If I define the dimensionless concentration, r by R, that is, r by capital R as 1.

So, this is the point 1. So, here you have the concentration 1; and then, r is equal to… Suppose if you have the center; there can be a symmetry. So, d C A by d r 0 here at the center; or, basically, you will have a kind of gradient, because of symmetry. So, the concentration profile will go like this and reach… It will approach to 0 or a minimum at this point. So, this is something like… where, r is equal to 0 – center of the pellet; and then, you have a symmetry on both sides. So, this is important to find the concentration profile of the reactant material or limiting component that, a gas A in the pore of a catalyst.

So, theoretically, what we want? Theoretically, we want something like that; not too much drop; so, otherwise… Suppose the diffusion resistance is very high, then it may drop like this just at a half of the center or half of the distance, the concentration becomes 0. So, rest of the surface of the catalyst is wasted; we do not need that. So, this is very important. So, effectiveness factor or design of a good catalyst becomes very important in the case of trickle-bed reactor also. So, whether you look at the mass transfer resistance, you need to look at a definite size and shape of the catalyst, because you would like to have large interfacial area and the large surface area of the catalyst per unit volume – external surface area. And, that will depend on the shape of the particle, size of the particle. So, that is again important for the design of a catalyst particle.

So, simultaneously, for internal diffusion, you need to look at this factor – effectiveness factor; we have already discussed this. So, this effectiveness factor in general if I say, eta is… When you have a diffusion limitation, eta is going something like this – 1 upon phi – Thiele modulus. This is phi – Thiele modulus. If this is the case, for different cases, you have seen. So, phi is related to the size.

So, first thing is that, take a smaller particle if this is very large – size of the particle. And also, simultaneously, it depends on the rate constant and there are several… Actually, when you write it based on the volume, it is simply k by d for a first-order reaction. If you write it based on some surface area, based on mass, you have a different expression in that form; otherwise, it is same right. So, whatever this is a surface rate constant here; and, this is the density of the catalyst. So, k s times rho times De. Or, when you write it… because you know this relationship. So, that choice is yours.

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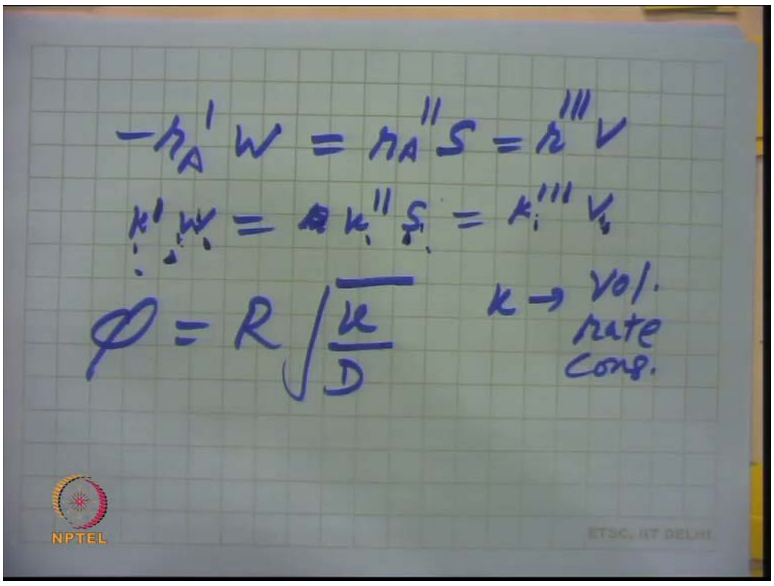

$$-r_A' W = r_A'' S = r''' V$$

$$k' W = k'' S = k''' V$$

$$\phi = R\sqrt{\frac{k}{D}}$$

k → vol. rate cons.

So, r A dash into mass of the catalyst is equal to r A double dash into surface area of the catalyst is equal to r A triple dash into volume of the catalyst. So, one can write the relationship, which is related to… So, it means k dash. So, the mass transfer… The rate of reaction based on the mass of the catalyst times W is equal to k double dash rate of reaction, which is based on surface area. So, k S also you write – times the surface area of the catalyst. So, sometimes, the surface area of the catalyst if you write – BET, which is meter square per gram; so, multiplied by the mass of the catalyst also here. And, that is equal to k triple dash, which is based on the volumetric rate constant times the volume. So, one can very easily write these relations.

So, k double dash S is simply k dash times W divide by s; that is, the mass of the catalyst divided by the surface area of the catalyst. Or, if you write k triple dash and V; so, k triple dash is equal to k double dash times S divided by V. So, generally this S if you write; based on the surface area, meter square per gram of the catalyst. So, here it will be per unit volume of the catalyst. So, this volume will be in the denominator. So, this becomes k times S times rho; BET surface area multiplied by that density of the catalyst. So, likewise, this is what the term written here. So, k double dash, which is surface area times the rate constant based on surface area times the density of the catalyst. So, it is basically the S, which is written, is the surface area of the catalyst and this is density of the catalyst basically divided by De.

So, one can write it or one can write this phi directly R under root of k by D; where, this k is based on volumetric rate constant. So, this is very simple to remember. So, this is based on volumetric rate constant. And, one can very easily convert this k from this relation. So, this is surface area of the catalyst; this is volume of the catalyst; and, this is mass of the catalyst. So, one can very easily… So, if I write mass per unit volume of catalyst; so, k triple dash can be written k dash times rho – density of the catalyst. So, one can write it k dash times rho also. Or, when you write it in terms of k S; so, k triple dash is k S times S divided by V. So, if I write S in terms of BET surface area, then S, which is meter square per gram and this is volume. So, that becomes density. So, surface area and the… So, surface area here given in meter square per gram and this is the density. So, the term should be dimensionless; that is important. That consistency of the unit should be checked in order to make this phi a dimensionless unit. D is the diffusion coefficient; all of you know. R is the size of the pellet. So, one can know that, for a spherical pellet, this is the definition – cylindrical pellet is R by 2 surface to volume ratio basically. And, slab – it is the characteristic length; that is, width of that slab.

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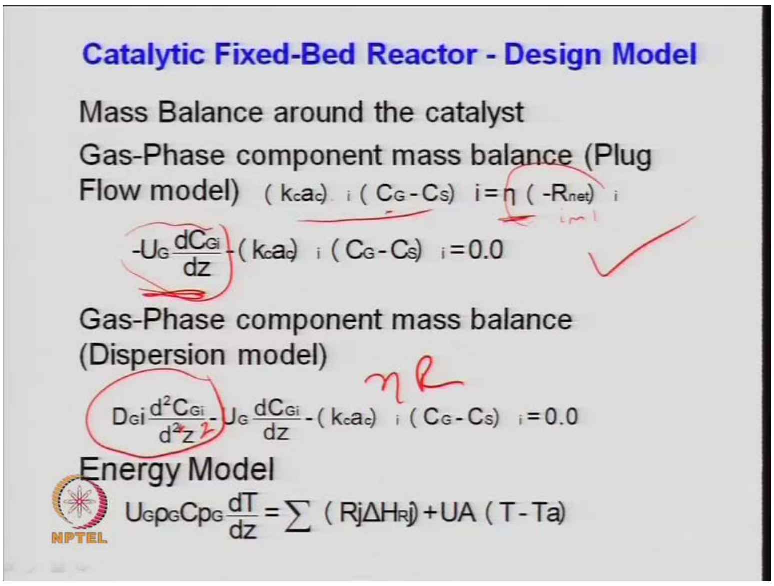

Catalytic Fixed-Bed Reactor - Design Model

Mass Balance around the catalyst

Gas-Phase component mass balance (Plug Flow model) $(k_c a_c)_i (C_G - C_S)_i = \eta(-R_{net})_i$

$$-U_G \frac{dC_{Gi}}{dz} - (k_c a_c)_i (C_G - C_S)_i = 0.0$$

Gas-Phase component mass balance (Dispersion model)

ηR

$$D_{Gi} \frac{d^2 C_{Gi}}{d^2 z} - U_G \frac{dC_{Gi}}{dz} - (k_c a_c)_i (C_G - C_S)_i = 0.0$$

Energy Model

$$U_G \rho_G C_{pG} \frac{dT}{dz} = \sum (R_j \Delta H_{Rj}) + UA(T - T_a)$$

So, this kind of expressions have been used. And then, reactor design models for defining what I have done earlier that, steady state – all these rates are equal; but, there can be the axial dispersion terms; there can be radial dispersion terms. So, depending upon the non-ideality parameter, which can be studied based on the hydrodynamic study or RTD study. So, by using these residence time distribution study in a multi-phase reactor, one can find out the value of non-ideal parameter, that is, axial dispersion coefficient in terms of the peclet number, in terms of dispersion number. And, these factors can be introduced when you write the moles in; moles in because of convection, moles in because of the dispersion term. And, there can be different kind of systems: open-open, close-close. These I am not going to discuss in this. But, one can write that boundary conditions also accordingly.

So, a simple mass balance as I discussed now that, whether you write the mass transfer or a chemical reaction at a steady state, all these rates are equal. So, whatever you need; the input minus output minus disappearance because of chemical reaction in a reactor at a steady state is 0. That is very standard design equation. Whether it is a fixed bed or multiple, the design equation will based on the mass balance and the energy balance. So, same thing – energy balance means energy input minus output minus disappearance because of chemical reaction. And, that is again at steady state if you talk is 0.

So, these steps have been discussed. So, something, where worst thing I told that, k c a c at the interface if I calculate – times C G – concentration in the gas phase – minus concentration at the surface of the solid. So, this is just a simple gas-solid reactor; just a simple packed-bed reactor, where you have a gas, you have a solid; and, gas is diffusing through that. So, C G is the concentration at the gas phase minus C S is the concentration at the surface of the solid.

And, at any point, if I just talk height of the reactor at any differential fraction; so, that will be the effectiveness factor – pellet effectiveness factor times the net rate. And, this net rate we got from the expression; that is what I wrote; at a steady state, all these rates are equal. So, eta times – basically, this is the intrinsic rate here measured at the surface condition. So, if you have an equation for reactor design; so, you know that, now, the input minus output minus disappearance because of chemical reaction, is equal to 0. So, the input, which we are writing here, is just because of the convective flow. So, F A z, which I have already discussed earlier.

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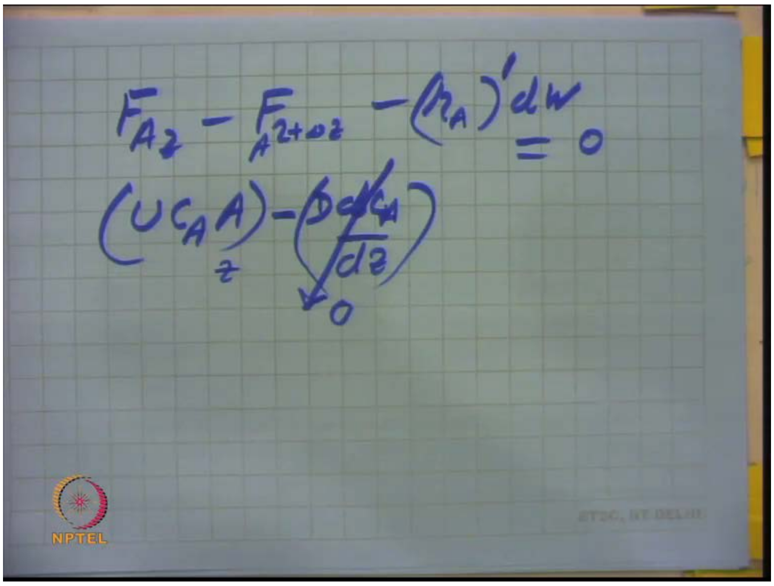

$$F_{A_z} - F_{A_{z+\Delta z}} - (r_A)' dW = 0$$

$$(uC_A A)_z - \cancelto{0}{\left(D\frac{dC_A}{dz}\right)}$$

So, F A at z minus the same thing F A at z plus delta z – input minus output minus disappearance because of chemical reaction r A dash in d W is equal to 0. All of you know this thing. So, now what is F A z? It is because of the convective term and because of the dispersive term. So, I told you earlier that, it is simply U times C A times the area of cross section of the bed. So, this is at z if I do not have any dispersion term. So, there is no dispersion term here. So, one can very easily… If there is a dispersion term, I will write plus minus or minus D d C A by dz. This is the axial dispersion term, which has been evaluated from the RTD study. So, most… So, this can say that, this is 0. Then, you have already this term. So, this thing at z and same thing evaluated at z plus delta z. Area of cross section is constant.

So, one can have the expression, which is related here, because this is given in terms of this W, which is mass of the catalyst. One can write in terms of the density of the catalyst and volume of the reactor. So, in that case, you have minus U G d C G by dz. This is the convective term because of that – convective. And, this is the disappearance, which has been written in terms of this, because this whole term is equal to this mass transfer – the same term. If there is the term mass transfer is the controlling, that rate is given by that. So, k c a c times C G minus C S at the surface. So, it is something like a non-porous catalyst pellet also; where, you have concentration at the gas phase, concentration at the surface. So, we can do it for the monoliths also or any non-porous solid catalyst. So, expression will come like this.

And, you should have a dispersion model, which I was talking just here. So, you will have additional term, which is because of dispersion. So, D d C A by dz at z and same thing will be evaluated at z plus delta z. So, ultimately, you get DG, which is the dispersion coefficient times d 2 C A by dz square. So, this is dz square here. And, other terms are similar – U G D G by dz. And, this is the third term, which is the reaction term. One can write either this equation or one can write eta times r also; both terms are same, because in steady state, both these rates are equal. So, this is what here.

And, the energy balance is also required. So, I told you that, heat input – it can be because of the convective transport. So, you need a kind of term MCP dt. It can be because of conduction also; then, you need lambda dt by dz, what we write here similar to that. So, you have the equations something like… And, plus heat generated because of endothermicity or exothermicity plus there may be some kind of cooling coil or heating coil. So, heat is supplied from the outside. So, all this terms may come there; and ultimately, if you write the heat balance equation, which you must have learnt before. So, heat is minus heat out minus heat disappeared because of chemical reaction or plus heat generated because of the chemical reaction. So, that will be the term.

And, if there is some heat added plus Q if I write; that is equal to 0, if there is no accumulation of heat within the system. So, U G P G times C P G dt by dz is sigma of all these heats because of chemical reaction for all reactions plus U times T minus T a. So, this is a simple energy balance, which you must have learnt during your other courses – heat balance, heat transfer courses. So, you can very easily write the balance – energy balance. And, one can find out the temperature profile from this equation, because the basic idea is that, when you have an exothermic reaction or endothermic reaction; so, for exothermic reaction, the heat will generate during the system. So, how much heat is to be removed from the system in order to maintain the reactor at isothermal condition; that is important. So, that is to be calculated. So, you need to provide a jacket along with some cooling device or cooling arrangement.

So, you need to find out. Or, you need to check what is the temperature profile; so, whether it is an isothermal operation or adiabatic operation; so, what will happen in the system when the heat is generated or heat is being released from the system or not; so, you need to check that. Or, simultaneously the endothermic – temperature will drop. If you want provide heat, then it will keep on dropping. So, performance will be affected. So, one needs to check that.

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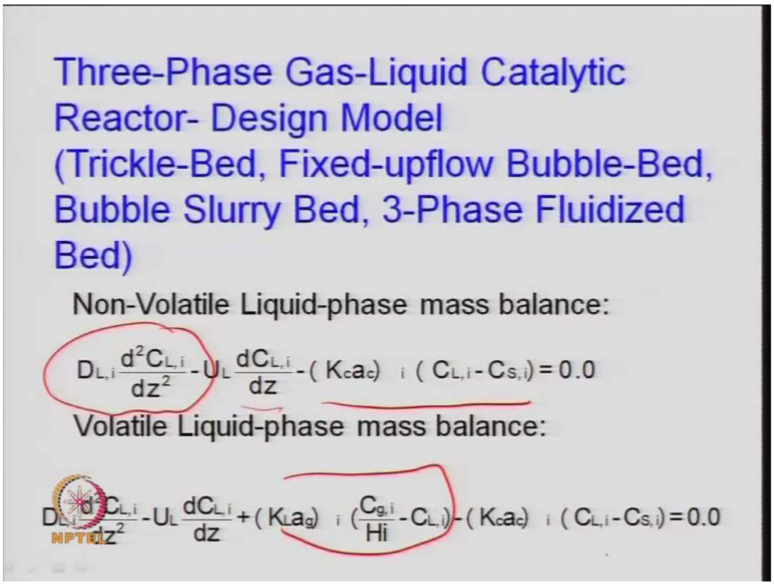

Three-Phase Gas-Liquid Catalytic Reactor- Design Model (Trickle-Bed, Fixed-upflow Bubble-Bed, Bubble Slurry Bed, 3-Phase Fluidized Bed)

Non-Volatile Liquid-phase mass balance:

$$D_{L,i}\frac{d^2C_{L,i}}{dz^2} - U_L\frac{dC_{L,i}}{dz} - (K_c a_c)_i\,(C_{L,i} - C_{S,i}) = 0.0$$

Volatile Liquid-phase mass balance:

$$D_{L,i}\frac{d^2C_{L,i}}{dz^2} - U_L\frac{dC_{L,i}}{dz} + (K_L a_g)_i\left(\frac{C_{g,i}}{H_i} - C_{L,i}\right) - (K_c a_c)_i\,(C_{L,i} - C_{S,i}) = 0.0$$

So, in general, if you look at the reactor design – a three-phase gas-liquid catalytic reactor design, which is a multi-phase reactor; so, whether it is trickle-bed, fixed-upflow, bubble flow, slurry, three-phase fluidized bed, I will take separately, just some basics of that. But, in general, if you look at, the expressions will remain same. So, this is the dispersion term. Here it is written axial dispersion term. So, this is the axial dispersion mass transfer; this is the convective mass transfer term, which we have already discussed; this is the chemical reaction term. This will be 0. So, basically, input minus output minus disappearance because of chemical reaction is equal to 0.

And, we are assuming that, liquid is not transferring into the gas. So, this is a mass transfer of a gas from the liquid, that is, bulk liquid and to the surface of the solid. So, basically, it is from bulk to the surface of the solid. And, if it is volatile, then you have to just contribute that, what is the loss of liquid into the vapor phase. So, you will have some additional term, which is here written in terms of the Henry law constant; so, when the liquid is partially transferring into the gas phase. So, what… That is the liquid transfer.

So far, we are not considering that. So, D – again the same term; this is again the same term – convective. And, this is what reported as because of the transfer of the material from liquid. So, liquid phase mass transfer coefficient. And, this is transferring into the gas and times whatever the P A minus P A i or in terms of the concentration Henry law. So, C G i minus C L. And, same thing for the… This term is common here again. So, I stop here and I will just continue it in my next lecture.

Thank you for today.