Chemical Reaction Engineering

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Lecture No. #31

Case Study- Hydrogenation of Oil

Friends, let us continue our discussion on the reaction reactor design case study number two, namely hydrogenation of oil. Now, last time we mentioned why hydrogenation of oil is important, and when you hydrogenate essentially the natural oils that you get have lot of di unsaturated fatty acids, and you do not want that anyone to hydrogenate it to get monounsaturated as well as saturated fatty acids.

Now, it turns out that as far as the final product is concerned, you do require some polyunsaturated fatty acids and that is from the health perspective. As well as you require some monosaturates as well from the consistency and higher melting point of view, which means that if we are trying to hydrogenate the di unsaturated to completely saturated that is not what our market demands, and so we have to keep that aspect in mind while designing the reactor.

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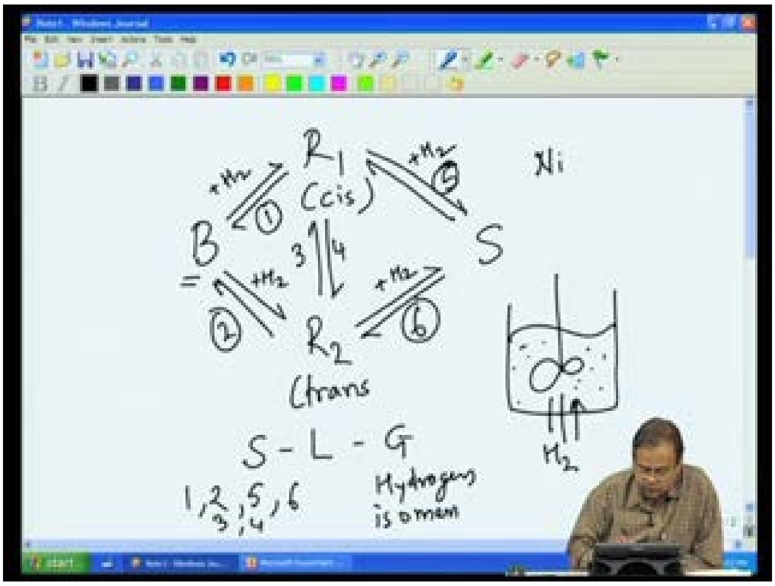

So, let us start our discussion by looking at what exactly is happening, when we are trying to hydrogenate this oil. So, we can represent our reaction scheme for example, let us say this is my diunsaturated B. So, in the first set of reactions that is where hydrogen is added we get mono unsaturated, and this is a cis form of mono unsaturated and we have a transform its isomer.

So, we have cis and trans. So, once again plus H 2 and there can be an isomerisation between these two forms and these in turn gets further hydrogenated. So, let us say plus H 2 to give fully saturated fatty acids. So, the species that are of interest to us are this B di unsaturated R 1 R 2 mono unsaturated fatty acids and S saturated fatty acids as well as hydrogen.

Now, I also mentioned that this reaction takes place in presence of catalyst and in nickel or nickel you know micron sized particles is often used as the catalyst. So, design of this reactor therefore, involves looking at solid liquid and gas reactor and slurry reactors are most commonly used or in other words we have a stirred tank reactor in which let us say oil is present.

A batch reactor we are talking about so there is no addition or removal of oil, but we are continuously bubbling hydrogen and there are catalyst, because of which this set of reactions is are taking place. So, now let us start our discussion on designing this reactor by looking at kinetics of this kinetics of this process. So, our first task is to develop the kinetics, not worrying about mass transfer at the present time and we will worry about the kinetic aspect.

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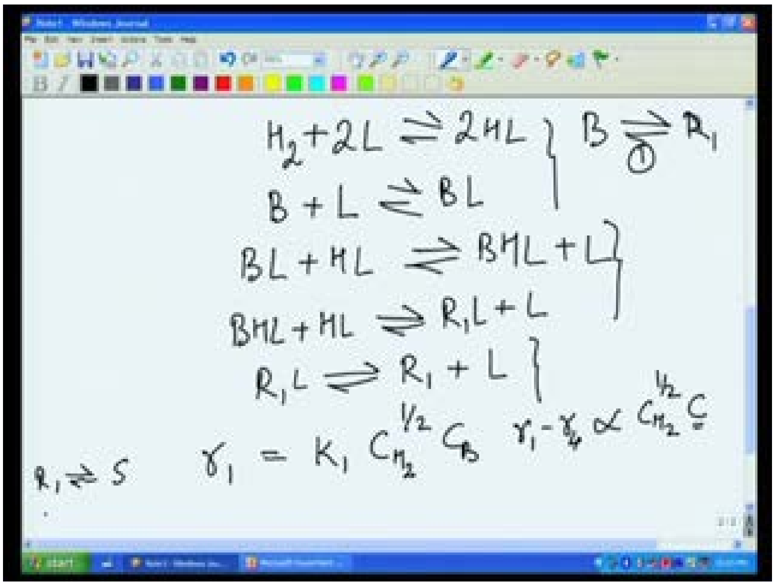

$H_2 + 2L \rightleftharpoons 2HL$

$B + L \rightleftharpoons BL$

$BL + HL \rightleftharpoons BHL + L$

$BHL + HL \rightleftharpoons R_1L + L$

$R_1L \rightleftharpoons R_1 + L$

$B \underset{①}{\rightleftharpoons} R_1$

$R_1 \rightleftharpoons S$

$r_1 = K_1 C_{H_2}^{1/2} C_B$

$r_1 - r_6 \propto C_{H_2}^{1/2} C$

So, the first step is for example, hydrogen gas. So, we will write our mechanism of the reaction and this is absorption with dissociation. So, on two active sides hydrogen molecule gets dissociated into atomic form and occupies each of the active side so H L. Similarly, we have let us say B plus L, B is our diunsaturate gives us B L, then B L plus H L gives us B H L plus L and B H L plus H L gives us the required product R 1 L plus L. R 1 L dissociates to form R 1 plus l.

So, what we are looking at is the individual reaction B going to R 1 that is the first one of the hydrogenation steps. So, we have absorption, we have surface reaction, we have desorption, the similar kind of mechanism that we saw earlier when we were discussing the kinetics. So, one can apply quasi steady state or quasi equilibrium approximation.

Here, quasi equilibrium approximation was applied and what we get is the rate of these reactions let us call this as first reaction is equal to K 1 C hydrogen raise to half into C B after certain simplification. So, this is my reaction 1 if you if you let just go back let us say that this is my reaction 1, reaction 2, reaction 3 and 4 and reactions 5 and 6. So, I have this reaction mechanism. So, one can write for each of these reactions notice here that reactions 1 2 5 and 6 are hydrogenation reactions whereas, reactions 3 and 4 are isomerisation reactions.

So, what we just wrote was the typical mechanism for isomerisation reaction for hydrogenation reaction and we get this kind of rate laws. In fact, rate laws for all the four reactions R 1 to R 4 are of the same form namely, these rates being proportional to concentration of hydrogen raised to half and corresponding substrate reactant. Now, we can do the same thing for second set of reactions namely R 1 now binding with L and eventually getting hydrogenated to the saturates.

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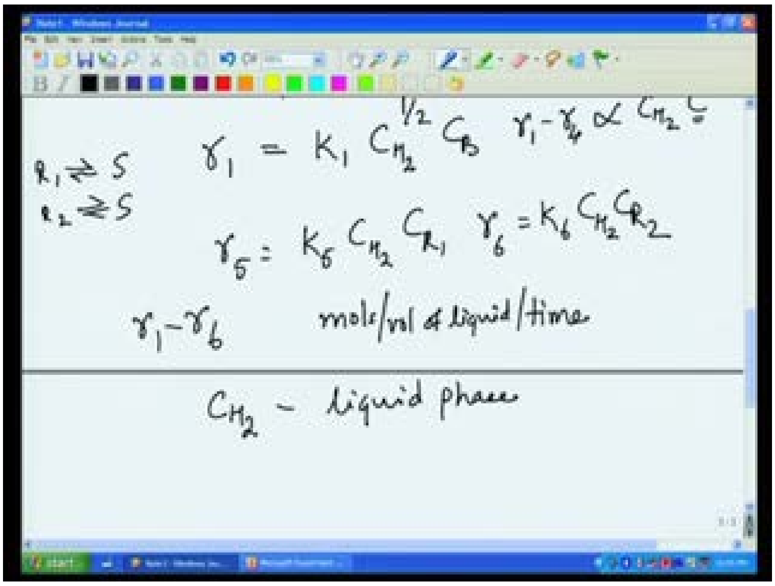

$R_1 \rightleftharpoons S$

$R_2 \rightleftharpoons S$

$r_1 = K_1 C_{H_2}^{1/2} C_B$ $\quad r_1 - r_4 \propto C_{H_2}$

$r_5 = K_5 C_{H_2} C_{R_1}$ $\quad r_6 = K_6 C_{H_2} C_{R_2}$

$r_1 - r_6$ mole/vol of liquid/time

C_{H_2} – liquid phase

So if you do that, if you will consider reactions 5 and 6 which were namely r 1 to S, and r 2 to S. We will get rate r 5 for example, being equal to K 5 hydrogen concentration into C R 1, and similarly r 6 as K 6 C hydrogen into C R 2 for these two reactions. So, we have basically the kinetics of the reaction, think to notice here is that my r 1, r 2, r 3, r 4, r 5, r 6; for example, r 1 to r 6 are my intrinsic kinetic rate expressed as moles per unit volume of liquid per time. And C R 1, C B, C S, C R 2 are all concentrations of my different species r 1, r 2, B, and so on. Hydrogen concentration C 2 that we have written here is the liquid phase concentration that is not the gaseous concentration. So, we need to find that liquid phase concentration.

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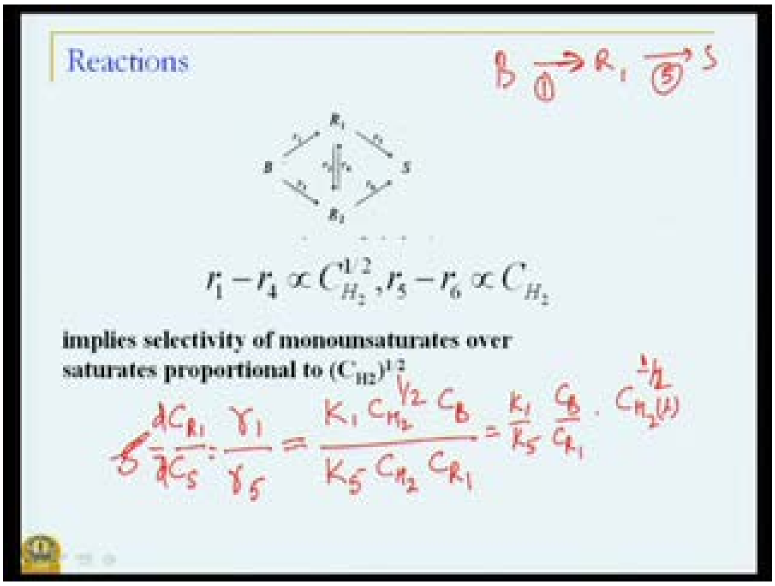

Reactions

$B \xrightarrow[①]{} R_1 \xrightarrow[⑤]{} S$

$$r_1 - r_4 \propto C_{H_2}^{1/2}, r_5 - r_6 \propto C_{H_2}$$

implies selectivity of monounsaturates over saturates proportional to $(C_{H2})^{1/2}$

$$S = \frac{dC_{R_1}}{dC_S} = \frac{r_1}{r_5} = \frac{K_1 C_{H_2}^{1/2} C_B}{K_5 C_{H_2} C_{R_1}} = \frac{K_1}{K_5} \frac{C_B}{C_{R_1}} \cdot C_{H_2(l)}^{-1/2}$$

Now, if we look at these rates and let us go back to our slides. So, once again this is my reaction scheme B going to R 1, B going to R 2, R 1 going to S, R 2 going to S hydrogenation reactions and then the isomerisation reactions. As I said earlier that R 1 to R 4 are proportional to carbon hydrogen concentration raised to half and R 5 to R 6 are proportional to concentration of hydrogen raised to raised to 1 fourth raised to 1. Now this implies that selectivity of mono unsaturates over un over saturates.

So for example, if you are to look at ratios of R 1 to typically that of R 5 it will be for example, let us look at what happens to r 1 by r 5? So, if you take this segment B going to R 1 going to S this is my reaction 1 this is my reaction 5. So, what this would this would imply is that this is K 1 hydrogen concentration raised to half C B this to R 5 is K 5 hydrogen concentration C R one. So, this now we can write as K 1 by K 5 into C B by C R 1 into concentration of hydrogen raised to minus 1 half.

So, what does it mean, it means that selectivity of R 1 over S, remember this is the indication of selectivity of that is let us say concentration of R 1 over concentration of S in a crude way or d c R 1 by d c S if you look at the point selectivity. So, now, this selectivity is inversely proportional to hydrogen concentration in the liquid phase. So, what does it means that if you want higher selectivity of R 1 over S then the concentration of hydrogen should be lower, otherwise you will get results differently.

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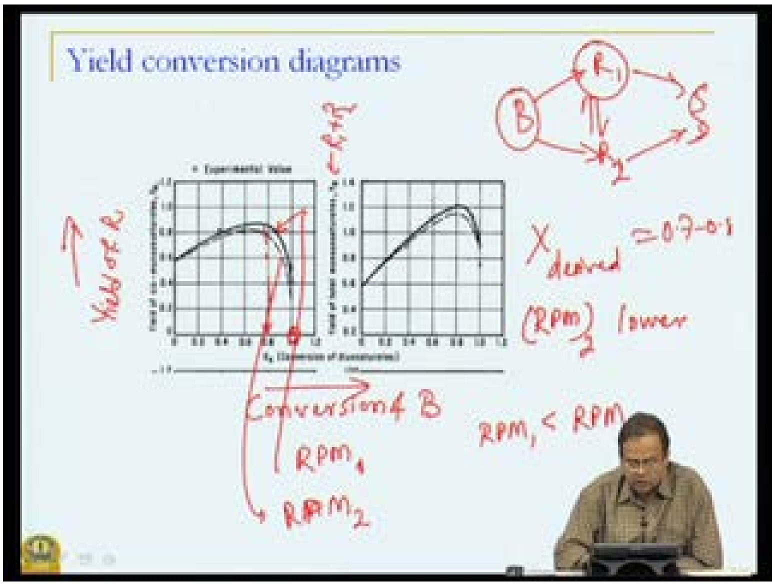

Yield conversion diagrams

So, let us look at when you actually do batch experiments, how does this results look like in the domain of yield conversion diagrams. So, what we are looking at here is the conversion of mono unsaturated conversion of B versus yield of R 1 and this is yield of R 1 plus R 2 put together, once again our scheme is these hydrogenation reactions with some isomerisation reactions.

So, if we look at conversion of B on the x axis against R 1 that is on the y axis over here or R 1 plus R 2 which is on in the second plot, we see the following. As conversion increases initially the yield increases, because more and more of B goes to R 1, but if you wait long enough for entire conversion of B that is if you go to this point, we see that the yields start decreasing and that is not what we what we want.

We want certain concentrations of R 1 and R 2 also in our reactor or in other words we are not going to aim and we also want certain quantity of B. So, we are not going to aim at hundred percent conversion of B, but where the optimal yield of R 1 is obtained. So, our reactor design now desired conversion is not hundred percent conversion of B, but certain 80 percent or 70 percent depending on whatever may be the results. So, that is point number one. So, in other words our x desired is in the range of 0.7 to 0.8. So, we should not design our reactor.

So, that we get hundred percent conversion that is one aspect and other aspect also is apparent in this figure is this particular solid line is a result for or these two different curves solid line and dotted line are results for different RPM.

Let us say the solid line is for RPM 1 and the dotted line is for another agitation rate RPM 2 and it turns out here that RPM 1 is greater than RPM 2 or in other words solid lines are the results where you have agitated system more and you get or other you have agitated system less, I should I stand corrected these are the results for RPM being less than RPM 2. So, if you agitate more you get lower yields now at first glance these results may look paradoxical.

Generally we assume that if we agitate system more, you will have uniform mixing and therefore, between the gas phase and the liquid phase and therefore, you should get better mass transfer and better kinetics or yields or selectivity, whatever we are looking.

While the first part of this is true that is you agitate more you will have better mass transfer between gas phase, that is hydrogen and the liquid you will have higher concentrations of hydrogen in the liquid, but as we just now saw few minutes back, that in order to get higher selectivity or yield of R 1 over R 2, we need lower hydrogen concentration, because that selectivity was inversely proportional to hydrogen concentration.

So lower RPM, lower hydrogen concentration, higher is the selectivity. So, another lesson that is to be learned from this example is that when you are trying to design heterogeneous reactors achieving uniformity highest degree of homogeneity mass transfer is not necessarily always the design criteria. So here among the two, RPM 2 or the lower of the RPM is to be selected, because that gives you higher selectivity. So, this brings us now to what happens to the mass transfer aspect. So, this is as far as the kinetics is concerned.

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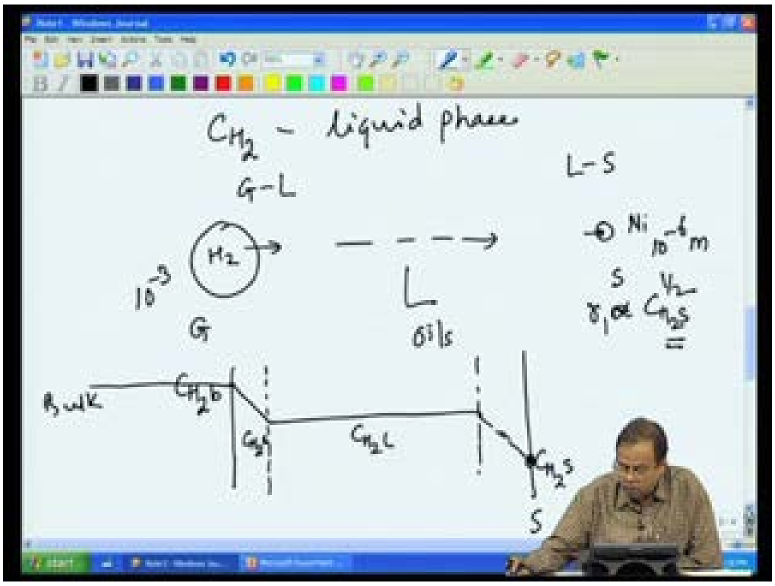

So, let us go back and look at how we handled the mass transfer aspects in this system. As I said earlier we have a gas, liquid, solid system. So, here is my solid catalyst, nickel catalyst, here is my gas phase and separating the two is the liquid. So, now for this reaction to take place the following things must happen, hydrogen is over here, my oils are over here and this is my nickel catalyst. So, the reaction has to occur by interaction with the catalyst or in other words hydrogen has to get transported from the gas phase to liquid phase.

So, gas liquid mass transfer then in the bulk due to the motion of agitation then to the catalyst and then further reaction in presence of the catalyst or in other words we have now three step process of which important are these two mass transfer processes. So, now to handle these processes now we have a gas liquid reaction.

So, let us say that we now represent this by assuming that there is this is a gas liquid interface, we will analyze this situation in the framework of two film theory. So, let us say that this is my concentration of hydrogen in the bulk gas phase; I am going to indicate the gas side mass transfer resistance and assume that the concentration in the bulk is same as the concentration at the interface. Then due to mass transfer interface concentration drops down and let us say that this is my concentration C 2 L in the bulk liquid the resistance is negligible.

So, we say that the concentration is same as C 2 H L and then once again, this is my solid interface and again mass transfer resistance and this concentration of hydrogen on the solid surface.

So, once again I repeat we have two interfaces gas liquid and liquid solid and therefore, two mass transfer resistances namely from the bulk gas to the bulk liquid. All mass transfer in this thin film bulk liquid transport is or mixing is good. So, we do not assume any further drop and but from the bulk liquid or the again bulk liquid to the solid entire mass transfer in these boundary layer and we have concentration C 2 C 2. Now all the kinetics that we wrote that is R 1 R 2 and so on.

We said R 1 is proportional to C H 2 raised to half that concentration must be concentration on the surface of the catalyst. Now here once again we are going to make another assumption. Typically, what is seen is that this is a micron sized particle and these are millimeter sized bubbles.

So, gas bubble is typically much bigger than the particle. Particle is really micron sized so diffusion of oil in the nickel particle as it is it will be a tough preposition. So, whatever is the reaction occurs at the surface of the nickel catalyst and therefore, corresponding surface concentrations are what determine the kinetics. So, now let us try to write down the mass balance equations for these processes by looking at first gas liquid interface.

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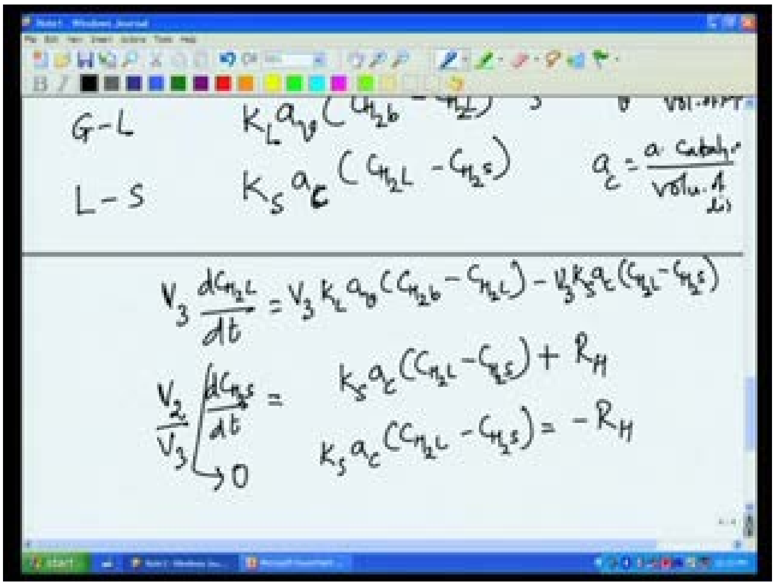

G-L $K_L a_v (C_{H_2b} - C_{H_2L})$

L-S $K_S a_c (C_{H_2L} - C_{H_2S})$

$a_c = \frac{\text{a catalyst}}{\text{volu. liq}}$

$$V_3 \frac{dC_{H_2L}}{dt} = V_3 K_L a_v (C_{H_2b} - C_{H_2L}) - V_3 K_S a_c (C_{H_2L} - C_{H_2S})$$

$$\underbrace{\frac{V_2}{V_3} \frac{dC_{H_2S}}{dt}}_{\to 0} = K_S a_c (C_{H_2L} - C_{H_2S}) + R_H$$

$$K_S a_c (C_{H_2L} - C_{H_2S}) = -R_H$$

So, what is happening at gas liquid interface? The rate at which hydrogen is getting transferred across the gas liquid interface much can be represented as K L into a v into C H 2 bulk minus C H 2 L. The concentration difference between these two levels is my driving force and that driving force times the area available for the area available for mass transfer so a v.

So, a v here is the surface area of the bubble per unit volume of the liquid and K L is the mass transfer coefficient. Similarly, what happens at the liquid solid interface, we can write this as once again the driving force for mass transfer the concentration gradient between the interface or the film and the interface. So, times the area a c is the area of the catalyst per unit volume of the liquid because, we want to maintain all rates in terms of volume of the liquid.

So, now let us write down the mass balance for the bulk liquid. So for example, bulk liquid mass balance assuming the volume is v 3 C H 2 liquid dt must be the rate at which gas hydrogen is coming from the gas phase to the liquid minus the rate at which it is going from the liquid to the surface of the surface of the catalyst. So, this is my mass balance equation for the liquid.

Now let us write down the similar balance, for the concentration on the surface and this must be again, this is the rate at which hydrogen from the bulk liquid is coming to the surface plus the rate at which hydrogen is getting generated at the surface, this must be the rate at which my hydrogen is getting accumulated. Now, I am expressing my rate in terms of volume of the bulk liquid.

So, now if we look at this solid balance, if you look at the balance of hydrogen on the solid so, we can take v 2 by v 3 over here and remove v 3 and now we see that v 2 by v 3, what is v 2? v 2 is the volume of the catalyst which will be much smaller than volume fraction as compared to the bulk liquid.

So, we can assume that this is close to zero and the rate of mass transfer K S a c into C H 2 L minus c H 2 S must be equal to minus R H. Now what is R H? Remember, if we go back to our reaction scheme over here, then the rate of hydrogen generation. Of course, it will be consumption in this particular case must be minus R 1 plus R 2 plus R 5 plus R 6. Because, that is the reactions R 1 2 5 and 6 are the reactions in which hydrogen is consumed.

So, the net rate of hydrogen consumption must be summation of all these rates, so now going back to our set of mass balance equations.

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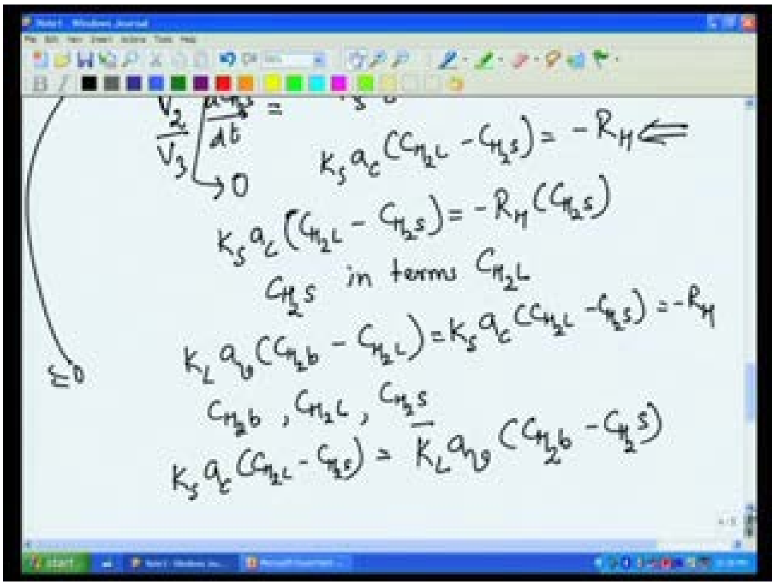

$K_S a_c (C_{H_2L} - C_{H_2S}) = -R_H \Longleftarrow$

$K_S a_c (C_{H_2L} - C_{H_2S}) = -R_H (C_{H_2S})$

C_{H_2S} in terms C_{H_2L}

$K_L a_v (C_{H_2b} - C_{H_2L}) = K_S a_c (C_{H_2L} - C_{H_2S}) = -R_H$

$C_{H_2b}, C_{H_2L}, C_{H_2S}$

$K_S a_c (C_{H_2L} - C_{H_2S}) = \overline{K}_L a_v (C_{H_2b} - C_{H_2S})$

So, what we have first is K S a c into C H 2 L minus C H 2 S is now, I will just write this I know what this R H is, but this has C H 2 C H 2 S into a. So, that is in terms of hydrogen concentration at the surface. So, now in other words we know concentration of hydrogen on the surface in terms of concentration of hydrogen in the bulk liquid, but we do not know what is the concentration of hydrogen in the bulk liquid that is not very difficult we have already written a mass balance equation for that.

So, in this mass balance equation for example, I can just simply substitute this for R H s, but we can also make an further assumption, that is the due to the dynamics of mass transfer this accumulation of hydrogen in the bulk is zero or it has reached a what we can call a quasi steady state or in other words d C H 2 d L with dt is close to 0. So, if we said this term equal to 0, then from this mass balance equation on bulk hydrogen, we will get K L a v into C H 2 bulk minus C H 2 L equal to K S a C into C H 2 L minus C H 2 S equal to minus R H from this two balances.

So, we have two relationships now and therefore, we can eliminate for example, so we have three concentrations of hydrogen bulk this will be determined by the partial pressure of hydrogen.

Then we have C H 2 L and we have C H 2 S that is on the surface. So, in the gas phase liquid phase and on the surface three concentrations and we can use these relationships to eliminate one in terms of other and if you do all that exercise, we actually get K S into a c into C H 2 L minus C H 2 S.

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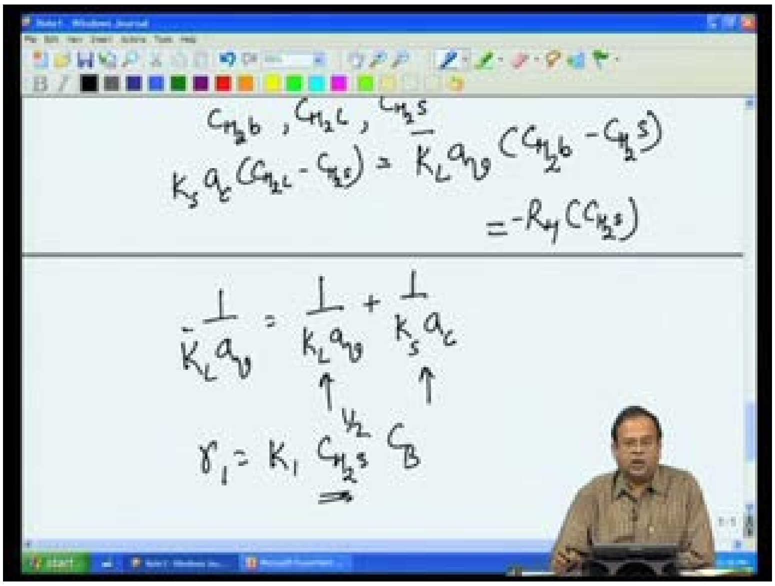

$$C_{H_2b},\ C_{H_2L},\ C_{H_2S}$$

$$K_S a_c (C_{H_2L} - C_{H_2S}) = \bar{K}_L a_v (C_{H_2b} - C_{H_2S})$$

$$= -R_y (C_{H_2S})$$

$$\frac{1}{\bar{K}_L a_v} = \underset{\uparrow}{\frac{1}{K_L a_v}} + \underset{\uparrow}{\frac{1}{K_S a_c}}$$

$$r_1 = K_1 \underset{\Longrightarrow}{C_{H_2S}^{1/2}} C_B$$

That is the oxygen transfer across the liquid solid interface, as over all mass transfer coefficient K L a into C H 2 bulk minus C H 2 S. This to you will be somewhat familiar concept that is let us go back to this. So, if you look at this is gas liquid and then liquid solid processes in series resistances addition of resistances and therefore, it are not surprising that we get our overall mass transfer coefficient.

This is resistance representation of resistance in terms of gas liquid interface resistance across liquid solid interface. Once again what are K L and K it should be K S is the mass transfer coefficient across liquid solid interface K L is the mass transfer coefficient across gas liquid interface and a v and a c are, a v is the area per area of the bubbles per unit volume of the liquid, a c is the area of the catalyst per unit volume of the liquid.

So, as a result now we have which is a function of c 2 S or in other words in our kinetics. Which we had for example, what is this value of c 2 H? That value of c 2 H at the surface of the catalyst which we cannot measure is related to the concentration of hydrogen in the gas phase in the in the in the in the gas phase c H 2 B not a direct relationship, but implicit relationship. So, that is sufficient for us to write down our mass balance equations.

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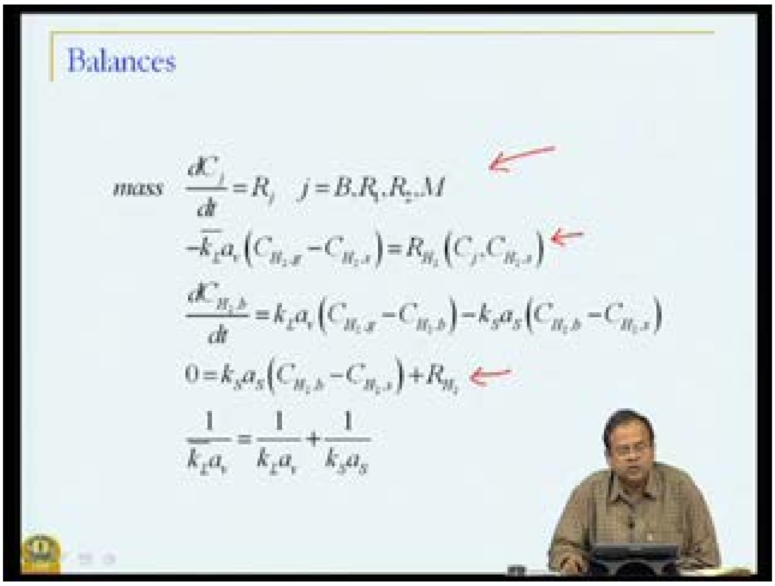

Balances

$$\text{mass} \quad \frac{dC_j}{dt} = R_j \quad j = B, R_1, R_2, M$$

$$-\bar{k}_L a_v \left(C_{H_2,g} - C_{H_2,s}\right) = R_{H_2}\left(C_j, C_{H_2,s}\right)$$

$$\frac{dC_{H_2,b}}{dt} = k_L a_v \left(C_{H_2,g} - C_{H_2,b}\right) - k_S a_S \left(C_{H_2,b} - C_{H_2,s}\right)$$

$$0 = k_S a_S \left(C_{H_2,b} - C_{H_2,s}\right) + R_{H_2}$$

$$\frac{1}{\bar{k}_L a_v} = \frac{1}{k_L a_v} + \frac{1}{k_S a_S}$$

So, now the next step of our design would be to write the mass balance equations. What are our mass balance equations? for components in the liquid phase that is those four components B R 1 R 2 and S, we have d c j equal to R j corresponding rates then we have this we just now saw as a result of assuming steady states for hydrogen concentration in the liquid as well as hydrogen concentration on the surface of the catalyst palette and there thereby combining these two we have the final form of this with overall coefficient defined in this manner.

So, I can now simulate my reactor, if I know the initial concentrations of B R 1 R 2 m or saturate S and the hydrogen concentration in the gas phase. Because, we just now saw that hydrogen concentration in the gas phase is in turn related to the concentration in the liquid.

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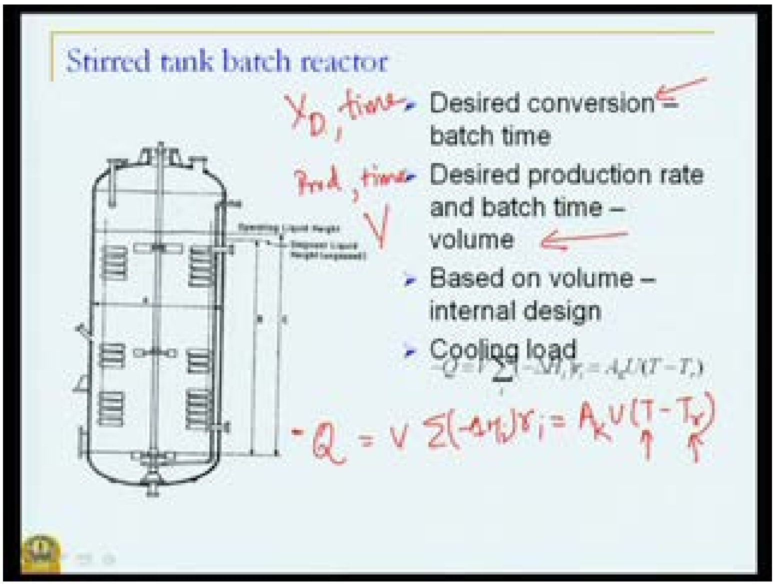

Stirred tank batch reactor

X_D, time
- Desired conversion – batch time

Prod, time, V
- Desired production rate and batch time – volume
- Based on volume – internal design
- Cooling load

$$-Q = V\sum_i(-\Delta H_i)r_i = A_c U(T - T_c)$$

$$-Q = V\sum(-\Delta H_i)r_i = A_c U(T - T_c)$$

So, how do we go about designing this reactor? So, essentially it is a typical stirred tank batch reactor, in which we have multiple stirrers, because the height to diameter ratio is not always one. In fact, that would make the reactor will occupy much more horizontal space. So, it can be the height to diameter ratio can be in excess of 1 typically 2 and in which case we need multiple impellers.

So, we have multiple impellers with standard design of their locations, clearances, their diameter which obvious diameter of the whistle and so on. So, now in the design this is how we can go about designing the process. So, let us recap what we have seen so far, before we go on to this process.

So, what we had is a hydrogenation of oil which is a solid liquid gas phase reaction. The kinetics of this process being a catalytic process is represented by interaction of the active site of the catalyst with the different species that we have and so on. The mass transfer aspect is represented by assuming the resistance to mass transfer along the thin film which surrounds the interface, particularly on the liquid side between gas liquid and once again on the liquid side between liquid solid and doing certain manipulations such as steady state assumption and so on.

We come up with the mass transfer rates couple it with the kinetics. So, now let us try to design this reactor. So, as we saw in these result there were two aspect which came out that you do not want the conversion to go to hundred percent.

So, you have certain desired conversion in mind. So, with our model on hand we can now simulate this process and look at what is the time that is required to achieve the desired conversion and that will fix our batch time. Now, knowing the batch time and knowing the desired production rate typically, you will be asked design thousand tons per annum or whatever that quantity is. Then you will decide on what is the working days, that are that are available to you, what is the batch time based on this two and the production rate that you have you will decide, how many batches you have to do.

Basically, you will do number of batches based on the time available in the year and the batch time. So, that gives you number of batches, you have your total desired production. So, that will give you what should be your production per unit batch and based on that you will decide on the volume of the reactant. So, here based on desired conversion we found time of operation, based on desired production and the time of operation we found a volume of the reactor.

Now once you know the volume then all you are either heuristic empirical approach or in todays age say of dissimulations or whatever you want to do. One can design the internals that is what should be the diameter, height to diameter ratio, diameter of the impeller, diameter of the vessel ratio, clearances, baffle sizes and so on.

The last thing that one needs to design, because this is an exothermic reaction and if you go back to our energy balance and the fact that we want to run this as a isothermal reactor, we would like to find out what is the cooling rate that is required and this cooling rate this has got jumbled up. So, the cooling rate that will be required is minus delta H. This we had done earlier for all the reactions, each of these reactions will have heat of reactions.

So, rate of the reaction into heat of particular reactions summed over all reactions, is how much is the energy that is getting liberated and this has to be removed and therefore, by knowing what temperature we want to operate this reactor, what coolant we have. We can find out both the area of the mass transfer and e k u and deciding upon what will be the heat transfer coefficient, we can find out how much area is required. So, that will complete the design of the internals. So, this in short is the kind of exercise that one would have to do, if you were designing a batch reactor.

The case we saw was the hydrogenation of oil which was gas liquid solid reaction. So, we have seen two case studies so far. One reaction in an empty tube or homogeneous gas phase reaction namely, cracking of ethane to ethylene; the second case we just now saw in this session is hydrogenation of oil using nickel catalyst. So, slurry reactor gas liquid solid case in which kinetics transport reactor design all come together.

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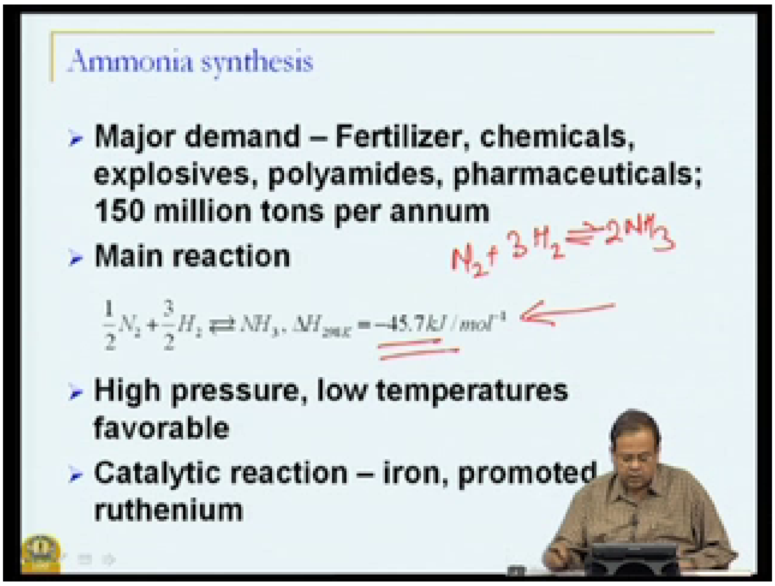

Ammonia synthesis

- Major demand – Fertilizer, chemicals, explosives, polyamides, pharmaceuticals; 150 million tons per annum
- Main reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3,\ \Delta H_{298K} = \underline{\underline{-45.7 kJ/mol^{-1}}} \longleftarrow$$

- High pressure, low temperatures favorable
- Catalytic reaction – iron, promoted ruthenium

Now, let us turn our attention to another case study and this case study will be using extensively for illustrating various aspects of reaction. This is a reaction of ammonia synthesis a simple reaction. The reaction process is nitrogen and hydrogen in appropriate stoichemetric quantities gives you a mole of ammonia that is the main reaction. Now why do we need to synthesize ammonia is it tremendous demand for ammonia in fertilizers, chemicals, explosives, polyamides, pharmaceuticals and so on.

And typical production sizes are about hundred and fifty million tons per annum worldwide may be in slightly in excess, but that is the kind of numbers that you are looking. So, for this reaction if you look at reaction what is happening on the reactant side we could write this reaction also as in N 2 plus 3 H 2 giving 2 N H 3. So, what is happening there is a decrease in number of moles.

So, compared to what we had for ethylene ethane cracking where it was increase in number of moles here we have decrease in number of moles from 4 to 2.

So, thermodynamics immediately tells that we must use high pressures. The reaction is exothermic reaction is exothermic. So, once again thermodynamics tells us that lower temperatures will result in higher equilibrium conversion. It is a catalytic reaction where iron or promoted ruthenium this type of catalyst are used.

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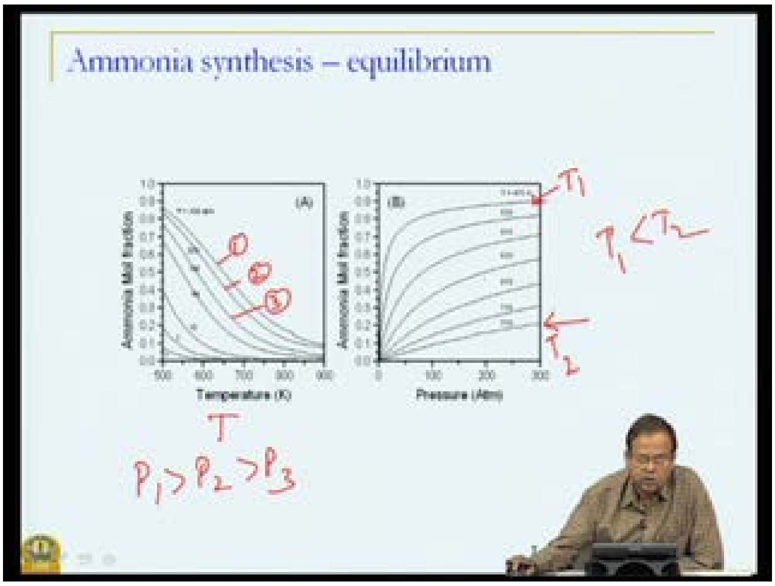

Ammonia synthesis – equilibrium

So, let us look at first the thermodynamic aspect, what we are seeing here is the temperature on the x axis, and ammonia mole fraction that is the equilibrium relationship for different pressures. Let us say 1, 2, and so on, and pressure 1 is greater than pressure 2 greater than pressure 3; these are in fact 300 atmospheres, 100 atmospheres, and so on.

And as we can clearly see that, first of all as temperature is increasing the equilibrium conversion is decreasing and this is what is to be expected of an exothermic reaction. We also see that, as we increase the pressure that is equilibrium conversion at three hundred atmospheres is higher than two hundred atmospheres and so on. So, as we increase the pressures we are getting higher conversions.

So, typical operating conditions that we are looking at are higher pressures and lower temperatures the same effect is also seen from another aspect, if you look at equilibrium mole, ammonia mole fraction versus pressure at different temperatures.

So, this is lower temperature T 1 to a higher temperature T 2 in a land and in general T 1 is less than T 2. So, as we are increasing the pressure conversion is increasing and conversion is also increasing as we are lowering the temperature.

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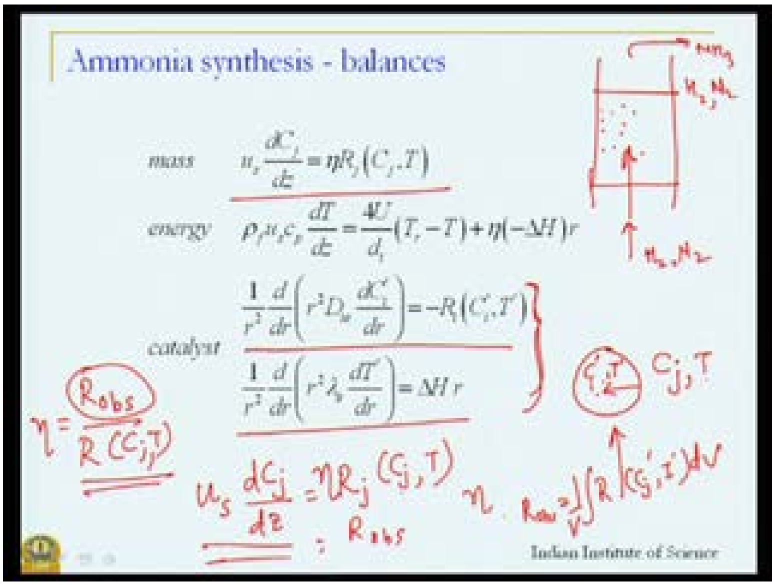

Ammonia synthesis - balances

mass $$u_s \frac{dC_j}{dz} = \eta R_j(C_j, T)$$

energy $$\rho_f u_s c_p \frac{dT}{dz} = \frac{4U}{d_t}(T_c - T) + \eta(-\Delta H) r$$

catalyst
$$\left.\begin{aligned} &\frac{1}{r^2}\frac{d}{dr}\left(r^2 D_{ej}\frac{dC_j'}{dr}\right) = -R_j(C_j', T') \\ &\frac{1}{r^2}\frac{d}{dr}\left(r^2 \lambda_e \frac{dT'}{dr}\right) = \Delta H\, r \end{aligned}\right\}$$

$$\eta = \frac{R_{obs}}{R(C_j, T)}$$

$$u_s \frac{dC_j}{dz} = \eta R_j(C_j, T) \quad ; \quad R_{obs}$$

$$\eta \qquad R_{obs} = \frac{1}{V}\int R(C_j', T')\, dV$$

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So, let us setup the mass balance equations, for this particular reactor. Now what do we have here? We have a fixed bed reactor here and let us say that we are passing hydrogen and nitrogen here and ammonia and unreacted nitrogen and hydrogen are coming out of the of the reactor. There are catalyst particles and this is a bed of this catalyst particle and the reaction is taking place. It is an exothermic reaction; so first I have to setup the mass balance equations for the catalyst.

So, if we say that this is my catalyst and concentration inside is c prime, temperature is T prime and we have several components. So, c i prime is the concentration of components such as hydrogen, nitrogen, ammonia inside the catalyst pillar. T prime is the temperature and what is happening steady state diffusion and reaction. This we had seen when we had talked about individual catalyst.

Similarly, non isothermal catalyst pillar, so energy balance heat of reaction times rate is your conductive heat transfer. So, this is as far as the catalyst is concerned, but the gas is full outside this catalyst and the concentrations of the gaseous components are let us saying c j. So, we now need to link the flow phenomena in the reactor or transport phenomena in the reactor to the transport phenomena in the catalyst.

And the way we do this is for sake of simplicity, we will use the concept of effectiveness factor. So, if we look at this mass balance equation for, I am going to assume a pluck flow reactor or a pluck flow in the fixed bed reactor. So, what we have is we had seen this earlier. Let us say R of species j where R j is a function of concentration and temperature in the bulk, but now I also know that my reaction is not taking place in the bulk, this would have been the case balance, if the reaction was taking place at in the bulk or at least at the bulk conditions.

But the reaction is taking place at concentrations c i prime and T prime and that is where we bringing the concept of effectiveness factor and we say that the reaction rate is actually eta times R j of c j anti and that is that mass balance.

What is my eta? Eta is my effectiveness factor namely R observed to R at bulk conditions that is if mass transfer resistances were negligible. The rate should have been the rate at bulk concentrations and bulk temperature. So, at bulk c j and bulk temperature would have been the rate the actual rate is R observed eta is my effectiveness factor and therefore, in my balance it is actually nothing, but R observed.

But that I have related through concept of effectiveness factor. Now there are two ways, one can simulate this if you know effectiveness factor of put that in or if you do not know then at each simulation time step. You will have to solve these equations for the catalyst palette evaluate the effectiveness factor or if you do not want to evaluate effectiveness factor, just evaluate rate average rate.

That is why observed rate if that is there is some rate associated with this concentrations and temperature, average they were the entire volume of the catalyst palette is my observed rate. So, this is how I would simulate the ammonia synthesis reactor. We stop here for this session, and start looking at how this reactor behaves when we try to simulate this reactor, a non isothermal reactor, a fixed bed non isothermal reactor for ammonia synthesis. So, that is what will be topic of our discussion for the next session. Thank you.