Chemical Reaction Engineering 2 (Heterogeneous Reactors)
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Lecture-21.
Inter and Intraphase Effectiveness Factor.

Professor: Yah, I think you have seen the assignment and all those rates that we have developed using that assignment, I think I last class also, last-minute when I was about to leave, I said all those glasses are called, I mean all those reactions are called intrinsic rate of reaction, okay. So the meaning of intrinsic rate of reaction is no mass transfer coming in. But in reality you will have definitely some mass transfer all the time, okay. So that is why now we will take the other 2 steps in the beginning that the mass transfer through the film and also diffusion to the pores and of course, same mass transfer steps even at the end also for the products, so same analysis is also valid there.

Why should we do this, you know the mass transfer step? Mast transfer steps give to do because the mass transfer is rate controlling, the entire surface area, the way we imagine in the LA HW models may not be covered with the molecules, because you do not have sufficient amount of reactant A or reactant B which is going through the surface, I mean which is going through the pores and then there sitting on the surface. So that is why all the surface area that is there inside the catalyst particles might not have been used for reactions and that is really very bad, particularly when I have noble metals, noble metal catalysts.

Noble metal catalysts are very very costly, platina misused as a catalyst, okay, in many reactions. So if Platinum surface only 10 percent covered or 50 percent covered, the remaining 50 percent of the Platinum is waste. So that is why it is always better to have an idea how, how can we say that my catalysts is 100 percent, effectiveness factor is equal to1 or 100 percent it is useful for only 50 percent is useful or only 80 percent is useful. That is why we define it called effectiveness factor, okay. Effectiveness factor, I thing in your understanding can it be more than 1 or less than 1 or there is always one or any, what is your understanding till now?

Always? There is no other condition? Less than 1 under what conditions, you are saying for anything it is less than one?

Student: (())(2:30).

Professor: Mass transfer only, If mass transfer is not coming into picture, then you have intrinsic rate where theatre surface area is useful, effectiveness factor equal to1, okay. But I am saying this 1, is it same, the definition wise is it valid for, under any conditions or lesser some conditions where it is not valid? How do I define effectiveness factor?

Student: Actual rate upon intrinsic rate.

Professor: Yes, excellent. Actual rate of reaction divided by intrinsic rate of reaction, okay. Or reaction evaluated that the bulk condition, that means all the bulk of gas, whatever concentration we have in the bulk, that is also there on the surface. Which means absolutely there is no mass transfer, resistance, otherwise same consideration will not have within the pores, right. Okay, that is also but these, it is restricted to a particular thing or generally we can define like that? This definition, this intrinsic rate is evaluated at what condition?

Student: Taking into account only single particle.

Professor: Single particle only, that is what it is, but what are the conditions? Because I told you also, the dinner matter, intrinsic rate is always evaluated at, yah, only for isothermal case it is Eta equal to1. Or Eta to1 if you do not have mass transfer coming into picture. At less than that, if you have, then you will have Eta less than 1 but if you have exothermic reaction for example, non-isothermal, okay, exothermic reaction, then the reaction is taking place on the surface, it might have not completely occupied by these molecules of reactants, the surface.

But still it is an exothermic reaction and when the reaction is taking place, even with 50 percent of area covered, the temperature will increase and we know this R always has the effect of increasing the rate of reaction because of Arhenius equation. So under those conditions, many times, the effective factor can go to even thousand times, okay. That means the rate of reaction inside the particle you know when it is highly exothermic, the temperature is so high the rate of reaction within the particle will be very very high when compared to bulk rate, right.

So bulk, that means when you are talking about nonisothermal effectiveness factor, we are talking about the actual rate of reaction divided by the rate evaluated at bulk temperature and bulk concentration, okay. So that is what you know next few classes we will focus on, how do you evaluate the effectiveness factor so that I will find out for my catalysts what is the effectiveness. But equally all this catalysts are very very costly, that is why we should have an idea how the catalyst is performing. That same thing, you know people say that we are using our 1 percent of our brain, so what will be effectiveness factor, 0.1. Okay, most of the time that happens, 0.1…

Student: 0.01. 1 percent.

Professor: Okay, 0.01, 10 percent a larger, 10 percent means all of you should have done Ph.D. already. So we are not doing that, yah, so 0.01 percent, so 0.01 at the effectiveness factor. So like that it is better to have some idea about our catalyst, other than that the another advantage you know because many people do not know what is the use of effectiveness factor, we will simply derive equation, nicely but when are you going to use, we do not know. That is why I am trying to tell in the beginning itself what is the use of this effectiveness factor. One is to find out whether we have a very good catalyst or not.

The other one is if someone has already given an intrinsic rate, that means there is no, without any mass transfer is controlling the rate and entire surface area is used but the catalyst manufacturers will say that, depending on the pores because he has to manufacture the catalyst. Normally take the powder and then compresses it and while compressing, if he used too much pressure, then the pores will be very very small and then mass transfer will automatically come in the future. If he does not pressurise much, then particles will fall, the strength of the catalyst will not be there, then went and then tons of this catalysts are put inside the reactor, particularly packet bed and all that, so they will be crushed.

That is why mechanical strength also is required. At least for that sake you have to pressurise to certain pressure and then you have to also sinter and when you are sintering the particle, that is you know to form mechanical strength, for sintering the particles again the pores may close. Some of the pores may close, so that is the reason why always there will be some mass transfer effect in the actual particles, right. So what the catalyst manufacturers tells is that my effectiveness factor for this catalyst is 0.5, okay. But you have for the same reaction the intrinsic rate of reaction. So then what is the actual rate of reaction now, 0.5.

So that is the actual 0.5, that rate, you know 0.5 into that rate equation, that is what what you use in the design expression. That is also another advantage of, or another use of effectiveness factor. Okay. So this is what what we will do now and the 1st thing what we will do is we take independently the 1st step, that means only film controlling, okay. If I have film alone controls, what will be the effectiveness factors, then we will go inside, you will forget film and then you take only the pores and if there is only mass transfer resistance in the pores, then how do you develop effectiveness factor. Now there are 2 steps pore diffusion and also film diffusion. Now combining what will be the overall effectiveness factor?

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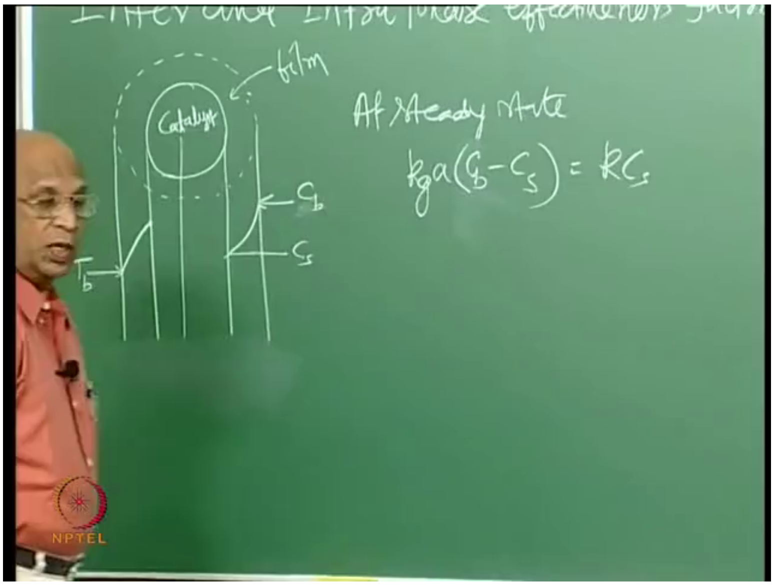

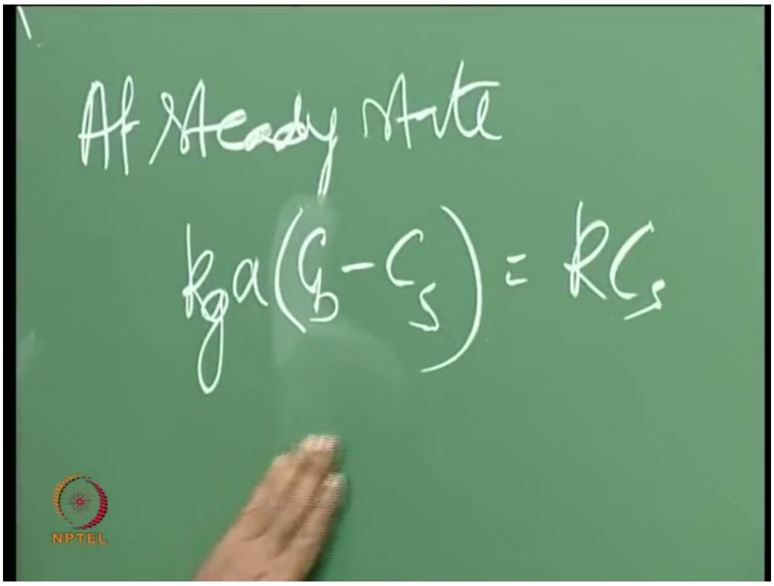

So that means when you have some film control, some diffusion controls to the pores, then how do you calculate the overall effectiveness factor for the particles. Okay, this is what what we will do in the next few classes. So to start with now we will have the 1st film control alone. So we will call this one Inter and intra phase effectiveness factor effectiveness, okay, good. So what we will do is, we have the particle, we have the film surrounding this, this we have done many times. Like for example if I have, if I have only porous particles, sorry nonporous particle okay, there is no diffusion, you know the 2nd mass transfer effect will not be there.

And we also have some catalysts nonporous catalysts. Reaction was occurring only on the outside surface, so when you have that kind of catalyst nonporous particles, then we know this I do not have to ask you, many times we have discussed this, this may be CB, bulk concentration, then this will be CS, that is surface concentration, this is the catalyst, this is film. So we can also have here temperature profiles, okay. How do I draw temperature profile here?

Student: Is the reaction exothermic?

Professor: Yes, that is the question you have to ask. Is the reaction exothermic or endothermic. First I will say exothermic, you have to start only from here 1st know, T b, yah so it may increase it, exactly how the function increase it depends on the equation, okay. Like this, only reaction is taking place there, okay, this is exothermic, if I have endothermic, decreases, correct on the surface. We should develop an equation for effectiveness factors, taking these 2 account, 1st let us take isothermal particles, okay, then we can go for non-isothermal particles.

The analysis you have done already, that under steady-state conditions, the rate of mass transfer must be equal to rate of reaction at steady state, okay, at steady state rate of mass transfer, I will not write the words but straightaway I will write the equation because already we have done so many times, as this is CB minus CS, as usual I will take first-order reaction, this is K CS. This a is centimetres square per centimetre cube of the particle, that means surface area per unit volume of the particle, okay. So then with this, there will be a lot of confusion, so that is why I am just pointing out this, even though it is very simple but I think you will make a lot of mistakes. Yah, then now tell me what will be the units of this K without a, with A. Yah without a and with A. Quickly, time is going, you cannot simply because you apply them and tell me. Because it is? Per second yah, why this is per second? What is this, what are the units of this?

Student: (())(12:57).

Professor: Yah, concentration is for per metre cube… Yah, but who told you that, what is your overall dimension here for this rate? This is read, this is R ob observed…

Student: (())(13:14).

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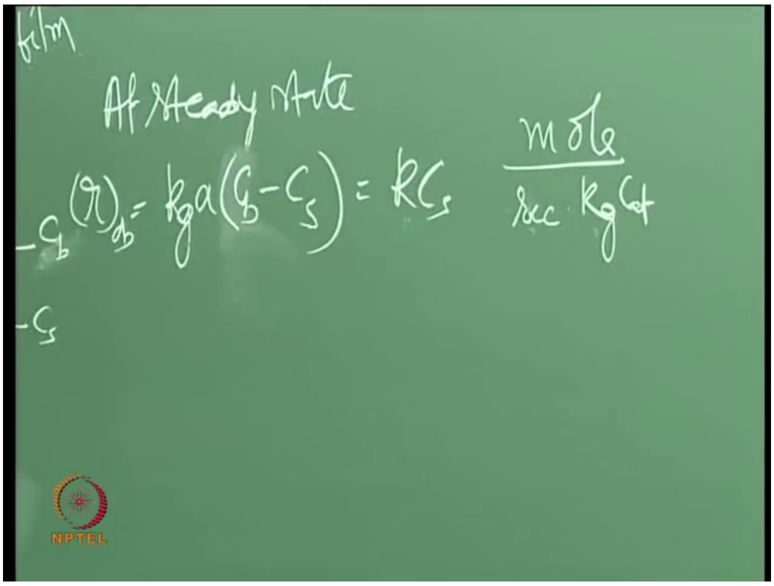
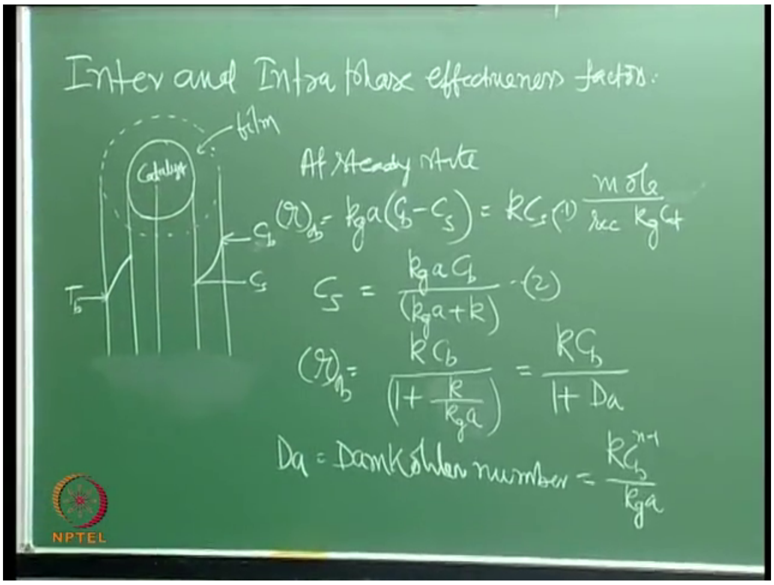


film

At steady state

$-C_b$ $(r)_{ob} = k_g a (C_b - C_s) = k C_s$ $\frac{\text{mole}}{\text{sec} \cdot \text{kg cat}}$

$-C_s$



Inter and Intra Phase effectiveness factors:

At steady state

$$(r)_{ob} = k_g a (C_b - C_s) = k C_s \quad (1) \quad \frac{\text{mole}}{\text{sec} \cdot \text{kg cat}}$$

$$C_s = \frac{k_g a C_b}{(k_g a + k)} \quad (2)$$

$$(r)_{ob} = \frac{k C_b}{\left(1 + \frac{k}{k_g a}\right)} = \frac{k C_b}{1 + Da}$$

$$Da = \text{Damkohler number} = \frac{k C_b^{n-1}}{k_g a}$$

Professor: Moles per? Yes, moles per, yah, now you understood no what is the problem? It depends on 1st of all how to define the rate and for catalytic reactions what is the logical way of defining the root? Yes, maybe area, area is more difficult to use, in the sense that you have to measure that, wet will be the simplest one. So now if I have a rate as moles per second, second per kg catalyst. Not depending on this you have a corresponding, you know dimensions for KG a and K, please remember that. Please remember that but the moment I also expressed this KG catalyst, okay. The moment I also expressed this moles per seconds per centimetre square, okay.

Imagine that we have moles seconds centimetres square, what will be the units of this, what are the units of this? Centimetre square of catalyst surface I can always know, what Sarita, you are not able to follow? Follow the equation. See the rate in heterogeneous system can be written in many forms, one way of writing is moles of A reacted per unit time per unit weight of the catalyst. We can also write moles reacted per unit time per unit area of catalyst. That is why I said it is moles, seconds, metres per centimetre square, okay.

So now what will be the units of this KG and K, KG and KA? You are, metre per seconds and metre per seconds, under those conditions this is not required, okay. And particularly when you are solving the problems he will make these mistakes and then using that you currently they did but basically you made a mistake, dimensionally also, okay. So that is the reason why I am pointing out this. Okay, anyway, so these are the simple thing but number of times I have to point out because you know otherwise you may not remember things, okay. So solving this CS, we know already, this is KG a CB by KG a plus K, this already we have done.

I think K-1, this is equation 1, 1, 2, yah, Southern R OB is given by KCB by 1 by K by KG a, okay, this is what you get no after substitution I am just dividing. Correct, you got it? So this is the equation where this also can be written as KCB by 1 plus DA, where DA is equal to Dam Kohler number defined here as K CB to the power of N minus1 by KG, okay. This is another form of Dam Kohler number. What is the tell me? If I say that I have Dam Kohler equal to 1000, large number, which one is controlling? Mass transfer is controlling, okay. If Dam Kohler is small, 0.01, reaction is controlling, okay.

So that is the meaning of that, rightful so so you also had another Dam Kohler number, K Tao CA 0, C0 to the power of N minus1, that is another form of Dam Kohler number. What does that tell you? If I say that I have K times C0 to the power of N minus1 is very large, what is the meaning? That is strictly used for homogeneity actions. For first-order it is K Tao, for second-order it is K Tao CA0, what is the meaning of that? If K Tao C a 0 is very large, what is the meaning of it?

Student: Conversion (())(17:56).

Professor: Conversion will be very high. And K Tao small means conversion is small, okay. So that gives an indication, okay, this factor has very high Dam Kohler number, homogenous system, so that means you are getting very large conversions. Okay, yah but the 2nd form of

Dam Kohler number is for heterogeneous system, that is for homogenous, heterogeneous systems where this will give us an idea of how the reaction, you know, which one is controlling, mass transfer is controlling or reaction is controlling. You know generally in an academic institution we never bother about these numbers but an industry it is generally a lot of some rules there for them. Okay.

Biot number so much, buyout number also will come sometime later. That given an indication, buyout, buyout number so much means, okay, 1000, okay you do not have to worry, the things are going on very well. Like for example K Tao CA0 is very large for homogenous reaction means conversion is very high, we do not have to worry, very nice. So that kind of things, good.

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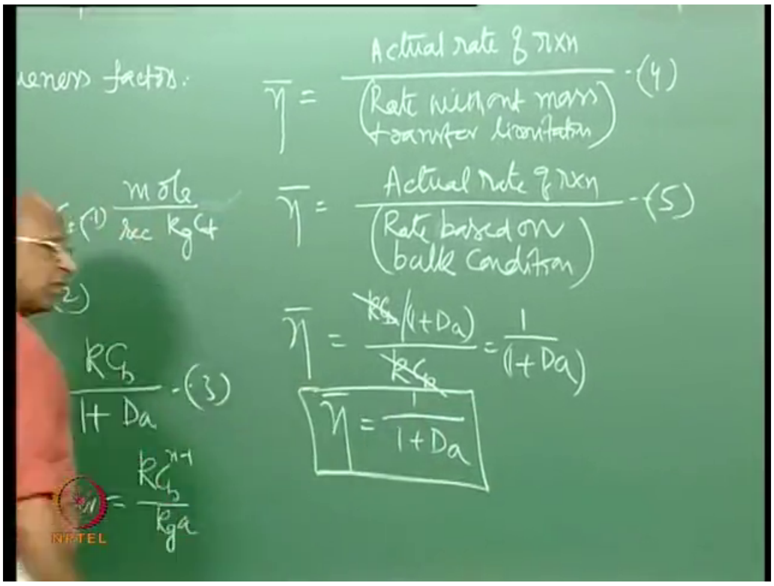

So this is the one Dam Kohler number destination and now we will define eta bar is effectiveness factor, eta bar, effectiveness factor as actual rate affection, you have all the names the actual rate of reaction, global rate of reaction, observed rate of reaction common thing you can write. Actual rate of reaction, shot form I will write, divided by rate without mass transfer, without mass transfer limitation. Okay, of course we can also write ETA bar as actual rate of reaction of limitation divided by divided rate, without any limitation means the concentration must be same throughout the particle, okay, must be same, that is what what we expect.

But in reality that may not happen, so that is why the effectiveness factor less than 1 means if it is isothermal system, then we will know how much less, okay. So this is the rate of, rate with, rate, rate based on bulk conditions, based on bulk conditions because some books write like this, some books write like this. This is equation, Dam Kohler number equation, this is 3, this is for, this is 5. Good. So now, this have taken first-order reaction, okay, I can also take second-order reaction and then you know how to solve correspondingly. Now for this example what is effectiveness factor? What is the actual rate of reaction, R observed, correct no.

Actual rate of reaction is R observed, so R observed is written as KC be divided by 1+ DA, correct no? Good. The other one?

Student: KCS.

Professor: By S? K CB, because evaluated under conditions, that bulk conditions, so KCB, this we can get cancelled out, then we will have 1+ DA. So effectiveness factor for first-order reaction is this equation, okay. So this is equation number, that is equation number 6, okay, good. So now what normally can happen is that if I know Dam Kohler number, this is the Dam Kohler number and for first-order this simplifies only K by KG a, yah KG a, then KG is the mass transfer correlation which I can get and K must be, yah intrinsic rate constant, please remember that is intrinsic rate constant, this K.

That means what is the meaning, without any mass transfer effect coming into picture like we had imagined our language Institute kinetics. Language Institute kinetics we never thought is first-order reaction. By the way what is the order of reaction in those cases in language, language Institute kinetics, what will be the order of reaction? For LA HW kinetics? 1, why 1? What is the meaning of 1 when you say order? Yah, but then what is the order with respect to you know the equation which you have derived. For example 1st equation A plus B going to R plus S, you have developed a big equation no.

Student: (())(23:19).

Professor: The order of rate (())(23:26), surface reaction we have taken 1st case, you see what is the equation you got, you have the notes no. This is very important, I think I have to connect you every time, I have to connect you every time because the order of reaction, there is very interesting point here, that is why I am trying to tell you? Yah, what is the equation Anurag? Final rate only know? Yes, that is what what you are asking. That is intermediate rate where I do not know anything (())(24:03), yah, rate equal to? CACP minus but then all that, then what is the order of reaction? You said 1, now it has gone to 2, after I ask another 5 minutes, it will go to 3, okay.

Why it is 2, why it is 1?

Student: (())(24:29).

Professor: So it should be 1.

Student: No sir it is not fraction, it is not an integer.

Professor: So what it should be? You cannot say any order for that kind of equations. It is purely for the power law model where rate is defined as minus R equal to K into CA to the power of something CB to the power of something, okay. Of course, even if you have reversible reaction also we can say but for heterogeneous systems you cannot, unless you take out all the terms, neglect one term you know in the denominator, except one come all other terms are neglected. Okay, I am just, just trying to tell that, so then you will have only one at the bottom, right.

Then you remove also the backward direction, then what is the order, you can say. It will be second-order because CA to the power of 1, CB to the power of 1. So that is why you cannot say for any rate equation what is the order of reaction, unless you have power law model, it should be highly restricted. This is one of the basic things even when I am sitting in Ph.D. interviews, when I asked also via in Ph.D. interviews, 2 degrees already they have got, okay, that is why I am telling. So after getting 2 degrees also (())(25:57) is not there for many people in the mind.

That is why I try to tell all the simple things, complicated things anyway you can learn later if you know simple things. So that is why order of reaction means image and you know, what we say is first-order or second-order, okay. You cannot say anything for heterogeneous, particularly in NHHW kinetics what is the order of reaction, right. And I told you also there are some negative orders which is very funny, negative orders are really very good. If everything is negative orders, it will be very good. Why, as the concentration is decreasing, rate of reaction will be increasing.

That is excellent no. So you maintain 0 concentration, you will get infinite rate theoretically. So infinite rate means you do not need any reaction at all. Rate infinity means before you start the reaction, converted, so it is so nice. But you know in the nature, I do not have any negative order reactions, except in language Institute kinetics, when you take, I think you are going to solve the problems in the assignment. So when you are solving those problems, so sometimes you get in the denominator some terms very important, dominating terms, some terms can be neglected.

So under certain some conditions, you will have in the denominator you will have some terms and in the numerator you will have less number of terms. For example CA CB or simply only C a CB, here in the bottom as well as maybe Ca square and CB. Some conditions, it depends on you know how the actual reaction is taking place. We have taken a very simple case like one active site and one molecule absorbing. But if you take the hydrogen example, you see this book, you know as I mentioned kinetics Smith book and (())(27:54) has given this. Sometimes you get square root also in the bracket, in the denominator.

You would have seen in that table which I had given. Sometimes you will get square, so that depends, how that depends, that depends on how the molecules are getting absorbed on the active side and then getting dissociated or getting associated, all these kinds of situations will come into picture. Under those conditions you may get sometimes negative orders. And one reaction what I can mention Cadbury given that one is, I think CO going to CO2 on platinum catalyst under certain conditions, you will get some negative orders. Okay, it is given in Cadbury book also.

Okay, that is the only one example I can give but that is not straight getting. But after finding out the kinetics, finally you will end up some terms and that will result into negative orders. That means it will be again, it will become a power law model type where minus R a is equal to K by CA or C a square C to the power of N in general, okay. So that is what, that is the kind of thing. Okay, good, so I think we will stop here, Okay, we will stop here. And then I will give you the assignment for you to, you are not submitting anyway.

For second-order reaction and half order reaction in the same case here. Start second-order here, that means square and then you solve same procedure. And half order you solve for CS and then again same procedure. So this will be the exercises you have to do in your rooms. Okay, good, I think tomorrow we will meet anyway.