Chemical Reaction Engineering
Prof. Jayant Modak
Department of Chemical Engineering
Indian Institute of Science, Bangalore

Lecture No. #17
Problem Solving: Complex reactions

Friends, in last few sessions, we looked at what I would call our second module namely relating to the complex reactions. And in today’s session, we will look at few examples; we will solve few examples, in with problems related to complex reactions, their kinetics and so on. But before we do that, let us recap what we have seen in in this particular module.

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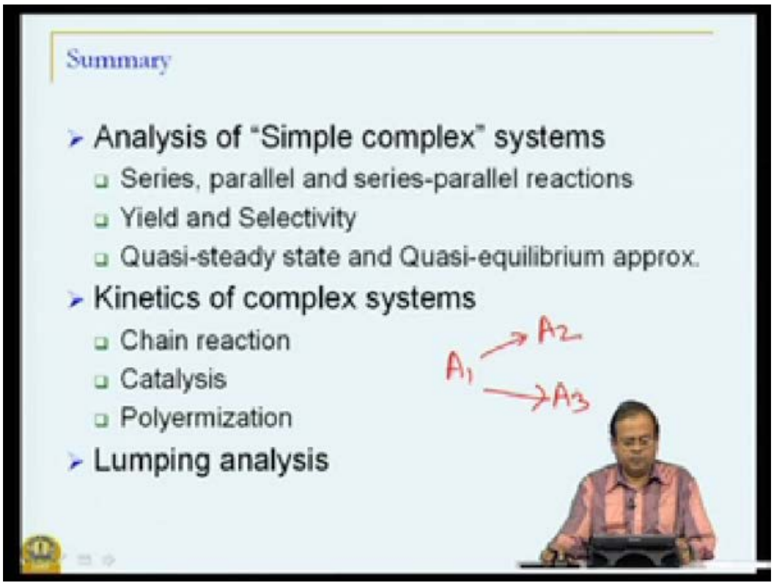

Summary

- Analysis of “Simple complex” systems
  - ❑ Series, parallel and series-parallel reactions
  - ❑ Yield and Selectivity
  - ❑ Quasi-steady state and Quasi-equilibrium approx.
- Kinetics of complex systems
  - ❑ Chain reaction
  - ❑ Catalysis
  - ❑ Polyermization
- Lumping analysis

So, we started by looking at analysis of Simple Complex systems. Now, you may wonder, what is Simple Complex system? Simple Complex system are the ones, where we said that there are few reactions, but they are enough to capture the complexity of the of the system. So we looked at, for example, series reactions, parallel reactions, series parallel reactions and few other cases. Now, the moment you have more than one reaction, your conversion alone cannot be your design criteria, because for A if reactant for example, is undergoing parallel reactions, so A 1 going to A 2 as well as A 1 going to A 3, then conversion of A 1 alone is not sufficient to tell us, what is happening with respect to A 2 and A 3.

And as it usually happens, one of these products and therefore, the reaction is an important or desirable reaction whereas, the other reactions are not desirable reactions. So under such situations, we need to go beyond conversion and start looking at, what is the yield of the product for example, or what is the selectivity. So in the example, we mentioned, suppose we have parallel reaction set, A1 going to A 2 and A 1 going to A 3, then we talk about what is the yield of A 2 on the total A 1 consumed or what is the selectivity of A 2 over A 3. And we start working working with those yield and selectivities, and these in turn often determine, how we can we can choose our our reactor, that is if you want to maximize yields, maximize selectivity and so on.

We then talked about two important concepts, which are required for arriving at the kinetic rate expressions for such complex network of reactions. Those two concepts were namely Quasi-steady state and Quasi-equilibrium approximations. What is a Quasi-steady state approximation? We said that there are few intermediates or few species in our in our scheme of things, whose turnover is very large that means they get formed, they get converted to other forms, and this is fairly a fast process.

So much so, that as soon as the reaction starts there is quote unquote steady state achieved, with respect to few of the species not all the species because, if there is a steady state with respect to all the species there is no net conversion. So, rate of reaction would be 0. So, it is with respect to few of the reactive species that we invoke a steady state approximation so its concentration does not change and therefore, we say that we have a Quasi-steady state approximation.

On the other hand, we also can think about reactions and their rates rather than focusing on the species and say that few of the reactions are very fast compared to other reactions. So the slow reaction is therefore, what determines the rate of the rate of the reaction and in the time scales of this slow reactions, the fast reactions has already achieved equilibrium and therefore, we say that those reactions are at equilibrium again not the entire reactions set or reactions at all reactions are at equilibrium, because if that is the case then the rate of the reaction would be would be 0. So, we have again what we call Quasi- equilibrium approximation.

Now, using these two ideas of Quasi-steady state and Quasi- equilibrium approximation, we looked at kinetics of few of the reactions or few types of reactions namely chain reactions, catalysis, some polymerization reactions and so on. We also then looked at certain class of complex reactions where you have large reactions, large number of reactants, large number of products as well as reactions, but what is further complicating the situation ,is that there is no way of defining the chemical species involved in these reaction just as we can do ethane, methane, propane and so on.

Take for example, crude oil now who knows what all things are there in the crude oil, but we have fairly good idea that it contains aromatics; it contains aliphatic; it contains branch aliphatic and so on. So can we for example, consider this code uncode unknown species as consisting of few groups of species rather than individual individual species and if that is the case so what essentially we are doing is whatever aromatics that are there for example benzene, phenol, xylem and so on. We will call these all the species as aromatics.

We will lump all this species into a single species which is not a real species, but an hypothetical species called aromatics and then have few such groups and see whether the reactions can be represented with the help of these few groups of species, this is what is called as lumping analysis and there we saw that what what is required for lumping to be possible? So what is the lump ability condition and so on. So, with this summary of things that we have seen let us try to address or let us try to solve few problems that one may encounter or few types of problems in this in this session.

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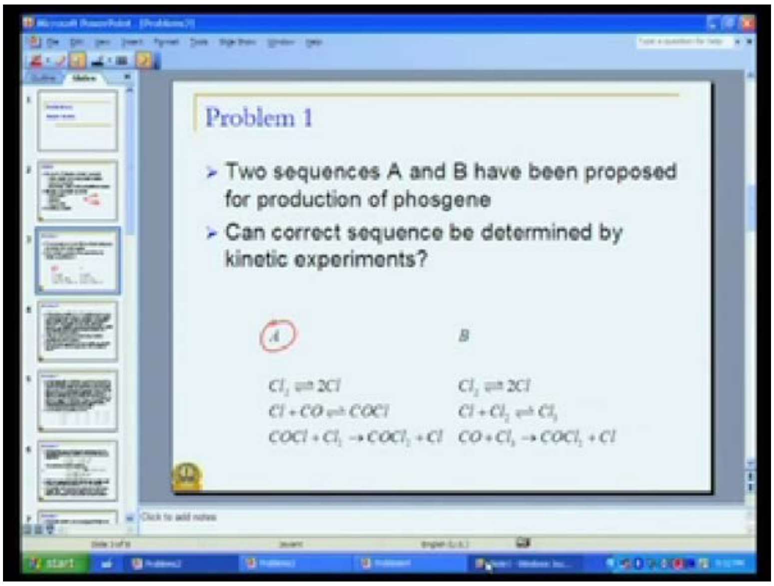

Problem 1

- Two sequences A and B have been proposed for production of phosgene
- Can correct sequence be determined by kinetic experiments?

A	B
$Cl_2 \rightleftharpoons 2Cl$	$Cl_2 \rightleftharpoons 2Cl$
$Cl + CO \rightleftharpoons COCl$	$Cl + Cl_2 \rightleftharpoons Cl_3$
$COCl + Cl_2 \rightarrow COCl_2 + Cl$	$CO + Cl_3 \rightarrow COCl_2 + Cl$

The first problem refers to that in the synthesis of phosgene COCl 2 from carbon monoxide and chlorine gas consist of several reactions, but in order to determine the kinetics of these reactions two mechanisms I have been suggested, mechanism A in which we have chlorine gas breaking down to chlorine atom, chlorine atom interacting with chlorine atom interacting with carbon monoxide giving COCl radical and this combining with another molecule of Cl 2 giving rise to COCl 2 .So this is mechanism mechanism A.

And mechanism B is also start starts with the same break down of chlorine atom and but this chlorine radical interacts with Cl 2 and then gives tri-chloride Cl 3 and the Cl 3 in turn interacts with carbon monoxide to give us phosgene gas. So we have this two sequences with us, the question is can correct sequence be determined by the experiments kinetic experiments whatever those experiments are are required. So, we have to if you recall we talked about what are the various steps in determining the determining the kinetics and one of the last step or one of the essential steps is that once you have proposed the mechanism it has to be verified experimentally.

How do we do that? So we have a mechanism, we make certain assumptions, we get the rate of the reaction and then carryout experiments and see whether our experiments match with our mechanism or the rate expression that we have got with mechanism and certain assumptions, if it matches that is not an guarantee that that is the correct mechanism, but if it does not match that is a sure guarantee that our mechanism or the assumptions involved are incorrect.

So, this example what we are trying to trying to figure out is that there are two different possible mechanisms and I have set of experiments I can do experiments with carbon monoxide and chlorine at different concentrations let us say measure their rate and so on. So can I differentiate between these two mechanisms by looking at the reactor the experimental data? So, the first step that we need to do therefore, is that for each of the mechanism we must determine the rate expression and we will start our problem solution with with this analysis.

Here again I would like to point out that, our question was only to just see whether we can differentiate so, on paper it looks like that is the only question, but we have to make a judgment what is the real question? So it turns now turns out now in this particular case the real question is to derive the rate of rate of the reaction based on the sequences given, that is part 1 and then part 2 to see whether both these rate expressions are similar or is there any difference so that we can design experiments to see what data we actually actually get and whether it matches with our with our sequences.

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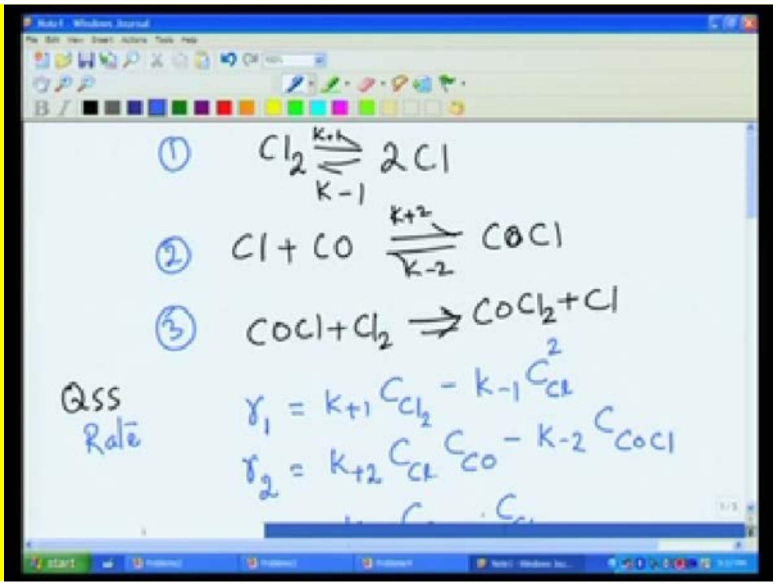

① $Cl_2 \underset{K-1}{\overset{K+1}{\rightleftharpoons}} 2Cl$

② $Cl + CO \underset{K-2}{\overset{K+2}{\rightleftharpoons}} COCl$

③ $COCl + Cl_2 \Rightarrow COCl_2 + Cl$

QSS

Rate

$r_1 = k_{+1} C_{Cl_2} - k_{-1} C_{Cl}^2$

$r_2 = k_{+2} C_{Cl} C_{CO} - K_{-2} C_{COCl}$

So let us start by deriving the rate expressions for the respective respective mechanism, so our first mechanism is our first mechanism is as follows: Cl 2 gives rise to 2 Cl, let us call forward rate constant of this as k plus 1 and the reverse one as K minus 1, so that is step 1 then the second step is Cl plus CO, COCl let us call the forward rate constant plus 2, the reverse rate constant minus 2 and then COCl plus Cl 2, COCl 2 plus Cl.

So, now let us let us try to derive the rate expression and we can we will try to do it by starting with Quasi-steady state approximation quasi steady state approximation so, what we will what we will do is we will try it to go in a systematic manner that having set these are three reaction. So we have reaction1, reaction 2, reaction 3 we have three reactions so, first let us define the rates of these reactions and the reason why we we we should do that will become become clear as we as we go along so let us say the rate of first reaction and remember we are talking of intrinsic rate is k plus 1 concentration of Cl 2 minus k minus 1 concentration of Cl and whole square assuming it is a it is a what is this? This is follows law of mass action mass action kinetics so, they are elementary reactions they follow law of mass action kinetics.

Let us write similarly, for r2 which will be k plus 2 concentration of chlorine concentration of carbon monoxide minus k minus 2 concentration of CO Cl. So this is my second second rate, second reaction and for third reaction we will have k 3, r into concentration of COCl into concentration of Cl 2. So, these are my three rates for three reactions. Ok

Now, let us so first step these are my rates, rate expression, now we will write our mass balances for three species now if you look at the look at the reactions we have chlorine which is our reactant, carbon monoxide which is our product, reactant also and phosgene COCl 2 which is our product. What are the other species in the in the reactions? It is chlorine radical and COCl radical. So, radicals being an active intermediate, we can invoke the Quasi-steady state approximation for these two radicals. So, I will write mass balance for d by dt of C cl this is this is assuming, this is assuming that I have I have this this particular reactions so what is happening?

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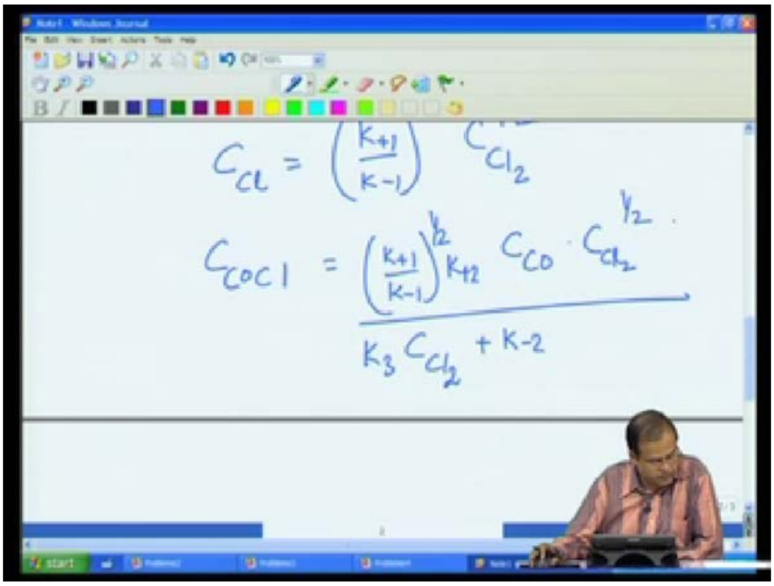

$$C_{Cl} = \left(\frac{k_{+1}}{k_{-1}}\right) C_{Cl_2}$$

$$C_{COCl} = \frac{\left(\frac{k_{+1}}{k_{-1}}\right)^{1/2} k_{+2}\, C_{CO} \cdot C_{Cl_2}^{1/2}}{k_3 C_{Cl_2} + k_{-2}}$$

Cl must be 2 into r 1 getting formed in the first reaction; getting consumed in the second reaction minus r 2 and again getting formed in the in the third reaction right. Let us write the mass balance for COCl, what is happening to COCl? It is getting formed in the first reaction and getting consumed in the in the second second reaction. So, r 2 minus r 3; so, this is this is how our ~~our~~ rate expressions will look like. And remember we have this two particular particular reaction reactionah sets, that is thatis r 1, r 2, r 3 and andandandand so on. So, let us invoke quasi Quasi-steady state approximation so, set it to 0 and solve it we will get the following:

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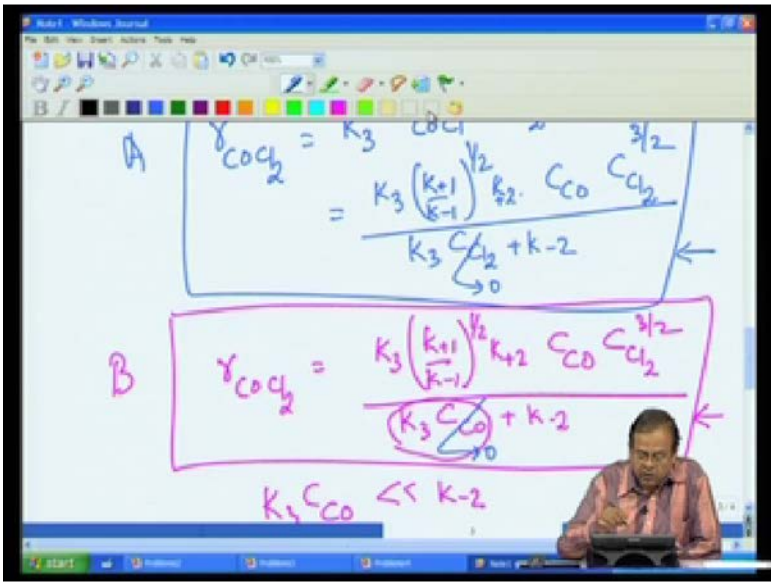

A

$$r_{COCl_2} = k_3\, C_{COCl}\, C_{Cl_2} = \frac{k_3 \left(\frac{k_{+1}}{k_{-1}}\right)^{1/2} k_{+2} \cdot C_{CO}\, C_{Cl_2}^{3/2}}{k_3 \underset{\to 0}{C_{Cl_2}} + k_{-2}}$$

B

$$r_{COCl_2} = \frac{k_3 \left(\frac{k_{+1}}{k_{-1}}\right)^{1/2} k_{+2}\, C_{CO}\, C_{Cl_2}^{3/2}}{\underset{\to 0}{k_3 C_{CO}} + k_{-2}}$$

$$k_3 C_{CO} << k_{-2}$$

So all allall we are going to going to do is this r 2 all all all, we are going to do is take these r 2 r 3 r 1 use the Quasi- steady state condition and solve this and this is what we will land up with, and from this my rate of phosgene production which is K 3 into concentration of COCl we will get as COCl into concentration of Cl 2. So we will get it as K 3 into all this terms, that we had before for concentration of so I am just substituting minus 2 and so this is my this is my rate for mechanism A. Now, if I go through the same same series of steps for mechanism 2 B which is given here Cl 2 going to 2 Cl Cl plus Cl 2 going to Cl 3, and Cl 3 plus CO going to COCl 2 plus plus Cl, we will end up with I would not repeat the same calculation. But same writing the rates and we will get the following: this should this should read plus 2. So, this is my rate for mechanism 2. So, now this is what we have got as mechanism mechanism2.

Now, our question is can our experimental experimental experiments distinguish between these two mechanisms. Now if you examine these two rate expressions a for mechanism A and B, one thing we notice that the numerator is same, it is some kinetic rate constant all this all this things kinetic rate constant concentration of C O into concentration of chlorine raise to 3 by 2, it is same in both of the cases. So if in our real reaction if denominator was some constant, denominator was some constant then these two mechanisms are indistinguishable.

Let us examine, the denominator of these two rate expression, the first one mechanism A: In the first mechanism the denominator has a term containing concentration of chlorine and in the in the second mechanism we have denominator which contains concentration of carbon monoxide and the second term is again a constant.

So this denominator terms if for example, this term was very small that is if k 3 C C O was very small compared to k minus 2 or for mechanism A, if k 3 C Cl 2 was very much smaller than K minus 2, then what will happen this term will be 0, this term will be 0. In which case both these reaction rate constants are both mechanism A and B are simply some rate constant K prime let us say concentration of carbon monoxide, concentration of chlorine raise to 3 by 2 indistinguishable.

What was the condition required for that? That K 3 C c o should be very small now, what does that mean in terms of mechanism? If we go back over here if we if wego back over here what does itwhat does it what does it mean K? What is K 3? First of all K 3 is this rate constant if K 3 is very small then what will happen? What are we actually doing? We are assuming that the third reaction is very slow that means we can go back and invoke Quasi-equilibrium approximation where we say that reactions 1 and 2 are at equilibrium. So r 1 is equal to 0, r 2 is equal to 0 this is my Quasi-equilibrium and the rate equal to K 3.

So, if indeed according to whatever mechanism the reaction is taking place, there is a rate determining step which is of the form of like a third reaction and the first two reactions are very fast, then there is no way we can distinguish between these two mechanisms. Ok But let us say, that that is not the caset hat is not the case, so these terms cannot be neglected. So they are they are there so let us let us go back and I will write these rate expressions once again.

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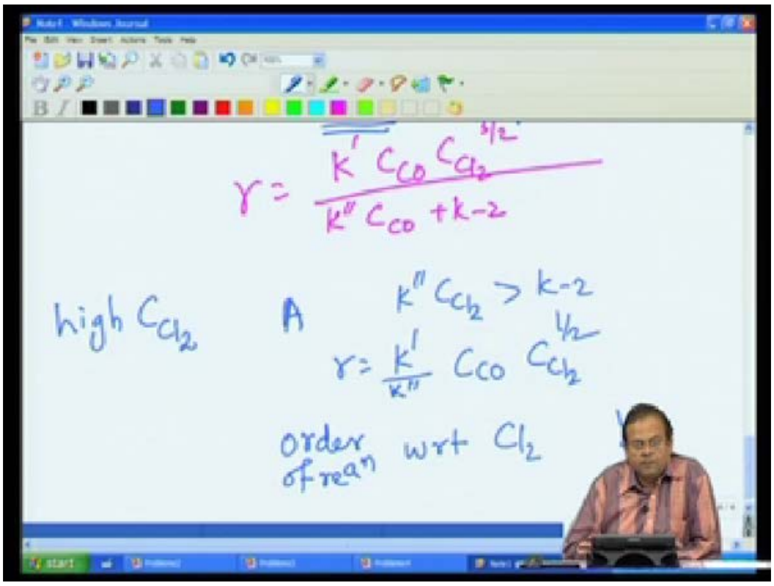

$$r = \frac{k' C_{CO} C_{Cl_2}^{3/2}}{k'' C_{CO} + k_{-2}}$$

high C_{Cl_2}

A

$k'' C_{Cl_2} > k_{-2}$

$r = \frac{k'}{k''} C_{CO} C_{Cl_2}^{1/2}$

order of rea^n wrt Cl_2

Mechanism 1 K prime C C O, C C l 2 raise to 3 by 2 some constant K double prime C l 2 plus K minus 2 and mechanism B some constant. So, let us say that this third reaction is not really as slow compared to other two reaction so Quasi-steady state is reasonable reasonable then is there any way of way of differentiating between between these two these 2 species.

Now, given that the rate these two rate expressions given that the rate expression is obtained in these two different forms, let us see whether we can we can do some experiments and let us say we do experiment, with high concentration of C l 2 ok. Now, if we do with very high concentration of C l 2 then what happens if for the mechanism A: for mechanism A, if this particular term is what does it imply? It implies that K very high concentration I mean that is all high low are all relative so, this is what we mean when we say high concentration.

Then what will happen to this mechanism, this term will go to 0 this second term and we will get r as K prime divided by K double prime C C O, C C l 2 raise to half because, numerator denominator will cancel. So at high concentration of C l 2 order of reaction with respect to C l 2 is half, at low concentrations of C l 2 again when this term is negligibly small with respect to k minus 2 what is the order so this is at high, so at low C C l 2 order with respect to C l 2 is 3 by 2.

So, indeed if we do the experiments experiments with high and low concentration plot l n C C l 2 versus l n r and we have seen that the slope of this line is what we call order with respect to chlorine, then if my data points are such that at low concentrations the slope is 3 by 2, but at high concentrations the slope becomes only half then my mechanism A is correct. What about with respect to carbon monoxide with carbon monoxide with high concentrations or low concentrations or whatever concentration the order is always 1. So, this is so what is the summary mechanism A is correct, if high C l 2, low C l 2 and carbon monoxide the orders are half, 3 by 2 and and 1 then mechanism A is correct.

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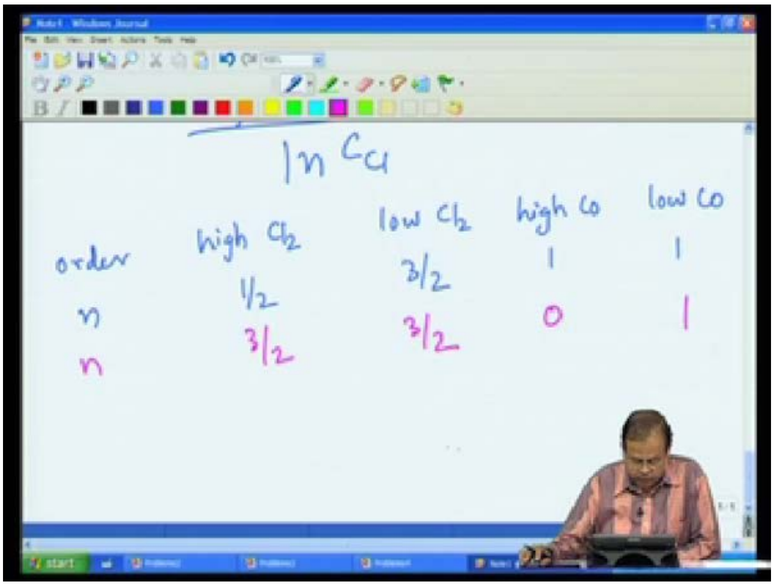

$\ln C_{Cl}$

order	high Cl_2	low Cl_2	high CO	low CO
	1/2	3/2	1	1
n	3/2	3/2	0	1
n				

On the other hand, what if mechanism B is correct what if mechanism B is correct so, what I will do is I will put, I will slightly modify this so that we get everything so let us say that we do experiments we do experiments and look at the order n, high C l 2, low C l 2, high C O, low C O and if the orders are half, 3 by 2, 1, 1 then mechanism A is correct. But if we use the same logic with respect to chlorine if the order is always 3 by 2 and with respect to high concentration of carbon monoxide order is 0. Now because both this terms will cancel this term is negligibly small and if with respect to low carbon monoxide the order is 1.

So, what are we what are we looking at if our experimental data experimental data follows this pattern as shown by the violet color this thing then we will say that our second reaction mechanism is correct. So this is how we can distinguish by designing appropriate experiments to differentiate between the two kinds of kindsof mechanisms. So this is our our first problem, let us look at another problem.

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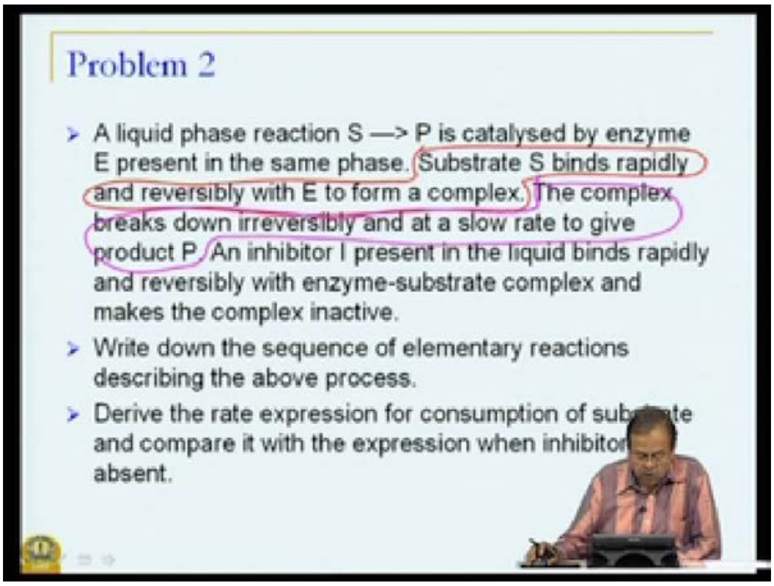

Problem 2

- A liquid phase reaction S —> P is catalysed by enzyme E present in the same phase. Substrate S binds rapidly and reversibly with E to form a complex. The complex breaks down irreversibly and at a slow rate to give product P. An inhibitor I present in the liquid binds rapidly and reversibly with enzyme-substrate complex and makes the complex inactive.
- Write down the sequence of elementary reactions describing the above process.
- Derive the rate expression for consumption of sub te and compare it with the expression when inhibitor absent.

And this example is from biology or biochemistry to be more specific, but again it has to do with chemical chemical kinetics. What does it say? It says that liquid phase reaction S going to P is catalyzed by an enzyme E present. So, catalyzed by an enzyme E that means enzymes E is is a catalyst substrate S binds rapidly and reversibly with E to form a complex, the complex breaks down irreversibly. And at a slow rate to give rise to product P an inhibitor I present in the liquid binds rapidly and reversibly with the enzymes substrate complex and makes complex inactive. So, this is a description of observed of our mechanism.

So, what is our problem now? Our problem is, write down the sequence of elementary reactions describing the above process, derive the rate of rate expression for consumption of substrate and compare it when inhibition is absent. So what it means is, what is written in English has to be translated in form of network of reactions which represent the mechanism of this reaction S going to P so let us see how we can we can do this the second part is deriving the rate expression for which we will use the same methodology that we have used in our first example. So, what is this liquid phase reaction S going to P so in presence of the catalyst or enzyme E. So, let us come to the second statement substrate S binds rapidly and reversibly with E to form complex, so let us put that put that information in the form of in the form of a reaction.

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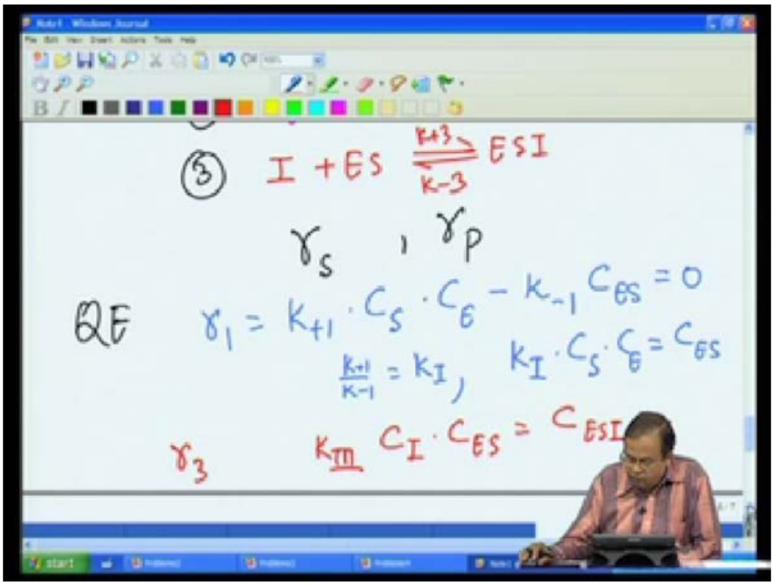

③ $I + ES \underset{k_{-3}}{\overset{k_{+3}}{\rightleftharpoons}} ESI$

$\gamma_S \,,\, \gamma_P$

QE $\gamma_1 = k_{+1} \cdot C_S \cdot C_E - k_{-1} C_{ES} = 0$

$\frac{k_{+1}}{k_{-1}} = k_I \,,\quad k_I \cdot C_S \cdot C_E = C_{ES}$

$\gamma_3 \quad k_{III}\, C_I \cdot C_{ES} = C_{ESI}$

So our reaction is S going to P in presence of this enzyme E and what is what is happening the first statement said S binds with E rapidly and reversibly. How do we put rapidly we cannot put rapidly, but we can put information reversibly that means, this is A reversible reaction giving rise to a complex ES. Then so we have we have taken care of we have taken care of the first part of the statement, not completely because we do not know what to do with rapidly, but let us letus do so what is the next information, the complex breaks down irreversibly and at a slow rate to give product P.

So, this complex which has been formed breaks down irreversibly to give rise to product P, and enzyme must be regenerated and it is a slow reaction. Now whether the information that is it is rapid slope we will use it while deriving the rate expression so this is my step step 2. So, we have taken care of we have taken care of our second piece of information, there is more an inhibitor I present in the liquid binds rapidly and reversibly with enzyme substrate complex and makes the complex inactive. So we have to incorporate this third piece of piece of information into our into our description of reaction.

So what happens some species inhibitor, I called inhibitor binds rapidly with substrate enzyme complex, rapidly reversibly to give let us say a complex ESI and makes this complex inactive that means no product can be expected from this complex. So, these are the three pieces of information that is that is available to available to us. So we have let us say our reaction 1, reaction 2 and reaction 3 and we want to find the rate of these reactions so the problem is what is the rate of substrate consumption or rate of product formation which should be one and the same because, the reaction is simple S going to P.

So let us see how we go about doing this, now what did our problem statement say and which we have not used so far it says that for example, the first reaction is rapid ,the third reaction is rapid what does it mean ? That means and the third second reaction is slow it means that we can use Quasi-equilibrium approximation for deriving the rate expression because, rapid two reactions rapid and the third one is slow is an indirect way of saying that the second reaction is the slow reaction is the rate determining step.
So we can invoke we can invoke that Quasi-steady state approximation.

So, once again if I write k plus1, K minus, and K plus 3, K minus 3 and K 2 as my reaction rates then I can I can write Quasi- equilibrium for for reaction 1, so what is my r 1 now? r 1 which is k plus 1 into concentration of S into concentration of enzyme minus K minus 1 into concentration of enzyme enzyme and and substrate is this is equal to equalto 0. Same thing for r 3,so what will what will this tell us this will tell us that if I write K plus 1 by K minus 1 equal to some rate constant K 1 capital I then this will tell us that K 1 into CS into CE equal to CES right. I can do the same thing for third reaction because, that also is a is a is a rapid reaction so for my third reaction if I do the same thing and denote the rate constant K 3 as K plus 3 by K minus 3 then K 3 into CI into CES is equal to CESI.

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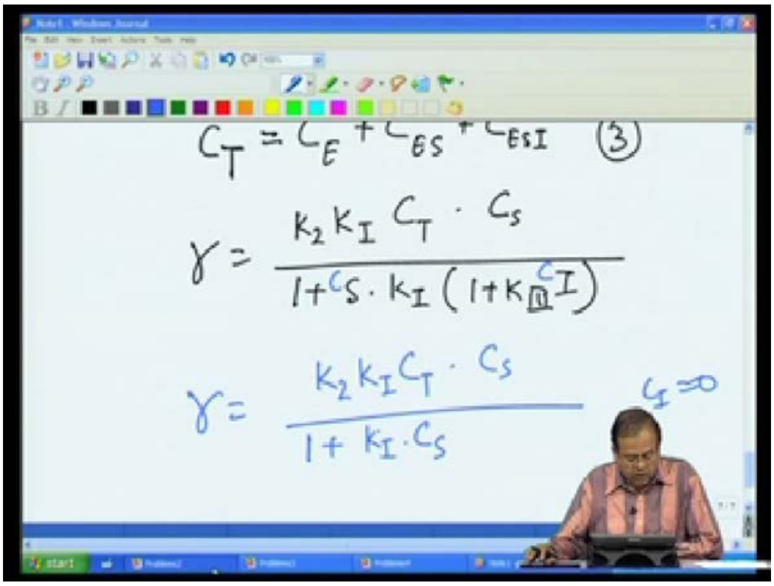

$$C_T = C_E + C_{ES} + C_{ESI} \quad ③$$

$$\gamma = \frac{k_2 k_I C_T \cdot C_S}{1 + C_S \cdot k_I (1 + k_{\square} C_I)}$$

$$\gamma = \frac{k_2 k_I C_T \cdot C_S}{1 + k_I \cdot C_S} \qquad C_I = 0$$

So I have two pieces of information I have 2 pieces of information and the third information namely we had used this earlier also that whatever may be the whatever may be the active site total active sites on my enzyme as per this mechanism. Some of these active sites have nothing bound to it, some of it has substrate bound to it and some of it has enzyme substrate, and inhibitor bound to it and there is no other possibility, why because that is what we had in our in our mechanism so now if I use information 1, information 2 and information 3 and do little bit of little bit ofalgebraic algebraic manipulation. I will get my rate as constant K 2 into KI into C S into let me first write c t C T into C S divided by 1 plus S into K I into 1 plus K 3 into I, this is my final final rate expression.

Now, you can see what is the effect of I for example, if I was not there inhibitor was not there then what would these rate expression, boil down to that is I is equal to 0 then this one would be K 2 K I C T into CS divided by 1 plus we should do it C S and C I K I into C S would be my rate expression. So, what has happened because of inhibitor? Because inhibitor this is the expression if C I is 0. So, what has happened? Because of inhibitor, because of inhibitor, our rate expression has become independent of or because of inhibitor the rate is now lower compared to if inhibitor was not there and hence the name inhibitor. Let us look at one more example which one shall we look at looked at this well there are several what I wanted to was I think I will I will just write it down over here the question, the next example although it is not there in that form is the following.

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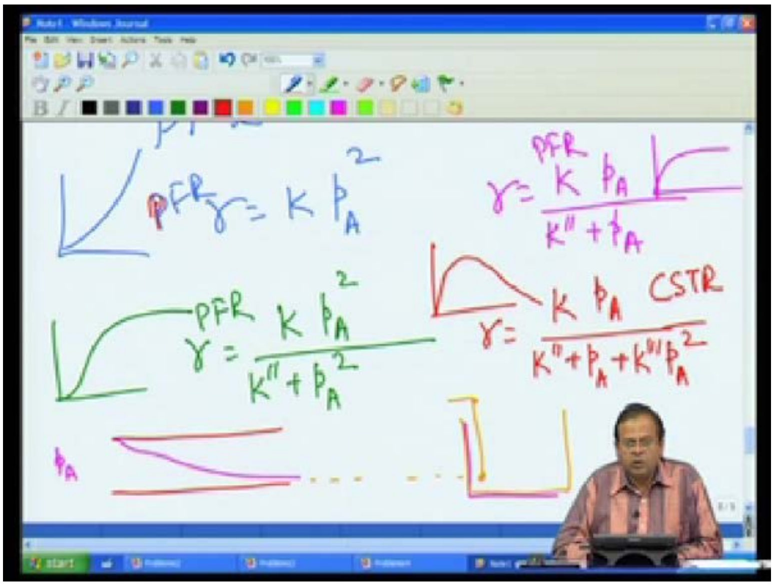

For which of the kinetics below, Plug Flow Reactor will be better than CSTR. We have a catalytic reaction whose rates are given, and they are three or four different types of rates so question is for which of this kinetics the Plug Flow Reactor is better than CSTR and what are what are those what are those rates, the rates we have is as follows. R equal to K into partial pressure of A square or R equal to K into partial pressure of A divided by some K prime plus partial pressure of A yet, another K into partial pressure of A the whole square divided by K double prime per partial pressure of A the whole square and yet another K into partial pressure of A plus K double prime plus partial pressure of A plus K triple prime partial pressure of A the whole square.

Now, this is all qualitative there are no numbers expected here so how do we how do we decide on this, so first thing that we have to recall is for what what kind kinetics PFR is better than CSTR even before with that let us recall the characteristic of PFR and characteristic of CSTR so what happens in a in a in a P F R, in a P F R, I am going to show now what will be my partial pressure along the length of the reactor partial pressure will gradually decrease from the inlet inlet condition and what happens in a CSTR in a CSTR what happens my partial pressure from the inlet decreases instantaneously to the lower value let us say that that lower value is same in both CSTR and Plug Flow Reactor.

So, in a CSTR there is a sudden decrease in the concentration and reactions occur at this lower concentration in a Plug Flow Reactor the decrease is gradual, and therefore, the reactions occur at concentrations which are gradually decreasing. So, when we want to answer this question, whether Plug Flow Reactor is better than CSTR the answer lies in realizing that if the rate of reaction is increasing with increase in partial pressure.

Then what will happen? The rate will decrease also gradually, but if for example, there are situations where the rate of reaction actually increases up to a certain point. And then starts decreasing so at high concentrations the rate is low actually and reaction rate is high at some intermediate concentration if such reactions exist then we have CSTR which is better than Plug Flow Reactor, because what will happen is at high concentration the reaction rate is low.

So, when the concentration reduces suddenly in CSTR the reaction rate will actually increase suddenly whereas, in Plug Flow Reactor the reaction rate will gradually increase so we need to examine these rate expressions in the light of this observation and see which one of them have rate increasing with increase in partial pressure. So, let us look at the first expression just a sketch this will be P A square, what about the second expression? second expression It will increase and reach a saturation what about the third one third 1also it will increase and reach saturation and S curve infect this will be hyper bola, this will be S curve but, what about the fourth reaction the fourth one you see numerator is going first order in partial pressure, the denominator is going in the second order.

So, initially rate will increase but, as partial pressures increases what will happen to the rate at very partial pressure rate will be inversely proportional to the partial pressure so rate will go down, I think the answer is clear now that for this it is a for this it is a PFR this is also PFR, this is also PFR, but only the third, the last one it is CSTR, so we have answer to our our question. So, these are the few examples which we saw which illustrate the ideas that we have seen in more more detail by looking at few of the examples. So we will stop here for this session and continue with our or initiate our discussion on heterogeneous catalysis in our next session. Thank you.