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**Lecture No. # 11**

**Complex Reactions – Quasi Steady State and Quasi Equilibrium Approximations**

Friends, let us continue our discussion on complex reactions and we are looking at simple reactions. Simple reactions in the sense that they are series parallel model type of reactions to see what kind of behavior we can expect, when we have complex reactions. And in our last session, we saw that even a reaction like series reaction  $A \rightarrow A_2 \rightarrow A_3$ ; we get yield conversion diagrams which we see in the industrial practice as well.

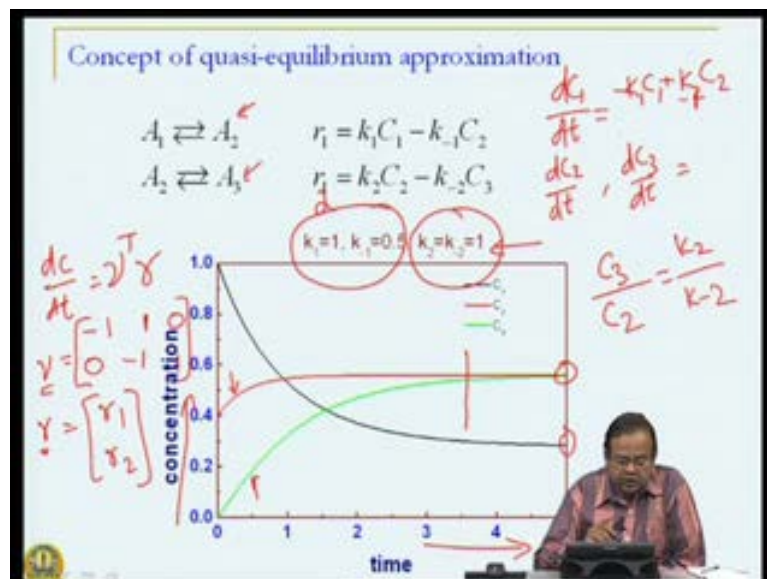
So, fall out of this is typically conversion is often considered as designed criteria, but when we have complex reactions, maximum conversion does not always lead to maximum product or yield of maximum product. And we have to now design our reactors may be for yield depending upon, what is more important yield of the desired product or the conversion of a reactant. We also saw that the type of reactor that we can use is not necessarily same, when we are maximizing the conversion or when we are maximizing the yield. Let us take this discussion forward and look at two important concepts which are often used in defining the rates of complex reactions. As we saw in the previous classes, complex reactions are large number of network of reactions and so on.

The question before us is that how do we determine the kinetics of such process or to be more precise, suppose if I have a reactant and it is going to some products, but while going from reactant to products, it undergoes a series of reactions. It could be series, parallel, connected complex reactions. My interest is to find out what is the rate of consumption of a reactant, what is the rate of consumption of as many reactants such are there as well as what is the rate of formation of a product.

Now, one simple way of doing this would be write down in detail all the reactions that you know, then find out the kinetics of each of this process and then there is nothing to do. We know already what is the rate of consumption of reactants. But it turns out, that many of the intermediates that is between reactant to product, there are several intermediates and many of these intermediates are not so easily amenable to measurements. So, we cannot really get the kinetics of such processes so quickly or so easily.

So, we need some assumptions, some reasonable assumptions, assumptions which we can justify, so that this whole analysis is simplified to a large extent. Let us try looking at what kind of assumptions we make or what kind of approaches that emerge as a result of this assumption. And the first approach that we are going to look at is what we call quasi equilibrium approximation or q e to be a short.

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So, let us take an example of our reactions which are series reactions. But this time, I have made these reactions reversible. And the reason for that will be clear as we discuss. So now, we can start looking at the reaction A 1 going to A 2. It is a reversible reaction, this one first reaction over here. And then the A 2 also goes to A 3 that is a second reaction that we have written. Both reactions are reversible and we are going to restrict our discussion to law of mass action kinetics. So, we can say that both reactions are a rather all reactions forward direction, reverse direction they are all first order reactions.

So, I have two reactions. I need two rates  $r_1$  and  $r_2$  and these are those two rates  $r_1$  is  $K_1 C_1 - K_{-1} C_2$ . I am using the subscript minus to denote that it is a backward reaction and same thing applies to second reaction  $r_2$ , this should read  $r_2 = K_2 C_2 - K_{-2} C_3$ .  $C_1, C_2, C_3$  is the concentrations of three species that we have  $A_1, A_2, A_3, A_4$  sorry  $A_1, A_2$ , and  $A_3$ . and let us say that these reactions are taking place in a batch reactor. What we are going to do is we start writing the mass balances for batch reactors. So, let us do that. Our first species  $\frac{dC_1}{dt}$ , what is happening to that. You can go back to your stoichiometric co-efficient matrix and rates and so on. That is in a compact form for example, we could write  $\frac{dC}{dt}$  as  $\mu^T r$ , where our  $\mu$  is a stoichiometric matrix we had discussed that earlier.  $r$  is my vector of 2 reaction rates  $r_1$  and  $r_2$ .

$\mu$  is a auto matrix, if you like we can write that matrix over here. The first element, first reaction stoichiometric coefficient is minus 1, first reaction, second species  $A_2$  stoichiometric coefficient is 1.  $A_3$  does not appear, so it is 0. And second reaction  $A_1$  is 0 minus 1 1. So, this is my stoichiometric matrix. If I take these two things together, I will get my mass balances and you can verify it for yourself. as minus  $K_1 C_1$  plus  $K_{-1} C_2$  that is all that is happening in the further first species. Similarly, I can write for  $\frac{dC_2}{dt}$ , I can write for  $\frac{dC_3}{dt}$  and then by assigning some suitable values of  $C_1, C_2$ , suitable initial values of  $C_1, C_2$ . That is let us say in this particular case are taken  $C_1$  as 1,  $C_2$  as 0.4,  $C_3$  as 0, these are some random values that we have given. And some values of the parameter set  $K_1, K_{-1}, K_2, K_{-2}$  and so on.

If you pluck that pluck these equations or pluck these numbers into these mass balances. And similar them, you will get concentration profile which looks something like this. So, what we have is on the X axis is the time. So, this is my time and this is my concentration. And there are three species. We are showing them by black, red and green lines  $C_1, C_2$  and  $C_3$ . As the reaction proceeds  $A_1$  decreases,  $C_2$  increases,  $C_3$  increases and after certain amount of time, as you can expect from a reaction of this kinds that we reach an equilibrium. Where there is no further increase or decrease of the species. And we see that  $C_2, C_3$  are both increasing and both are reaching same value.

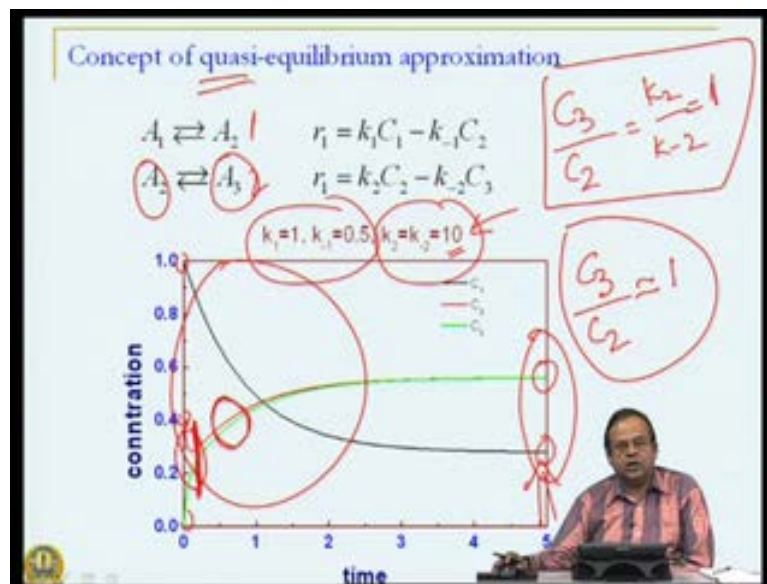
Now, when we reach equilibrium, remember we said that equilibrium is reached for each of these reactions. So for example, when equilibrium is reached  $r_2$  is 0. We have  $C_3$  by  $C_2$  as  $K_2$  by  $K_{-2}$  from this particular reaction  $r_2$  equal to 0 and since I have chosen  $K_2$  and  $K_{-2}$  values to be unity. We get equal value of  $C_3$  and  $C_2$  and that is what we see over here that is the equilibrium value. **All right** so, this is one particular scenario. Now, let us look at the same reaction scheme, but with different set of parameters. And we now simulate this process for  $K_1$ ,  $1$   $K_{-1}$   $1.5$ ,  $K_2$   $K_{-2}$  both being equal to 10. So, we have a new set of kinetic parameters. My initial conditions are still the same as before. And I find that my final value of  $C_3$  by  $C_2$  is still unity, because if you see here  $K_2$  and  $K_{-2}$  both are equal. At equilibrium both  $C_3$  and  $C_2$  are equal and I have the same value of  $A_1$  or  $C_1$  value is same as before. So, initially I started with same initial concentrations. Finally, I end up with same concentration. So, what is a difference between the two cases you may ask?

If you had noticed my previous closely, you would have now realized that for these set of parameters  $C_2$  and  $C_3$  values are much closer to each other, right through the entire time period as compared to the previous case. Let us go back to the previous case, here as I said the final values are same, initial values are same, but  $C_2$  and  $C_3$  values are significantly different for at least quite some time, may be up to here and then they merge unto each other.

So, that is a difference between these two conditions, these two simulations or these two reactions. Now, why is this happening or what is a difference between the two cases? We started with the same, we ended up with the same, and same mass balance equations except kinetic parameter values are different. If you notice here, my kinetic parameter values  $K_2$  and  $K_{-2}$ , where same order of magnitude as  $K_1$  and  $k_{-1}$  1.51 they are all same order of magnitude. But not in this second case, where  $K_2$  and  $K_{-2}$  are roughly 10 whereas,  $K_1$  and  $k_{-1}$  have not changed. So, they are same 1, means for this particular case, my there is order of magnitude difference between the rate constants of first reaction and that is this reaction over here and the second reaction over here. In fact, second reaction rate constants are order of magnitude higher than the first reaction rate constant.

So, what happens as a result of this? Now, if you look at over here you forget these initial time period. **Initial time period** there is a difference between C 2 and C 3. But for majority of the rest of the time period C 2 and C 3 are very close to each other, see C 2 and C 3 are very close to each other. Now, if you recall our equilibrium condition was C 3 by C 2 is K 2 by K minus 2. If C 3 and C 2 are very equal, both are equal they have to be because K 2 and K minus 2 are same.

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At long times they have to be equal, but even at short times C 3 and C 2 value are equal, which was not the case in the previous example. C 2 and C 3 were substantially different or in other words what is happening here is that even though the reaction is proceeding. How do we know reaction is proceeding? Because everything is changing, C 2 is changing, C 3 is changing, C 1 is changing, even though reaction is proceeding there is internally an equilibrium between species 2 and species 3.

The entire reaction has not reached equilibrium that is at this point of time, when the equilibrium is reached. But in this region A 2 and A 3 has almost reach equilibrium, because according to our parameter values C 3, C 2 is 1, when that reaction reaches equilibrium or in other words when we had a reaction, two reactions with differing order of magnitude of kinetic parameters. That means second reaction is much faster compared to the first reaction. So, when we had that scenario, we see that second reaction reaches equilibrium that is C 3 by C 2 equal to 1 much faster and for all practical purposes, that

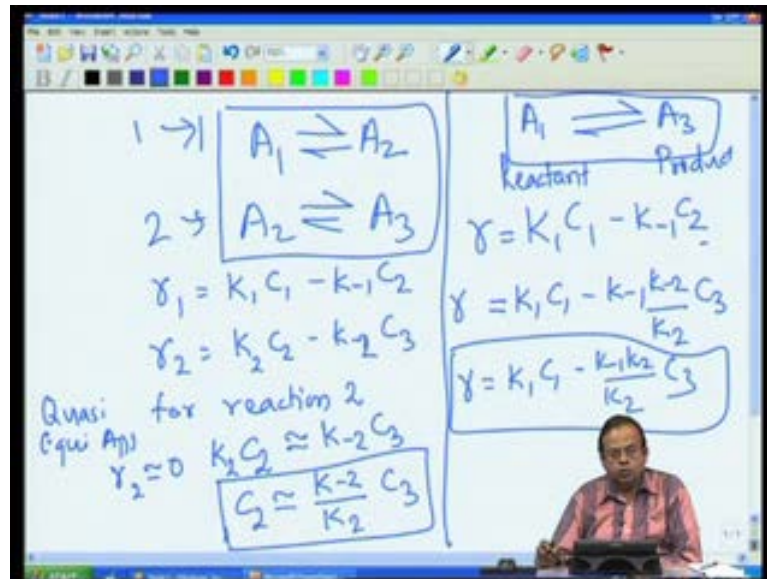
is except this time period over here the for the entire time period, I can assume that  $C_3$  by is by  $C_2$  is almost equal to 1.

There may be small variation, but being engineers we always talk about practical or practicality of the situation. So even though numerically or mathematical speaking there may be difference between  $C_3$  and  $C_2$ , they have reached almost equilibrium. This is what is known as quasi equilibrium approximation. So, let me refresh ourselves, what we just now discussed. We have two reactions, 1 and 2 these reactions order of magnitude of their kinetic rate constants are different. for this particular example reaction 2 is much faster compared to reaction 1.

When we have a scenario like this **when we have a scenario like this**, we can invoke what we call a quasi equilibrium approximation. Saying that the faster reaction namely reaction 2, reaches equilibrium in a very short span of time. And therefore, we can assume that see this reaction has reached equilibrium and we invoke the quasi equilibrium approximation.

What is a basic essential requirement for quasi equilibrium approximation? Among various reactions that we have, some reactions are much faster than other reactions and those faster reactions reach equilibrium. Now why we call it quasi equilibrium, because as you can see here they are still changing things are changing with time. Our concentrations are changing with time. So, we have not reached equilibrium, a true equilibrium, as what is happening at this particular time. So, this is equilibrium only for one set of reaction and not the entire reaction set. And therefore, we call such approximation quasi equilibrium approximation.

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What happens if we have quasi equilibrium approximation? Now, let me go back to **let me let me go back to** these reaction and write it, let us say we have A 1 going to A 2 and A 2 going to A 3. Now, I am going to slightly make a deviation, I am going to say that my main reactant is A 1, A 1 is my reactant. It is going to A 3 main product, but there is an intermediate A 2 and the reaction actually takes place from A 1 going to A 2, A 2 going to A 3. So, my interest is to find out what is my rate of consumption of A 1 or rate of formation of A 3. So, to do this, what I am going to do is that I have my  $r_1$  as  $k_1 C_1 - k_{-1} C_2$  same thing as before minus  $k_{-1} C_2$ .

So now, what I will say is that my reaction A 2 to A 3 goes to equilibrium much faster, so my quasi equilibrium approximation. Because rate constants  $k_1, k_{-1}$  are much smaller than  $k_2, k_{-2}$ . So, quasi equilibrium approximation for reaction 2. That means,  $r_2$  is very much close to 0 and  $k_2 C_2$  is almost same as  $k_{-2} C_3$ . So now, what happens? We have now  $C_2$  which is approximately equal to  $\frac{k_{-2}}{k_2} C_3$ . Now, how does this help? Remember our reaction network is A 1 going to A 3 and A 2 is an intermediate about which we do not know much. If I write my rate of this particular reaction that will be  $k_1 C_1 - k_{-1} C_2$  are according to this into  $C_2$ .

But if I would want to use this, I need knowledge of  $C_2$ . And this is an intermediate which I cannot measure or I do not know what are the rate constants and so on. So, what do I do? I can write this as  $k_1 C_1 - k_{-1} C_2$  and for  $C_2$  I am going to put  $\frac{k_{-2}}{k_2} C_3$ .

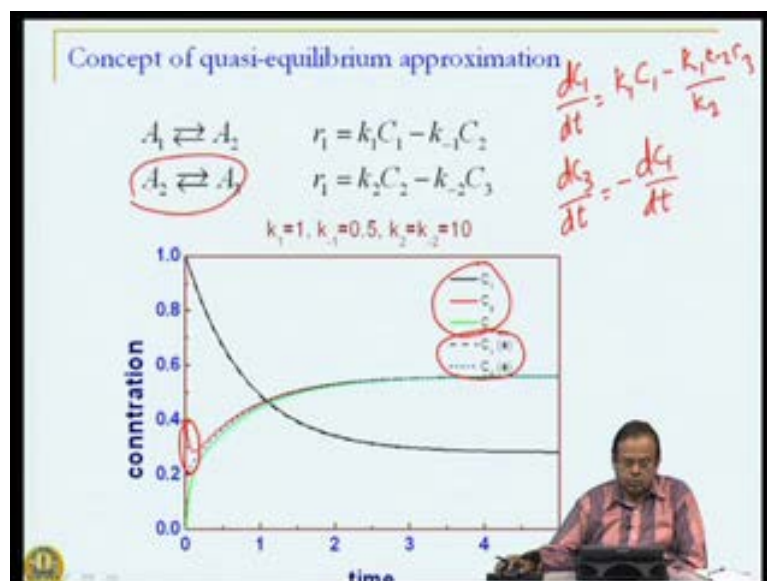


minus 2 by  $k_2$  into  $C_3$ . So, this is  $k_1 C_1$  minus  $k_{-1} C_2$  minus  $k_2 C_3$ . So, this is my rate of reaction. This rate now is known in terms of the concentrations of the species which I am able to measure, because my reaction is main reaction is  $A_1$  going to  $A_3$ .  $C_1$  I am able to measure,  $C_3$  I am able to measure. So, I have this particular set of reaction.

What did we do, we had original reaction, and its mechanism is of this kind. This reaction actually is not a single step conversion between  $A_1$  to  $A_3$  and  $A_3$  to  $A_1$ , but it is a multi step process. A complex reaction of  $A_1$  going to  $A_2$   $A_2$  going to  $A_3$ . And in this complex reaction, I want to find out the rate of reaction in terms of concentrations of species  $A_1$  and  $A_3$ . I have to look for ways of simplifying these kinetic analyses and one way I can do that is use quasi equilibrium approximation for reaction 2. This is my reaction 1, I can use it for reaction 2 and express  $C_2$  in terms of  $C_3$  and put it back in this particular rate expression and I get my kinetics of the **kinetics of the** reaction in terms of  $C_1$  and  $C_3$ . So I have two options actually now.

If I want to simulate this particular reaction, I have two options. Number 1, I can consider the detail network detail network simulates the process results of which we saw here or I can invoke quasi equilibrium approximation **quasi equilibrium approximation**.

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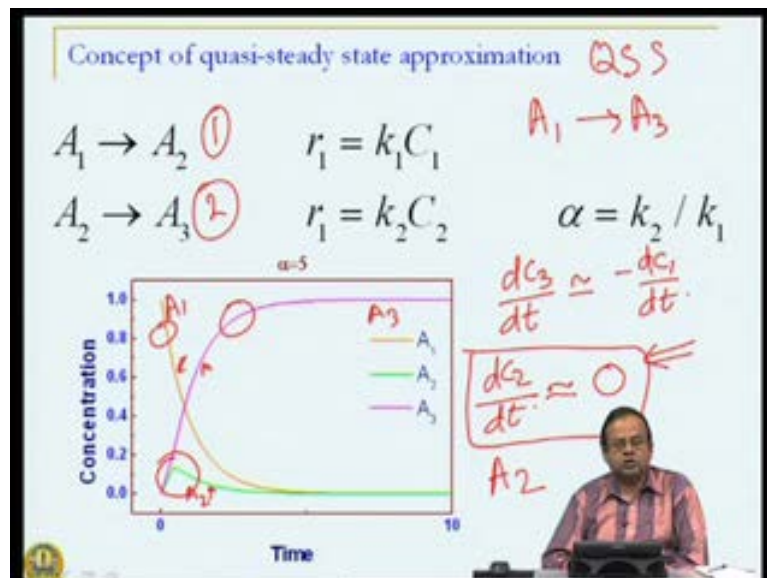


So, what do I do? my  $\frac{dC_1}{dt}$  is now  $k_1 C_1$  minus  $k_{-1} C_2$  minus  $k_2 C_3$  and  $\frac{dC_3}{dt}$ , as you would **as you would** imagine it would be exactly negative of  $\frac{dC_1}{dt}$ .



$\frac{dC_1}{dt}$ . What we can do is actually minus  $\frac{dC_1}{dt}$ , if you do all the simplifications. What we see here solid line, same simulations as before detail simulation, the dotted lines with quasi equilibrium approximation. And what we can see over here is that except. So, black dotted line and solid line all almost on top of each other. That means fairly good approximation for  $C_1$ . For  $C_2$  and  $C_3$  of course, if you see this red line and this blue line that is the dotted line for  $C_2$ , the slightly deviation is there in the beginning. But other than that the behavior is almost exact. So, fairly good approximation which case in which this reaction is or second reaction is much faster. So, we can invoke quasi equilibrium approximation. Let us look at the second approach, this is first approach.

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Let us look at the second approach of simplifying the reactions. This approach is what is known as quasi steady state approximation or QSS. Earlier one was q e this is QSS. To illustrate this approximation and to keep matter simple, let us go back to our same reaction 1, reaction 2. This time I have made them irreversible, but that is not required we will we can also do the same exercise with reversible reactions and you will get the same results or I should say similar results.

This particular diagram may have been familiar to you, if you recall our previous last session on complex reactions. we had simulated this reaction for ratio of  $K_2$  to  $K_1$  that is our alpha value, this two rate constants ratio of that alpha value equal to 5 and you also had seen this where we said that  $\frac{dC_3}{dt}$  is almost same as minus  $\frac{dC_1}{dt}$ .

Again, now we will go back to our earlier idea. That is my reaction of interest is actually this. But there is an intermediate that intermediate is A 2 and the real reaction is not one step conversion of A 1 to A 3, but rather A 2 step process of A 1 to A 2 and A 2 to A 3. Now, if you look at this alpha equal to phi result, we see that this A 1 and A 3 are almost mirror image of each other or  $\frac{dC_3}{dt}$  is minus  $\frac{dC_1}{dt}$ , we had seen that earlier. In fact, where did we see this? We saw this, when we discuss the rate determining step concept.

Now, if alpha value is large, that means second reaction is much faster than the first reaction. The first reaction is what determines the rate of the reaction not the faster reaction. But now, let us look at what is happening to C 2 and in particular  $\frac{dC_2}{dt}$ . Now, if you look at the slope of this A 2 line and slope of these A 1 and A 3, which are one similar to each other, we see that  $\frac{dC_2}{dt}$  or slope of this line is practically 0, if we compare it with slopes of A 1 and A 3. Or in other words even though reactions are reaction is taking place, A 1 is changing with time, A 2 is changing with time, A 3 is changing with time, A 2 is not really changing with changing with time. It is in fact, 0 for majority of the times only this small deviations in the beginning, which implies that we can approximate this as  $\frac{dC_2}{dt}$  equal to 0.

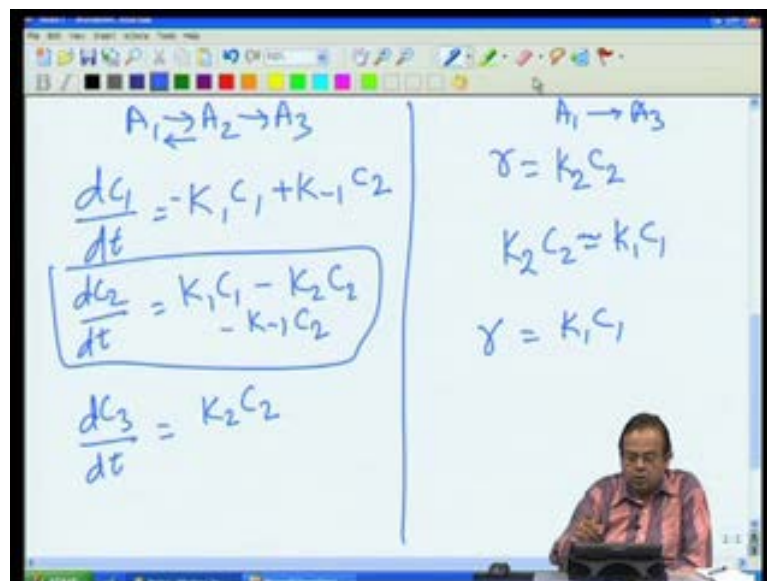
What is the condition?  $\frac{dC_2}{dt}$  equal to 0, we will arrive this condition **we will arrive at this condition** when we reach steady state or when we reach this condition we say that we have reached steady state. As far as A 2 is concerned it is almost at steady state all the time. But that is not the case with C 1 and C 3 and hence we call this condition as quasi steady state approximation. That is we can invoke a quasi steady state approximation for species too A 2 and say that its dynamics is much slower compared to that of A 1, A 1 and A 3. And therefore, say that  $\frac{dC_2}{dt}$  is almost equal to 0. This is what we call quasi steady state approximation.

Quasi steady state approximation is invoked for a species, not for a reaction. Quasi equilibrium approximation is invoked for the reaction, not in a species whereas; quasi steady state approximation is invoked for the species. Now, what was the condition under which we can invoke this was the case, when second reaction was much faster than the first reaction. Now, let us look at what is actually happening A 1 is going to A 2 at a relatively slower rate and A 2 is going to A 3 at a relatively faster rate, which implies that as soon as A 2 is formed from A 1, it undergoes reaction to form A 3. So, hardly

anything of A 2 is left in the reaction and we have direct conversion between A 1 and A 3. direct conversion in a mathematical sense strictly speaking, it is A 1 going to chemically, it is A 1 going to A 2, A 2 going to A 3, but A 2 going to A 3 is so fast that we hardly see any accumulation of A 2 and we see only A 1 and A 3 interchanging.

This is the basis for quasi steady state approximation or in other words, if I have reactant going to product through several intermediates. And if these intermediates are highly reactive, that means, as soon as they are formed something happens to them either they go from one form of intermediate to another form or some of them go to products whereas, different products. But that conversion process is very fast. If that is the case then we can invoke quasi steady state approximation for those highly reactive intermediate species.

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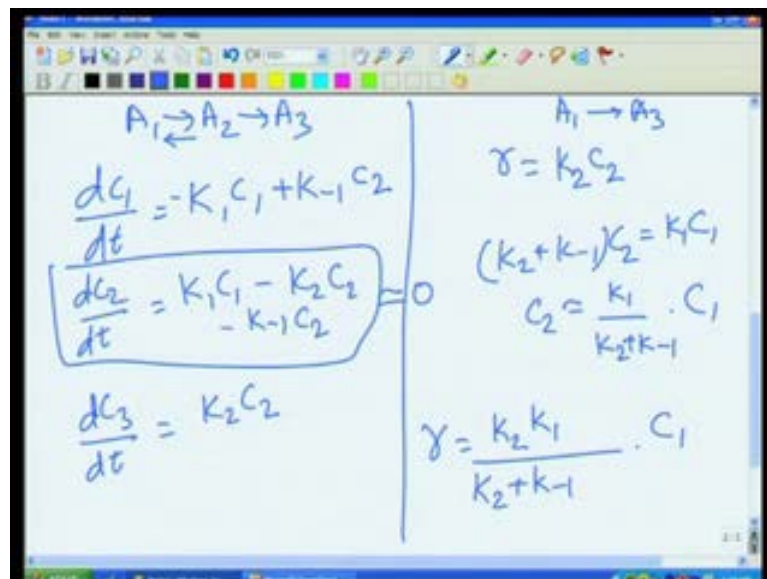
So, how do we use quasi steady state approximation? Let us go back to our reaction set once again. and this time let us say that I have A 1 going to A 2 going to A 3 is my mechanism of the reaction whereas, actual reaction is A 1 going to A 3. So now, if I write my mass balance equations, we know  $\frac{dC_1}{dt}$  is minus  $k_1 C_1$   $\frac{dC_2}{dt}$  is  $k_1 C_1$  minus  $k_2 C_2$  and  $\frac{dC_3}{dt}$  is  $k_2 C_2$ .

So now, I want to know the rate of formation of my A 3. And if I look at that rate of formation, it is actually  $k_2 C_2$ . So, when if I look at my rate, what is my rate determining step? My rate determining step in this case is the first reaction, but if I want

So look at the rate of these reactions, it is actually  $k_2$  into  $C_2$ . Now, I do not know what is this  $C_2$ . So, what I can do is, I can write, I can invoke quasi steady state approximation for this particular this particular species  $A_2$  or this equal to 0. So, if I say that this is equal to 0, then I have  $k_2 C_2$  is almost same as  $k_1 C_1$ . Therefore, the rate of formation of my product is nothing, but  $k_1$  into  $C_1$ .

Suppose, I make this little more involved. And say that this reaction is reversible. If that was the case, then I would add  $k_{-1}$  into  $C_2$ , reverse reaction then here also I will say  $k_{-1} C_2$  and rate of formation is  $k_2$  into  $C_2$ .

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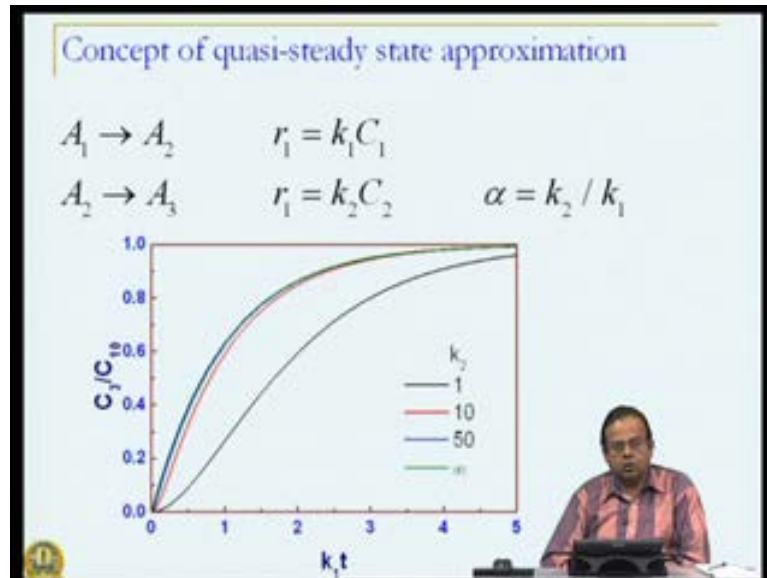


So now, for this particular reaction and if I again say that this quasi steady state approximation is invoked for the species 2, then this is almost  $\frac{dC_2}{dt}$  is almost equal to 0. Then I have  $k_2 C_2 + k_{-1} C_2$  is equal to  $k_1 C_1$  or  $C_2$  is almost equal to  $k_1$  by  $k_2 + k_{-1}$  into  $C_1$  and my rate of formation of  $A_3$  is  $k_2$  into  $C_2$ . So, that is  $k_2$  into  $k_1$  divided by  $k_2 + k_{-1}$  into  $C_1$ .

This rate of reaction is now known in terms of concentration of one species. So, this is how we use quasi equilibrium approximation. A quasi steady state approximation, quasi equilibrium for the reaction, quasi steady state for the species. So, let us go back to our reaction set once again **reaction set once again**. And if I invoke quasi steady state

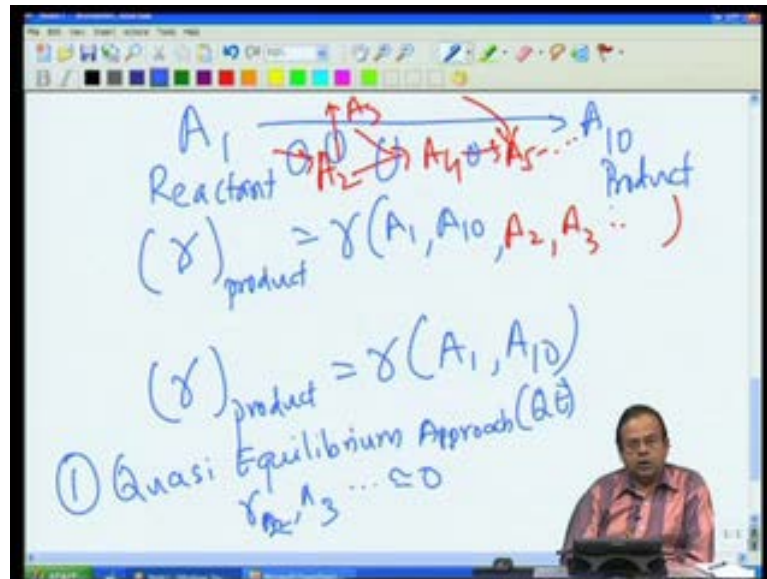
approximation and simulate the whole process, I find that my is this was this was when  $K_2$  was much higher.

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So, what we see here is the approximation that is how  $C_3$  is changing this is the case when  $K_2$  is very small, but as we keep on increasing the value of value of  $K_2$ , that rate constant we actually reach the saturation point. There are two different ways in which we saw in this particular class, how we can simplify the rate of formation of product or species. Let me recap once again, because this is an important concept which we would not be repeating again and again and again. So, let me recap these two approaches and put them in a perspective.

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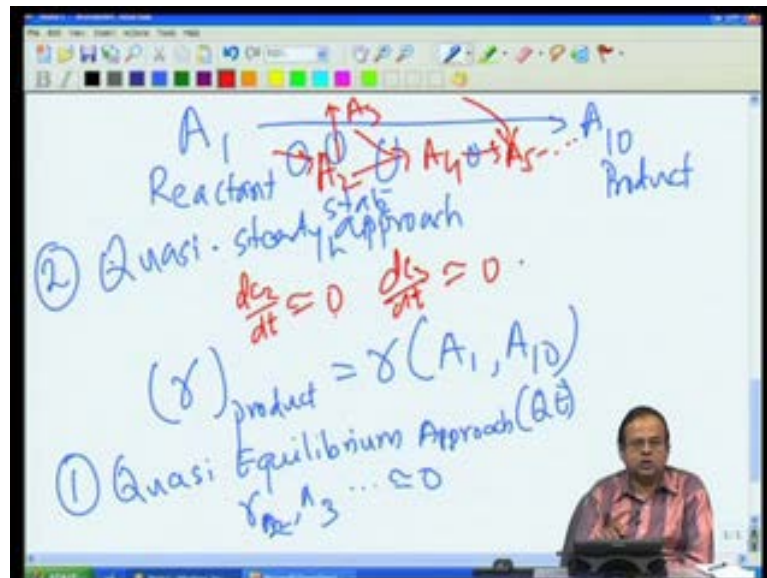
So, what is the problem that we are trying to address? We are trying to address, let us say my reaction A 1 going to some product. So, let me call give some number, it does not matter. So, my main reaction **my main reaction** is actually A 1 going to A 10. So, this is my main reactant this is my product. What is my objective, these are when I say this it is implied that I am able to measure my reactants and products, intermediates are something which I am not able to measure. So, this reaction from reactant to product actually does not take place as one step process as we saw here, but is actually may be goes to A 2 then A 2 goes to A 3, A 3 combines with A 2 to give A 4 to A 5 A 5 A 1 combines with A 5 and so on. A complex reaction network.

So, strictly speaking we can say that rate of formation of this product A 10, rate of this reaction this is a reaction or the rate of this formation of this product formation will be strictly speaking in general function of A 1, A 10 and all the intermediates that are there. But I am not able to measure these intermediates A 2, A 3, A 4 and so on. What is my objective? My objective is to express this rate of product formation in terms of things that I can measure A 1, A 10 and so on. That means I want to eliminate all these A 2, A 3, A 4 from my rate expression. So, how do I **how do I** do that. We saw we can do it in two different phases. Number one quasi equilibrium approach or approximation or Q e for short.



In this approach, what do we do? we say that these reactions whatever reactions that we see over here all these reactions over here, all these reactions are at equilibrium, that means, the rates of those reactions is all those  $A_2$ ,  $A_3$ , those two reaction 2 reaction 3 whatever may be there they are all 0. And then eliminate  $A_2$ ,  $A_3$  and so on.

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So, this is one approach, what is another approach? The approach, second approach that we use is quasi steady state approach **quasi steady state approach** or approximation steady state approach. So, what is **what is** that **what is that** approach? In that approach we say that these reactants  $A_2$ ,  $A_3$ ,  $A_4$  are highly reactive. And therefore, they reach quasi steady state much faster compared to some of the reactants and products and so on. So, we write for these highly reactive species  $dC_2/dt$  is almost 0,  $dC_3/dt$  is almost 0 and so on. And there by eliminate  $C_2$ ,  $C_3$  or all those reactive intermediates. So, two approaches quasi equilibrium approach, where we set the rates of these reactions to 0 quasi steady state approximations, where we set the rate of change of species to 0 that is a difference between the two approaches.

We will use both these approaches in the examples which we will see in our next session. We will see examples of chain reactions polymerizations catalysis and so on. So, this is these are the two approaches which we use for determining the rates of these complex reactions. **thank you**