Indian Institute of Technology Madras

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COMBUSTION

Lecture 9
Steady State Approximation
Partial Equilibrium Approximation

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We were looking at this model reactions this is basically three reactions A+A the forward reaction having a rate constant KF giving A*+A and the third reaction is A*which is of course it has a backward reaction there is a second reaction which is a reverse of the first one the third reaction is A* giving products with a rate constant of kf′ the second one having a rate constant kb, so we could write these rate equations for the production rates of net production rates of species A and A* like this and the course what you can do now is okay, we have two equations in CA and CA* dcA/dt and dcA*/dt.

So let us try to see if we can try to eliminate anything to do with A* therefore we now write from the first equation CA* in terms of CA and dcA/dt and then you plug that back in the equation for dcA*/dt wherever CA*appears and then you get a complicated looking expression that involves again only dcA/dt and CA wherever it shows up. So one possibility for us is to now plug back 3 and 4 into 1 okay, and so wherever you have a CA* you can now plug this over here and then what happens is you can get a very ugly looking equation and dcA/dt in terms of CA right.

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So plug1 and 2 to get a an equation relating dcA/dt to CA this is going to be a non linear second order ODE right, say very highly non linear second order ODE so you are going to have trouble solving that okay, so not easy to solve so the alternate approach is the steady state approximations this is a simplifying approach so this is a simplifying approach there that is we now say dcA*/dt is approximately equal to 0.

The moment you say that so we are now essentially trying to adopt a steady-state approximation and say dcA*/dt you should probably say this is quasi steady state, this is quasi steady it is not really steady but it is kind of like freeze frame a particular situation that is intermediate where the concentration of the intermediate is apparently not changing okay, change is sort of slowly there in this intermediate region so it is a it is sort of like a quasi steady state approximation rather than just steady state alone.

So if you now try to say that this is what we want to apply call this equation 5 and so what this means is A* is produced quickly in the first reversible reaction and consumed slowly right, so the moment you have A hitting A molecules hitting each other you produce A* all right but it is consumption with a the backward reaction as well as its decomposition to form the products it is relatively slow in that case then you now are producing a lot of A* but for awhile it is there but with a certain concentration that does not change a lot therefore we can now say on a quasi steady basis this is approximately 0.

Then so using 5 and 2 if you now apply 5 to 2 go back here right and say dcA*/dt is approximately equal to 0 we get CA*=kfCA^2/kbCA+kf′ not very difficult to figure that just how to pull out CA*wherever it appears said this equal to 0 on the left hand side so you can collect terms together and do this, now that is called a 6 and substitute 6 and 1 the first equation to get to get let us say –dcA/dt=ωA the reaction rate based on A that is equal to kfC2/kb/kf′ CA+1 okay, so we got something you got the answer there for dcA/dt so what we have done basically is we now have an expression for CA* from 6 which we plug in here and then you can rearrange because you know how a CA^2 there and then you have a you can plug in over here and then you should be able to get your dcA/dt right.

So what you are getting basically is KF is C2/kb/ kf′CA+1 okay, so what is this, where does this take us okay, what is our original aim we wanted to find out if this reaction set of three reactions will it behave like a first-order reaction or a second-order reaction or whatever okay, as far as like a global reaction is concerned. So the global reaction is A giving products but A* is like an intermediate right, that is showing up in a three-step reaction scheme and how do you now look at how the global behavior of the rate of depletion of A is going to depend on the concentration of A that is essentially the global question and the global question is it going to be a first-order or second-order and now you have an expression you see it is not so obvious we are now, we having some super-thin expression there with CA^2 showing up in the numerator and CA showing up in the denominator okay.

If you did not have the +1 right you would have canceled CA top and bottom and you will have the rate depends only on CA alone not CA^2 right, but if you did not have this term when you had only one in the denominator then you can see that dcA/dt is going to depend on CA^2. So in the first case you would have deduced that it is going to be a first order reaction the second case you would have deduced that it is going to be a second order reaction.

So depending upon whether it is going to be first order or second order what you will have to look for is how does this compare with unity there is a reason why we have rearranged things like that it is always good to compare things with 1 okay, to say whether it is going to be much larger than 1 or much smaller than 1 yeah, so if it is going to be much larger than 1 we ignore 1 if it is going to be much larger than 1 then we I am sorry I say the same thing if it is going to be much larger than 1 we ignore 1 if it is going be much smaller than 1 you ignore it right, so that is exactly what you are going to do.

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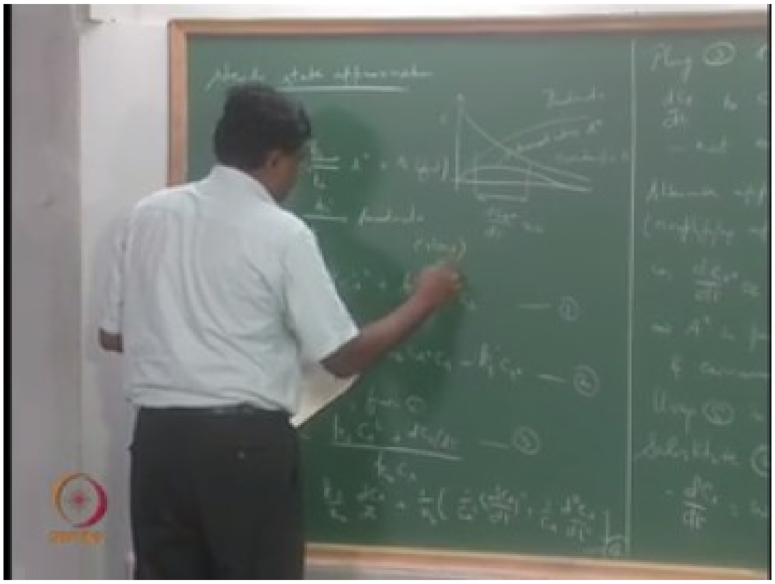

So at originally we said that this is this is going to be the fast and this is going to be slow so with this in mind we can now look at when would you when would you have which condition as far as this term comparison in comparison with unity.

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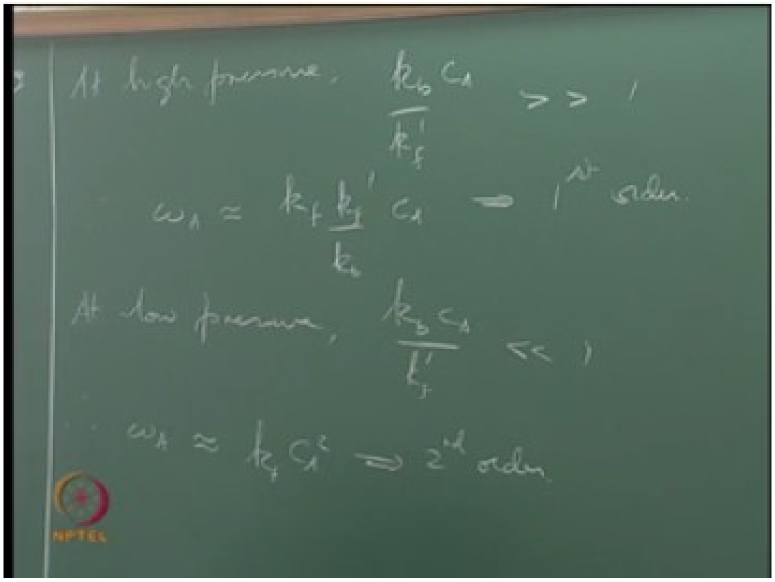

At high pressure, $\frac{k_b C_A}{k_f'} >> 1$

$\omega_A \approx k_f \frac{k_f'}{k_b} C_A \Rightarrow 1^{st}$ order.

At low pressure, $\frac{k_b C_A}{k_f'} << 1$

$\therefore \omega_A \approx k_f C_A^2 \Rightarrow 2^{nd}$ order

So at high pressure kbCA/kf′ kf′ is much greater than 1 okay, so what you are saying is kf′ is a unimolecular reaction okay, so it is going to go move as P whereas this is the reverse reaction but the competition is now between look at look at basically what is going on the kfCA^{2} is coming from producing A* with this forward reaction the first forward reaction the kbCA is coming from the reverse reaction okay well A* is getting consumed and the kf′ is actually coming from this one the third reaction there is also consuming.

So essentially in order for us to understand whether this is going to be larger than 1 or smaller than 1, much larger than 1 or much smaller than 1 we are essentially looking at how the competition between the two reactions that are consuming A* okay far in relation to the one that is producing A*, so there is one reaction that is producing A* there are two reactions that are consuming A* so between the two reactions that are consuming A* there is a competition on which one is doing a better job of consuming than the other okay.

How is that competition faring when compared to the production rate that is what this entire expression is all about, so if you want to now look at how this competition in the consumption is happening you have to understand that this reaction the backward reaction that is consuming A* is a second is a is a bimolecular reaction which is going to go as P^2 yeah, whereas the this third reaction that is a consuming A* is a unimolecular reaction which is going to go as P as first reaction rate therefore at high pressure you would expect that the backward reaction which is the second reaction is going to predominate over the third reaction that is very molecular.

And therefore we now expect that the top the numerator in this case is going to be larger than the denominator okay, therefore we expect that this should be much larger than 1 and therefore if you now plug that there then ωA then approximately becomes you just go back and get rid of the one okay, into this expression and so you now have a kfʹ/kb all right and then the CA it gets cancelled with one of the two CAs in the numerator to get only one CA this will behave like a first order all right.

At low pressure right, when the pressure is low then this square of the pressure will be lower than the pressure raise to 1 okay, that is what low that is what mean that is what it is been by low right, so when you now say at low pressure you have the other situation which is kbC/kfʹ is much less than 1 then therefore ωA so what you do is you drop the complete expression there in comparison with 1 and therefore you now simply get this is this is equal to $kfCA^2$ right, so this is this is first, this is second order.

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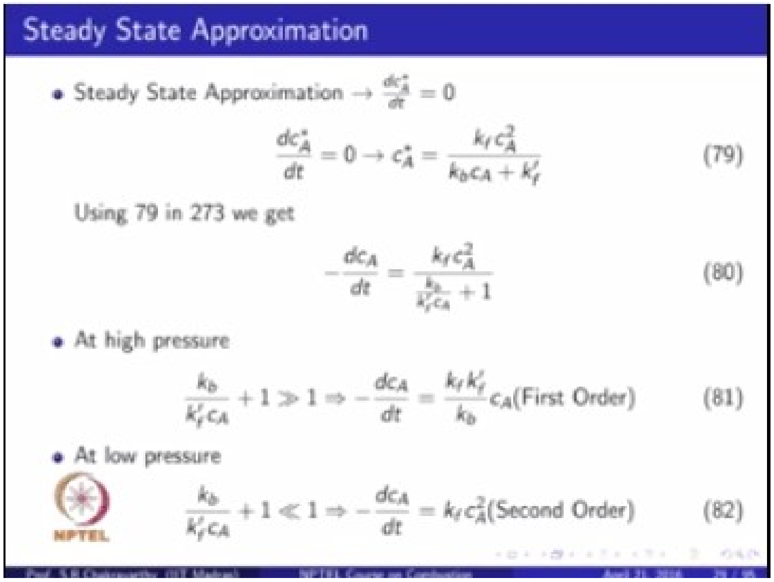

Steady State Approximation

- Steady State Approximation → $\frac{dc_A^*}{dt} = 0$

$$\frac{dc_A^*}{dt} = 0 \rightarrow c_A^* = \frac{k_f c_A^2}{k_b c_A + k_f'} \quad (79)$$

Using 79 in 273 we get

$$-\frac{dc_A}{dt} = \frac{k_f c_A^2}{\frac{k_b}{k_f' c_A} + 1} \quad (80)$$

- At high pressure

$$\frac{k_b}{k_f' c_A} + 1 \gg 1 \Rightarrow -\frac{dc_A}{dt} = \frac{k_f k_f'}{k_b} c_A (\text{First Order}) \quad (81)$$

- At low pressure

$$\frac{k_b}{k_f' c_A} + 1 \ll 1 \Rightarrow -\frac{dc_A}{dt} = k_f c_A^2 (\text{Second Order}) \quad (82)$$

So with just applying the steady-state approximation we should now be able to understand how the pressure behavior is going to happen when you are looking at two competing consumption reactions of the intermediates of different molecularities which will behave differently at different pressures this is essentially what you are trying to do that is not like a summary of what is going on good. Then let us now try to see how this works in the case of the HBR example, the HPR example.

Now let us look at the global reaction H2 +BR 2 is K 2HBR right, if this were a molecular level reaction if this were a molecular level reaction then what would you say for the rate that the reaction rate you would say the reaction rate would be the dcHBR/dt is equal to we still have to have the μ″- μ′ for HBR μ″ is 2 μ′ is 0 for HBR so you have twice yeah KCH 2 times CBR2 that means they will be the concentrations will be raised to powers one each right, if this were a molecular level reaction.

So if this were A we would write dcHPR/dt=2 kCH2 CBR$_2$ but this is wrong, another word why is it wrong it is because it does not happen at the molecular level not because of what we wrote right, this does not happen this is not what is observed that means if you were to do an experiment where you had a hydrogen and bromine and you know allowed the reaction to happen you now start sampling a hydrogen bromide okay, at different times you do not find that the rate of change of hydrogen bromide concentration to go linearly as concentration of hydrogen or concentration of bromine as you now do this experiment with varying concentrations of hydrogen or bromine.

This is how we would deduce this you actually find that the rate of rate of production of, rate of change of concentration of bromine is not going really as concentration of hydrogen and bromine so you in reality yeah.

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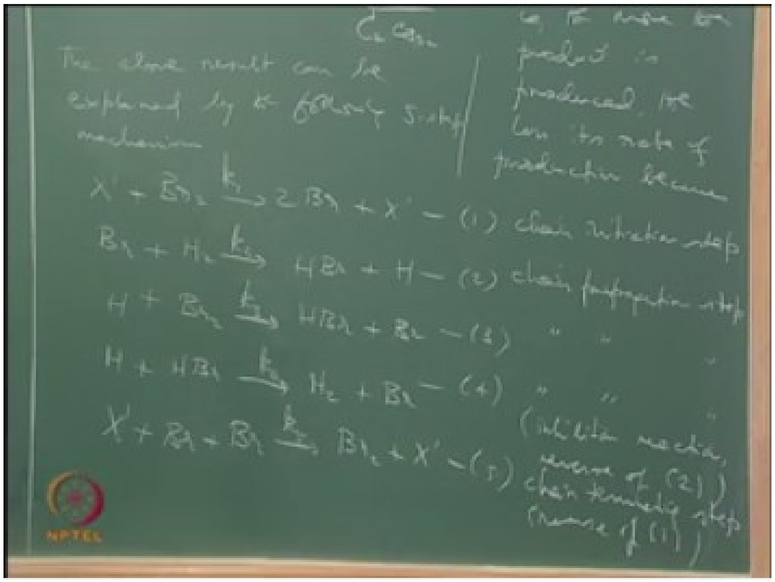

$C_{H_2} C_{Br_2}$

The above result can be explained by the following 5-step mechanism

i.e. the more the product is produced, the less the rate of production becomes

$X' + Br_2 \xrightarrow{k_1} 2Br + X'$ — (1) chain initiation step

$Br + H_2 \xrightarrow{k_2} HBr + H$ — (2) chain propagation step

$H + Br_2 \xrightarrow{k_3} HBr + Br$ — (3) " "

$H + HBr \xrightarrow{k_4} H_2 + Br$ — (4) " " (inhibition reaction, reverse of (2))

$X' + Br + Br \xrightarrow{k_5} Br_2 + X'$ — (5) chain terminating step (reverse of (1))

So experiments indicate the following results dcHBR/dt is some constant C1 CH2 $CBR2^{1/2}$ right, well you know now that is not the whole story because we now have this bar but as it is we are now finding that the rate of of production of hydrogen bromide is dependent on the concentration of bromine to the 1/2 rather than linearly right, but that is not the whole story hold your breath is getting a lot more interesting so we now have CHBR divided by another constant C2 well let us use capital C is here for these constants because we are using c for the concentration so this is just in case you are getting confused we will now have this little city font so this is C1 and this is C2, CBR2.

What does that mean this is a pretty wacky expression there okay, now if you were to be so intelligent has to immediately start thinking about what we did here right the moment you see a 1+ something you are like goodness I know what to do okay I am going to look at when will this be actually much larger than 1 okay, and then throw away the 1 and then I am going to you know rearrange things and what is going to happen so you are not going to say well this know this constant times BC, BCR2 is going to go up there and then it is going to become 1 and a ½, if I were to become like one that was that say the original production was that is still okay.

But that is not the morning to the most interesting thing the most interesting thing here is you know how CHBR in the denominator is that okay, what did he allow what well what would you want to keep in your final expressions for the production of the production rate of the product, the answer is like what and what an experimentalist would do which is you have to allow for the concentrations of stable species that is participating in the reaction and the stable species would be even reactants or products as well.

And here we now find that the concentration of the product is showing up as influencing the rate of production of the product itself, and how it is showing up in the denominator right what does that mean it means that if you now have a increase in the concentration of HBR the rate of production of HBR is going to decrease, you start out with new HBR he started now started out with only hydrogen and bromine he started producing HBR.

So the moment you start producing HBR you are now going to actually impede the reaction because the rate of production of HBR is going to come down because the concentrations of HBR is increasing, that is what is called a self inhibiting reaction okay, so this is an example of what is called as a self inhibiting right, that is the µ the product is produced well if you were not scientists before like advertising managers or something we would probably say the more the product is pretty is the less the product is videos that so much that is not what you should say the more the product is produced the less the rate at which it is produced okay, so we are now looking at how the rate of it is production is affected by how much of its produce so the more the product is produced the less its rate of production becomes right.

Now our problem is not just trying to reconcile a self-generating reaction our problem is no basic if I were to say that the actual experimental data were to show that the rate of production of HPR dependent on the concentration of bromine power half instead of one or 11/2 so the other possibility that I did not talk about is what if this entire thing will actually much less than 1 then you still have the concentration of the rate of production of bromine to be depending up on the concentration of bromine to the half which is not the case is what would the global reaction 6 right.

So you have a half or three halves depending upon this is great much greater than 1 or much less than 1 let us like the overall dependence if it is comparable to one you have to keep this as it is and we cannot resolve exactly between half and three halves its M where in between right, for the concentration of bromine depending influencing the rate and on top of it we have to explain in presence of CHBR. So how would you do this right, so this is possible the above result, the above result can be explained by the following five step mechanism right.

And we say five step mechanism we are now talking about things are happening at the molecular level, so far this was a global reaction that was not happening at the molecular level clearly because if you were, if it were this will be the rate reaction rate equation but that is not what is found in the experiments so something else is happening at the molecular level let us look at the five step mechanism. So if you now say there was some compound X' some species X' that bromine collided with to form 2BR.

That is an intermediate right, with a rate constant k1 and let us call this reaction 1 this is a chain initiation step and the intermediate BR now attacks this table reactant H2 to produce HBR+ another intermediate H which is a, which has a rate constant k2 and let us call this reaction 2, this is a chain propagating propagation step because we stopped started with a intermediate reacted with a stable reactant produced a stable product but produced another intermediate, so like the net gain and loss of intermediates is the same okay. So it is just propagating the chain and let us say we have a third reaction where H is reacting with BR2 to give you HBR+BR this is this is BR counterpart of H then the previous reaction so this is let us say reaction number 3.

This is also a chain propagation step and then we have H+HBR that gives you H2+BR right, look at what is going on right this is starting with a intermediate it is reacting with a stable product and producing a stable reactant and producing another intermediate so it is intermediate neutral if you just count intermediates blindly this is still like a chain propagation step alright but what is but it is actually consuming a stable power can producing a stable reactant that is simply that is simply because this is actually the reverse of reaction 2.

So you have reversible reactions that are happening okay, in trying to get into equilibrium under the given conditions right, and what is the flip side of that some of these stable products that you produce might actually get consumed right, so in this case we found that A+A these are the stable reactants producer A*+A right we are actually not producing any more reactants than we consumed stable reactants we have instead produced intermediates that is alright, okay that is like a chain initiation step and the reverse reaction A+A* gives 2A that is again producing stable reactants it is kind of like saying yeah I started with reactants and then did a lot of things and then got the reactants back okay.

So obviously is all over there you now have A* giving products now there is suppose that this was actually A reverse reaction then you would be consuming products to give you intermediates and that is when you will start looking at self inhibiting reactions so when you are having the stable products being involved in reverse reactions right, then they do consume and their concentrations affect your global reaction rate right. So this is a 4 alright but this is a chain propagating step alright, but there is this is the one that this removes of this is a inhibition reaction reverse of 2 okay.

And finally we now have X′+BR+BR gives of course the previous reaction had a rate constant K4 and this is a reaction rate constant k5, BR2+X ′okay. Now what is going on here we are talking we are starting with an intermediate to intermediate as a matter of fact and then producing it stable species, the stable species so we are actually killing the intermediates but this way of killing intermediates is to actually produce back the stable reactant yeah, so this is a chain terminating step and it is a reverse of 1.

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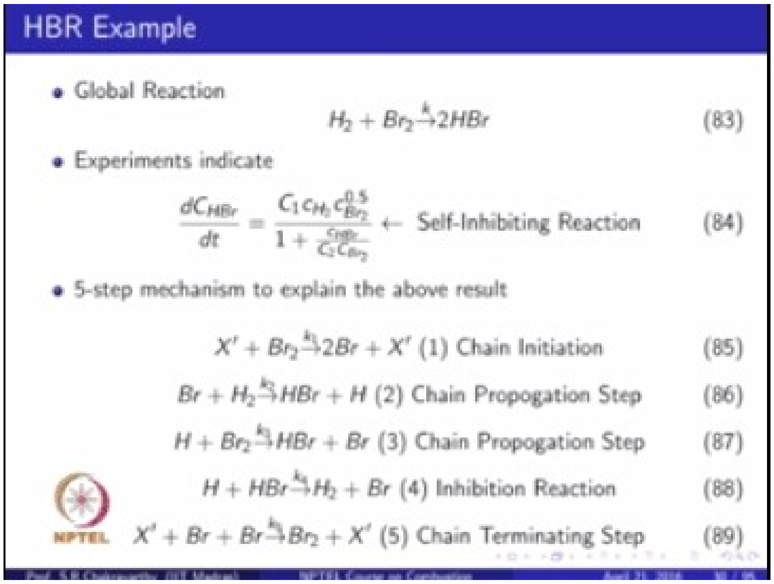

HBR Example

- Global Reaction

$$H_2 + Br_2 \xrightarrow{k} 2HBr \quad (83)$$

- Experiments indicate

$$\frac{dC_{HBr}}{dt} = \frac{C_1 c_{H_2} c_{Br_2}^{0.5}}{1 + \frac{c_{HBr}}{C_2 C_{Br_2}}} \leftarrow \text{Self-Inhibiting Reaction} \quad (84)$$

- 5-step mechanism to explain the above result

$$X' + Br_2 \xrightarrow{k_1} 2Br + X' \text{ (1) Chain Initiation} \quad (85)$$

$$Br + H_2 \xrightarrow{k_2} HBr + H \text{ (2) Chain Propogation Step} \quad (86)$$

$$H + Br_2 \xrightarrow{k_3} HBr + Br \text{ (3) Chain Propogation Step} \quad (87)$$

$$H + HBr \xrightarrow{k_4} H_2 + Br \text{ (4) Inhibition Reaction} \quad (88)$$

$$X' + Br + Br \xrightarrow{k_5} Br_2 + X' \text{ (5) Chain Terminating Step} \quad (89)$$

So you are having two reverse reactions in this out of 5, so effectively this is having the reverse here this is having the reverse here this is the one that is not having a reverse reaction yeah, and there are two reactions that are producing HBR there is one that is consuming HBR all right and finally something that you have to keenly note you now have a termolecular reaction here, so the moment you have a termolecular reaction as opposed to anything else that is bimolecular okay, the first thing that you have to think about immediately is effective pressure.

So anytime you see a unimolecular reaction versus a bimolecular reaction or a bimolecular reaction versus a termolecular reaction, whenever you are making these kinds of comparisons the first thing that hits and hits your head is pressure what is the effect of pressure okay, so that is one of the things that we will have to be looking at just like how we did previously for this example so the part that the answer the answer is are not going to work out the details that is going to be a homework for you secure the answer on how so what you do you now take each of those reactions right the where equation for whatever is its chief products in terms of its reactants concentration this is the molecular level things so law of mass action directly applies right.

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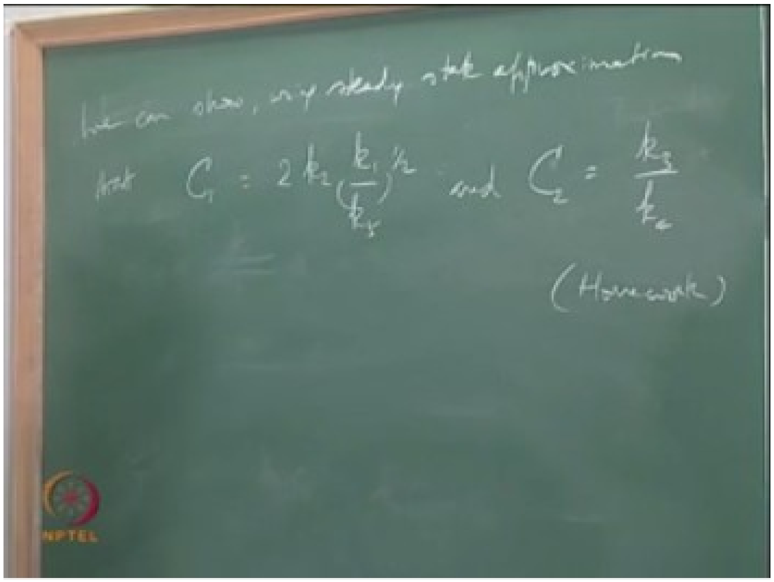

We can show, using steady state approximation

that $C_1 = 2k_2\left(\frac{k_1}{k_5}\right)^{1/2}$ and $C_2 = \frac{k_3}{k_4}$

(Homework)

And we can show we can show using steady-state approximation that C1 that we had before right, in the global reaction rate expression is 2k2 times k1/k5$^{1/2}$ and C2=k3/k4 so this is a homework for you, so whenever I say we can show which we mean you can show okay, so just go ahead and show yourself do not worry about this.

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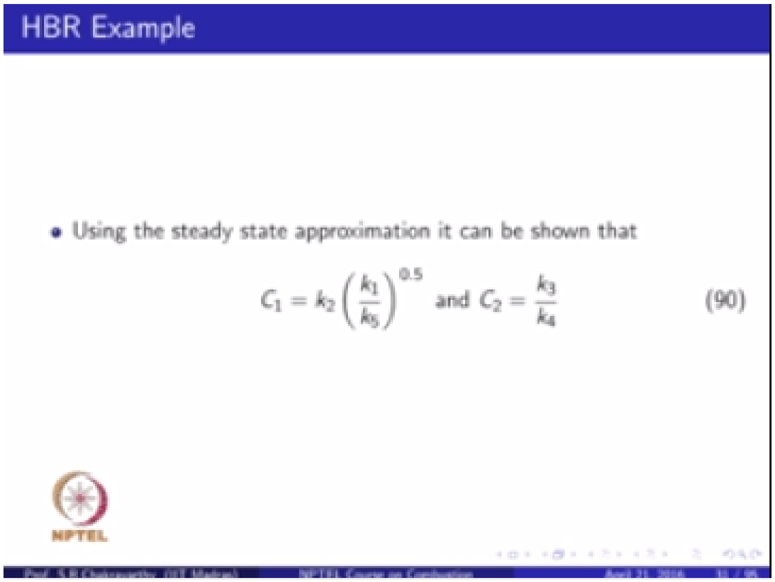

HBR Example

- Using the steady state approximation it can be shown that

$$C_1 = k_2\left(\frac{k_1}{k_5}\right)^{0.5} \text{ and } C_2 = \frac{k_3}{k_4} \qquad (90)$$

So you understand right that means if you now right throughout the rate equations for each of these and then pick out those rates that are based on intermediates that is ddcBR/dt or dcH/dt typically these are the two intermediates that are happening here okay, and then set them approximately equal to 0 you now get two equations and you have to try to eliminate CH and CBR in this expression and you had to play to all the gods that CX′ would vanish as well all right.

And then he will get something that looks like this after massaging all the remaining equations and so on do not do not over massage your because whenever you know the answer you try to actually try to fit it in but I but I have done this when I was a student okay, so he they design it is all it is not terribly bad you can you can show this yeah. So what else can we do so this is an example of how the steady-state approximation looks like, so now let us look at another approach where we try to simplify?

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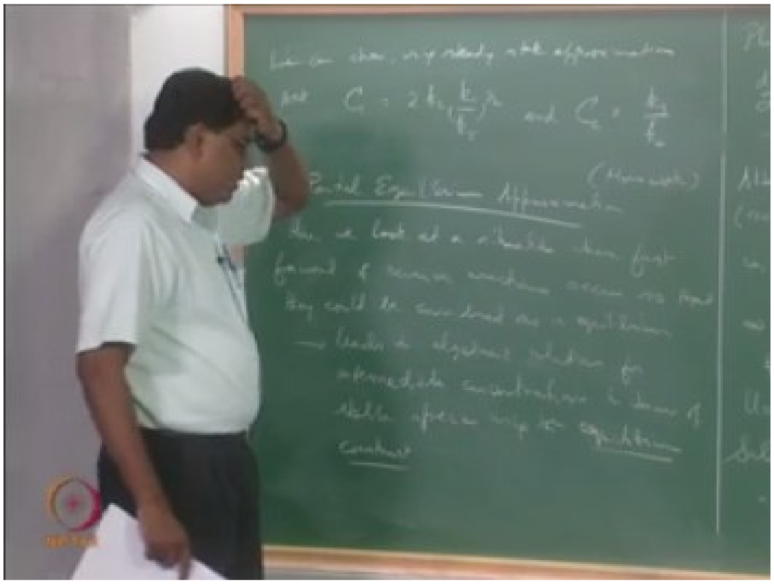

We just call the partial equilibrium, partial equilibrium approximation yeah, partial equilibrium approximation. Now this is a bit different from what we have done for the steady-state approximation but effectively leads to the same idea, the idea here is we want to try to get algebraic expressions for concentrations of intermediates as a function of concentrations of stable species does not have to be reactants okay. So this is our goal we do not want to deal with ODE for the concentration of intermediates, we do not want to deal with a expression there for dcA*/dt and then do a time integration of that and try to find out how the A*changes in time and so on okay.

So previously we said no change in time okay, approximately 0 for the rate and we just go with a algebraic expression is there another way whereby which we can obtain algebraic expressions for the concentrations of intermediates as a function of concentrations of these stable species reactants or products right, the answer is we will now try another approach do you remember these are based on some physics it so it is not like we are trying to do this just for the sake of getting these algebraic expressions okay. The previous case we said the intermediates are quickly produced and then they are there as a pool for some time when they are getting interchanged through the chain propagation steps right and takes a while for them to happen during this time their concentration is approximately constant okay, so that was a physics set. There is another thing that we can try to exploit which is the occurrence of these reverse reactions to forward reactions right, so typically when you now have two reactions that are forward and reverse pair and let us suppose that they are fast okay, like the first example that we had no A+A gives A*+A forward and backwards and that is fast and the second reaction A* giving products was the one that was slow.

So what happens there you now start with a, a bombards with itself like one molecule of a bombards with another molecule of a and quickly produces A* you now have an equilibrium that is established with A* and a like a soup and now he A* is around and it is an equilibrium with A right, and it just slowly gets consumed during the third reaction it to produce the final stable products right. So during this time is it possible for us to exploit the equilibrium between A* and A between the forward and the backward reactions.

Since if it is now so if effectively what we are looking for is if you now have fast reactions that are forward and reverse is it possible to actually apply equilibrium equation rather than rate equation. The rate equation is the one which has a dcA*/dt equals a function of CA and CA* okay, that is an ODE and we do not like ODE we want an algebraic expression. But the equilibrium equation for that assuming that it is actually in equilibrium right, would be you now have a KP or a KC that is equal to concentrations of reactants of the forward reaction divided by concentrations of the reactants of the reverse reaction raised to their respective stoichiometric coefficients right, that is an algebraic relationship you do not have a part we do not have a differential equation there right.

So this is essentially what you are trying to do, so here where forward and it is a fast forward and reverse this is not fast forward this is fast forward and reverse okay, reactions occur so that they could be considered as in equilibrium actually we are saying something about their rates it is not just that they are fast and therefore those reactions are in equilibrium essentially when you say something is in equilibrium we are saying that the forward reaction rate is equal to the backward reaction rate okay so we are basically saying let us not worry about how fast it is it is all fast okay, so they are all equal right that is exactly what you are what you are saying here so and this leads to algebraic relations for intermediate concentration in terms of stable species okay, using the equilibrium constant. So now you have the equilibrium constant we know is a ratio of the forward to the backward reaction rates constants okay.

So many times we find these kinds of ratios showing up you see so here as well we find these kinds of ratios that are showing up K1 over K5 for example is actually ratio forward to backward right, so that is exactly the equilibrium constant so we will simply be dealing with equilibrium constant instead of the ratio of the forward and backward reactions as if the two were in equilibrium.

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So let us now look at an example, so example or since example let us say let us look at consider have template reactions, template reactions let us say A+B2 gives let us say this is forward and backward so we call this AB+ B this is KF1 this is KB1 all right and let us call this 1 and B+A2 gives and takes AB+A and we call this KF2 KB2 let us call this reaction 2 and AB +A2 gives and takes A2B+A right and let us have rate constants KF3 and KB3 we will call this reaction 3 and finally let us have A+AB+M gives A2B+M that is reaction 4 that means the last reaction is not a reverse reaction see it forward it does not have a reverse reaction so strictly speaking the way you should look at it this is actually two reactions, two reactions, two reactions and one reaction so total it is actually seven reactions it is sort of like having five reactions but if you were to write it like this it would have been only three reactions this, this and this going together is forward and reverse this and this going together is forward and reverse and the last one right.

So it is just a different way of writing this and so let us call a rate constant for the fourth one so we do not have KB4 yeah, so all we are interested in now it depends on how you are I mean if you are like a chemistry kind of person like I want to see reality what is this A and B okay, they are not really happening in reality you might want to throw hydrogen for A and oxygen for B okay, and finally you might get you might be looking for H2O right, and then you can say AB is OH and so on.

So essentially what is going on is now you have a atomic species colliding with a molecular species to give rise to two atomic species so this is like a chain branching right, and this is again starting with one intermediate and this is this is supposed to be a stable species you are now getting two intermediates searching branching and this is a stable species here this is an intermediate this is the final product and that is an intermediate so that is a chain propagation it started with an intermediate reacting with a stable reactant producing a stable product and leaving another intermediate.

And MS any third body okay and you are finally getting a stable product so there is like a chain termination step you can see that sequence of events that happen that starts with the chain initiation branching, propagation, termination and so on. Now what you are interested in is to find out what is the net rate of production of the final product and how it depends on the concentrations of the stable reactants and the presence of the intermediates is spoiling the show we want to try to get rid of them yeah.

So what we want to do then is we say here we say KF1 CA CB2=KB1CAB CB right, that is for the first reaction okay, since you have the same molecularity on either side okay this will be SP^2 this will go SP^2 so concentrations can be written in terms of mole fractions and mole fractions can have pressures the total pressure so the pressure dependence is going to be the same on both sides so does not matter where you use a equilibrium constant based on pressure or equilibrium constant based on concentration I am just going to go back and use concentrate, equilibrium constants based on pressures okay. So this simply means that we now have CAB CB/CA CB2=P$_1$ right, K so K$_{P1}$ K represents equilibrium constant based on pressure.

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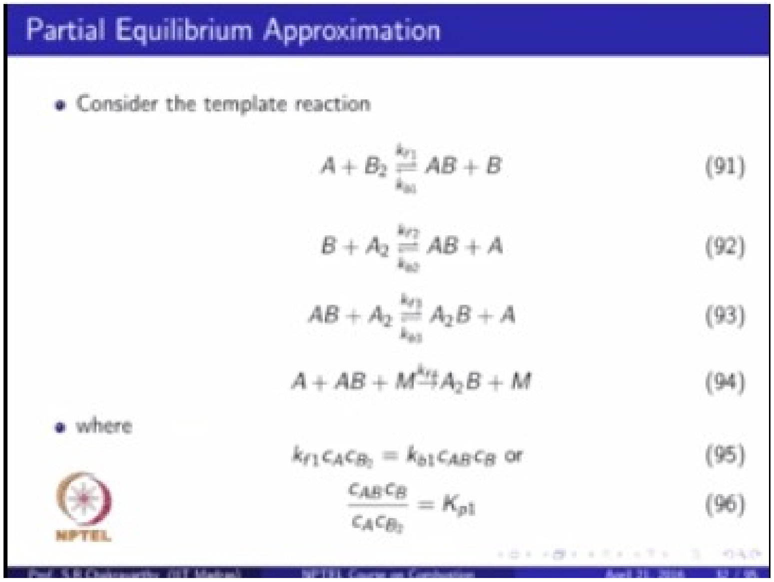

Partial Equilibrium Approximation

- Consider the template reaction

$$A + B_2 \underset{k_{b1}}{\overset{k_{f1}}{\rightleftharpoons}} AB + B \quad (91)$$

$$B + A_2 \underset{k_{b2}}{\overset{k_{f2}}{\rightleftharpoons}} AB + A \quad (92)$$

$$AB + A_2 \underset{k_{b3}}{\overset{k_{f3}}{\rightleftharpoons}} A_2B + A \quad (93)$$

$$A + AB + M \xrightarrow{k_{f4}} A_2B + M \quad (94)$$

- where

$$k_{f1} c_A c_{B_2} = k_{b1} c_{AB} c_B \text{ or} \quad (95)$$

$$\frac{c_{AB} c_B}{c_A c_{B_2}} = K_{p1} \quad (96)$$

And we have subscript 1 to denote this is actually the equilibrium for the first reaction. Similarly we can write for the second and third we can write CAB CE/CB CA2=KP2 and the third one CA2B CA= so divided by CAB CA2= KP$_3$ right.

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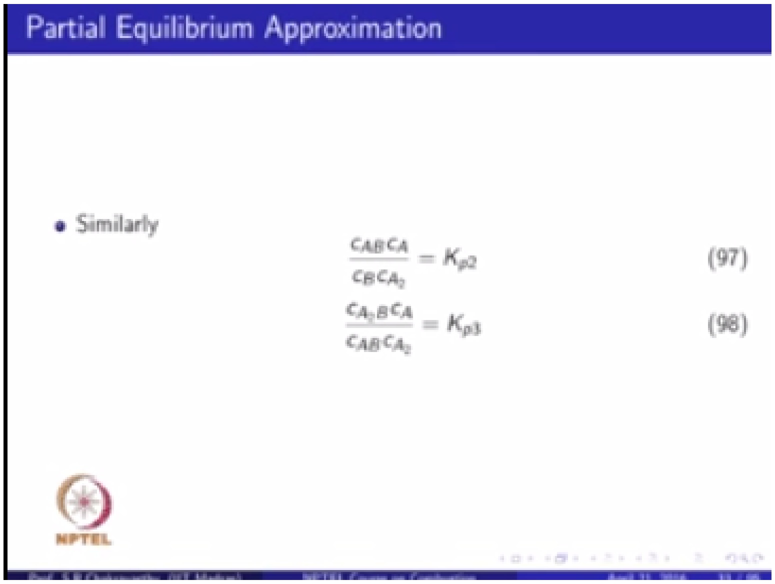

Partial Equilibrium Approximation

- Similarly

$$\frac{C_{AB}C_A}{C_B C_{A_2}} = K_{p2} \qquad (97)$$

$$\frac{C_{A_2B}C_A}{C_{AB}C_{A_2}} = K_{p3} \qquad (98)$$

So what was the purpose now we still understand we want to try to get rid of CB and CA in favor of by an CAB as well we want to get rid of CB CAD and CA in favor of CB2 CA2 and CA2B all right so this is something that we will do next class.

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