Indian Institute of Technology Madras

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COMBUSTION

Lecture 8
Reduced Chemistry, Steady State Approximation

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So the last class we have been talking about something called global reactions and what we found about global reactions was that they do not really happen in reality they are happening at some sort of like a conceptual level in our minds and we are trying to represent what is happening in reality at the molecular level by these global reactions, and therefore the kinetic parameters need to be obtained empirically for the considered species in those global reactions we also found that global reactions need not be single step they could be multi step as well.

In order to take into account some of the intermediates that are not necessarily highly unstable but those that we want to keep track off for some purposes, but in reality what we have in having is reactions actually happening at the molecular level and these are what we call as elementary reaction steps.

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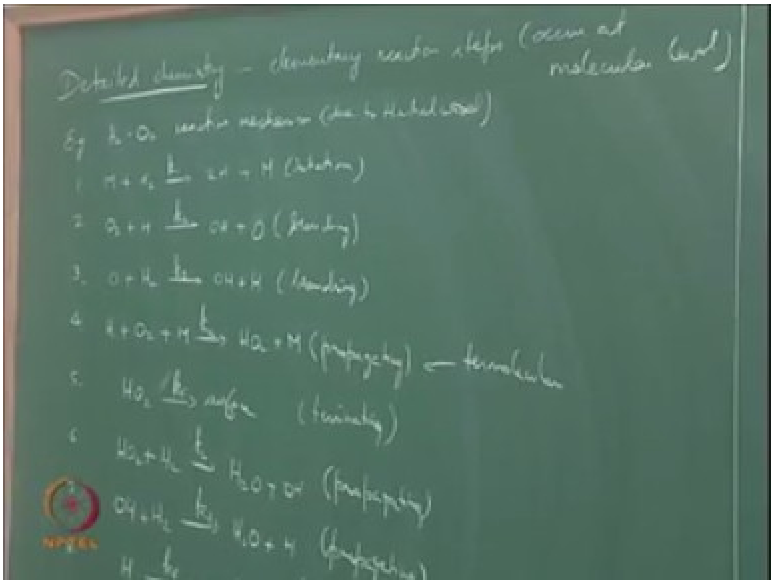

Detailed chemistry – elementary reaction steps (occur at molecular level)

Eg H_2-O_2 reaction mechanism (due to Hinshelwood)

1 $M + H_2 \xrightarrow{k_1} 2H + M$ (initiation)

2 $O_2 + H \xrightarrow{k_2} OH + O$ (branching)

3. $O + H_2 \xrightarrow{k_3} OH + H$ (branching)

4 $H + O_2 + M \xrightarrow{k_4} HO_2 + M$ (propagating) ← termolecular

5 $HO_2 \xrightarrow{k_5}$ surface (terminating)

6 $HO_2 + H_2 \xrightarrow{k_6} H_2O + OH$ (propagating)

$OH + H_2 \xrightarrow{k_7} H_2O + H$ (propagating)

$H \xrightarrow{k}$

So if you have to consider reactions happening at the elementary reaction elementary reaction level then what we have to do is we have to look at what is called as detail chemistry, so in general what happens with these reactions is there are typically a huge number of reactions that happen and involve a considerable number of species, so typical numbers we are looking at or tens of species or maybe up to 100 species and maybe about close to 100 or more or few hundreds of reactions that are happening.

Now many times it is either difficult for us to actually know what these reactions are or second thing is it difficult to actually get the kinetic parameters for each of those reactions okay so these are the first two steps for us to actually get information from the chemical kinetics and the third problem is let us suppose that the chemical kinetics were able to actually give you everything that they could possibly give right let us say that they say okay you are looking at this reaction mechanism and it involves at least about thousand reactions these are all the reactions and these are all the kinetic constants for those.

The question is can we handle them, so many times it is not possible for us to handle so many reactions in the first place, number one, number two we may not need to handle all the reactions as well okay, so just because that is what is happening in reality does not mean that we have to engineer from an engineering point of view consider all of them right. So many times what is typically adopted is reduced mechanisms.

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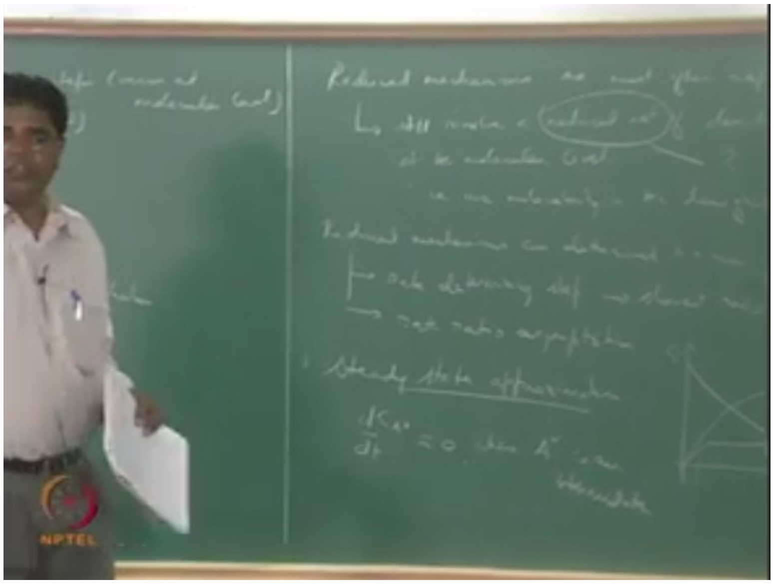

Reduce mechanisms or most often adopted so the difference between reduced mechanisms and global reactions are reduced mechanism still involve a reduced set of elementary reaction steps at the molecular level right, therefore we use molecularity, molecularity in the law of mass action right, that is we do not use orders for the reactants in the law of mass action we actually can go ahead and use molecularity for writing out the reaction rates for each of those elementary reaction steps in a reduced set right.

So that there is no ambiguity there about what we need to do and other than obtaining the reactions themselves from an empirical manner or getting the, where the element the kinetic constants empirically even for the molecular level reactions we are not necessarily looking at empiricism in order to get the orders, it is basically based on what happens at the molecular level so we just use molecularities rather than orders there.

But the key is what is this reduce set right, how do you determine this reduced set. Now that is actually something that is very difficult we do not want to get into that in this in this course so reduced mechanisms or determine in a number of ways the easiest I am not going to say anything much more about this but the easiest for us to think about is look at the rate determining step okay, the rate determining step is typically the slowest step that is happening. So if you now have a sequence of reactions that are happening right, so I have now a example of a reduced set that is put up here right for something as innocuous very simple as a hydrogen oxygen system and you would think that it is only hydrogen and oxygen there is nothing more right.

But look at how many things that are going on over there and this is like a one typical example of a reduced set of reactions that are happening with just hydrogen and oxygen to get you water as a ultimate goal okay, so we are looking at a global reaction as h2+1/2 O gives water or something like that but in reality you are having at least nine reactions that we need to consider for doing something sensible. Typically what is, how it is being done first of all what we have to look for is what does in is initiating this so there must be like one reaction or at least one or two reactions that initiates the reaction that means you start with a stable reactant and M corresponds to any species that this can bombard with.

So it could be it could be itself it could be O2 to begin with or once this is got started this reaction would still be happening so it could be any of those OH or O or H or those or even walls of the vessel okay, like the surface right and many times we have a dilemma for example if M is like a gas phase species then its concentration is important in determining the rate of this reaction okay, and we will go through these as we go along. But essentially that is how you start the reactions that is you now have a one of the stable reactants begin to decompose into atomic level radicals or intermediates.

So this is H for example as an intermediate in the big global reaction that we are looking at H_2+O_2 H_2O in whatever proportions H does not figure in, O does not figure in, OH does not figure in HO_2 does not figure in right, so all these things are essentially then intermediates that we have to recognize as such so you now have an chain initiation step this is a chain reaction and in all these things you have to stop start talking about chain initiation, chain branching, chain branching, chain propagating, chain propagate a chain terminating and so on okay.

So it is actually a reaction chain that is happening right, so when you say chain branching what that means is it actually multiplies the number of intermediates you see you started out with one stable reactant and one intermediate but it results in two intermediates that means it branches out okay, the third one is also actually multiplying the number of intermediates. The propagating steps are sustaining the number of intermediates that means you now start with H+O2+M gives HO2+M so it is like you had H2 start with O2 is stable M as a initial species which is staying there on the other side you started with one in intermediate you are sticking with one intermediate okay.

So you look at HO_2 + H_2+ H_2O+OH H_2 and H_2O are stable but HO_2 and O_2H are intermediates. So you are now propagating okay, that means you know you are not really branching you are not terminating but you are just propagating the number of intermediates keeps preserved righ,t so those are the propagating steps and finally you are also looking for some terminating steps and in some of these propagating steps is when you are actually beginning to produce the final product this table product okay.

So if you are really interested in finding out the rate of production of the final stable product in what you could think of the global reaction your mind you should keep these reactions if you throw away the elementary reaction steps that producing the final product in your reduced mechanism then you are not producing what you want right, so you how to allow to keep these and then you have to look at the rate at which these are happening and then what happens so you now look at H_2O that is being produced its depending on the concentration of HO_2 and the concentration of H2 concentration of OH.

So you have to now look for those reactions which are producing OH and HO_2 all right, now you might find that there are, there is only one reaction that is producing HO_2 when compared to a bunch of reactions that are producing OH, so obviously we might think that the root by which

H_2O is produced from H_2O is less important when compared to the route from which H_2O is produced from OH okay, that is one way of thinking about it.

The other way of thinking about it is look at the reaction that is producing HO_2 it is a term molecular reaction okay, that means H and O_2 have to bombard in the presence of M that means three bodies have to collide for you to be able to produce this, this is a highly unstable intermediate does not happen very prevalently right. So the reason for that is term molecular reactions are important mainly but high pressures so it is only at high pressures we are actually trying to put lot of species together in a much more compact region because you are trying to pressurize right, and that is when the probability of term molecular reactions actually increases otherwise it is pretty low.

therefore we could say at moderate pressures or low pressures let us not worry about this, example right so these are the ways by which you would think about trying to pick some reactions over the others. Among these one of the chief thinks that I am talking about this we now say k1, k2, k3, etc each of these is actually an Arrhenius expression that you can write which indicates the exponential dependence of these on temperature. So if you now have a temperature bath at which these reactions were to take place in reality for the flames that does not happen that way okay.

In reality for the flames the temperature continuously changes in space and for unsteady problems the way you want to post unsteady problems it might change in time right, so it is not like a nice constant temperature bath but if you want to do for kinetic purposes think about a particular temperature at which you want to compare the rates at which these things are happening we just which is already call simpler it is actually simpler to think about that way okay.

In reality it is possible that you have to have a chain you know like last time I said only if CO is produced can it get oxidized and then it is going to compete with the oxygen that that was used to produce it in the first place then in a flame you might find that depending upon the reaction rates of the two reactions that we are thinking about they could be spatially displaced, you might have like as the reactants are coming in you first have to have one reaction happen and then feed and convectively feet into the next reaction zone.

So the reaction zones could be separate it is not necessarily at the same place and therefore the temperatures of these two reactions maybe different and depending upon the temperatures at which these two reactions are taking place one of them could be faster than the other merely because the temperature was different right. So comparing these things at the same temperature is not a very straightforward thing but you could think about it from simpler for the purpose of simplicity right, let us say you did that other than having to sequence them because one has to be produced one has to produce H in order for it to be utilized okay.

So keeping the sequence in mind the next thing that you want to worry about is which one is actually the slowest okay, so when many things are happening in parallel okay if you now want to say I want to look at the whole thing as like one black box I am putting in hydrogen and oxygen here I want to get water there all this stuff is happening tell me how fast this is going to happen then all I am going to be thinking about is which of those reactions is the slowest to happen that is the one that is going to determine the rate at which the whole thing is going to happen, right.

Because until that is complete I am not going to get out water okay, so all other reactions could have already happened but it is waiting for this last reaction happens you see. So the rate determining step is the one that is actually the slowest we with the slowest reaction rate so you could also pick these reduced mechanism reactions based on their reaction rates okay, and a much more sophisticated way of doing these things is called rate ratio asymptotes that is something that quite a few people have done in the last many decades to try to deduce reduced mechanisms okay, to actually compare rates and then look at asymptotic expansions based on those and so on.

And we do not want to go further into that because it is a area that that can take pretty much all your time thinking about. So in what we have done we have we have introduced a couple of ideas here first of all the right thing to do instead of adopting global reactions is to actually adopt reduce mechanisms because the chemical reaction rates that you would want to write the law of mass action would be less ambiguous, but then what could be ambiguous as to how to reduce the reaction mechanism and there are people who work on this separately.

So if it is possible for you to actually look at the literature for your application let us say you are now looking at a partially prime flame under some conditions or something like that so particular situation there are people who work on this new experiments and deduce these things and so on and also do the analysis for this and try to recommend reduced mechanisms. Many times as we go along between the time I graduated or I went to grad school to now the last 15, 20 years for example things have actually grown.

So previously when two reactions was considered to be too much okay, now you your chemist is going to say take these 50 reactions again this just take it and then you like can I reduce further or maybe you do not have to so you have computer power to handle those 50 reactions so just go ahead and try to use it and so on. So it is an expanding area where things to keep changing what is required keeps changing with computer power and so on. So therefore the right thing to do is for you to actually try to keep as many elementary reaction steps as possible because they are closer to reality and the second thing that we have also come across is the nature in which these reactions happen right, that is the initiative the branch of then propagate and terminate so that sequence, right.

So in this sequence what is essentially crucial there is the role of intermediates the presence, the formation there are presents and the role of the intermediates in each of these because when we are now trying to identify a reaction is branching or you are propagating we are actually looking at how many intermediates are showing up on either side you see so we are now also started looking at intermediates as one of the important things in the reaction scheme. And finally I would like to point out that we now have a reaction scheme that put together is the one that is now going to give you the reaction rate expression that depends on the reactant concentration for the stable reactants the original reactants.

If you are now basically looking at H_2 and O_2 to giving H_2O you finally want an expression for the rate of production of water which depends on the concentrations of H_2 and O_2 right, but that is something that you want to deduce from this entire soup of reactions water is happening here it depends on this and this, this and this so this depends on this so it depends on this and this depends on this and this keep going back ultimately to wherever you are showing up as H_2 and O_2 the reactants.

So you want to find our job is finally to link up the rate of production of products to the rate of production of reactants through the rate of production of the net rate of production or depletion of the intermediates right. And if you now are able to actually look at how my global activation energy for example is going to fair given the activation energies of all these, you see because you have kinetic constants for these and finally we want to deduce a kinetic constant for like a global reaction from this let us suppose right.

What is going to happen is if you have more and more chain branching and propagating reactions the global activation energy will come down, that means its sensitivity the temperature actually diminishes. So there is a role for consideration of detail chemistry and the way you want to reduce the chemistry in how the, how it influences your global activation energy or the net activation energy for the entire system, net activation energy essentially tells you how the full system of border production from hydrogen and oxygen depends on temperature right, how the non linear dependence gets right.

So there is a significant impact that this has on the global performance or the system what we will then do is come up with a couple of approximations which we can try out with these intermediates in trying to quickly put together this connection between rate of production of products and concentrations of the reactants okay. So we are let us get into that game of getting like a global reaction rate based on the reactant concentrations through the intermediates right, so some easy ways of doing this is one steady state approximation, right.

So in steady state approximation what we are essentially saying is if you now or trying to plot your concentration of different species with respect to time right, initially at T= 0 you are starting with a bunch of reactants are there at some concentrations. Now let us say we have some reactant that we can follow and as the reaction proceeds the reactant concentration will decline right, with the time so that is not a you do not get any prizes for this right, now what happens to concentration of the products it will increase right, how does it increase?

It increases like that it should increase like this because ultimately at T at infinity it does lesson taught right, so well. Let us not worry about how in either in any inflection here and so on but ultimately we are looking at a picture that will emerge like that, now the story is about the intermediates it is not about what happens when you are born or when we die it is about like the life in between right, so that is the intermediates life, so all life is intermediate essentially so question is what are the intermediates do, they are born and they then and they die right, like all of us. So the question is how do they behave, they have a maximum right.

So it goes and comes down does it go up and then come down immediately or does it want to live for some time like us right, so it does that right so the intermediates you know they produced and then they want to stay for some time as long as they can, so it is not really like a peak at the maximum it is a plateau at the maximum okay, so they produced and then they are like yeah I am going to be here for quite some time yeah sure.

Let me let me have some fun that is the way it goes and then ultimately it does okay, so what we are looking for is it possible for us to exploit the situation say let us not worry about the initial transient when the intermediates are just beginning to get initiated and branch off okay, or let us not worry about when they are busy getting terminated okay, can we look at the region when they were actually simply propagating.

When the concentration is going to be more or less constant and if that is the case then we suppose that is around like a steady state things are not changing with time and so we approximate the concentration of an intermediate approximately equal to at the rate of change of concentration of an intermediate with respect to time as approximately equal to 0 where A store is an intermediate.

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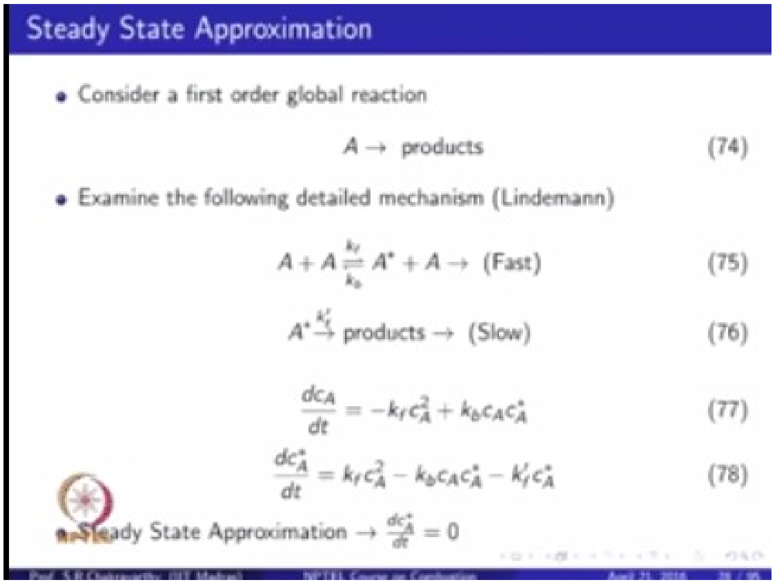

Steady State Approximation

- Consider a first order global reaction

$$A \rightarrow \text{ products} \qquad (74)$$

- Examine the following detailed mechanism (Lindemann)

$$A + A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} A^* + A \rightarrow \text{ (Fast)} \qquad (75)$$

$$A^* \xrightarrow{k_f'} \text{products} \rightarrow \text{ (Slow)} \qquad (76)$$

$$\frac{dc_A}{dt} = -k_f c_A^2 + k_b c_A c_A^* \qquad (77)$$

$$\frac{dc_A^*}{dt} = k_f c_A^2 - k_b c_A c_A^* - k_f' c_A^* \qquad (78)$$

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

This is the sub this is the essence of the steady-state approximation okay, so what are you get out of this is what we have to see right. So we use this we use this approximation.

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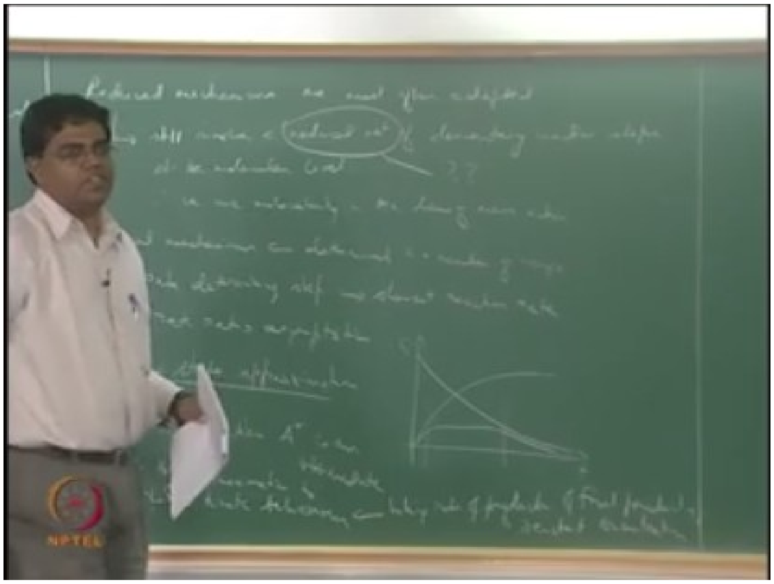

To obtain global kinetic behavior, what is meant by global kinetic behavior that is like linking rate of production of final products to reactant concentration, the reactant concentration that is like the global kinetic behavior, right?

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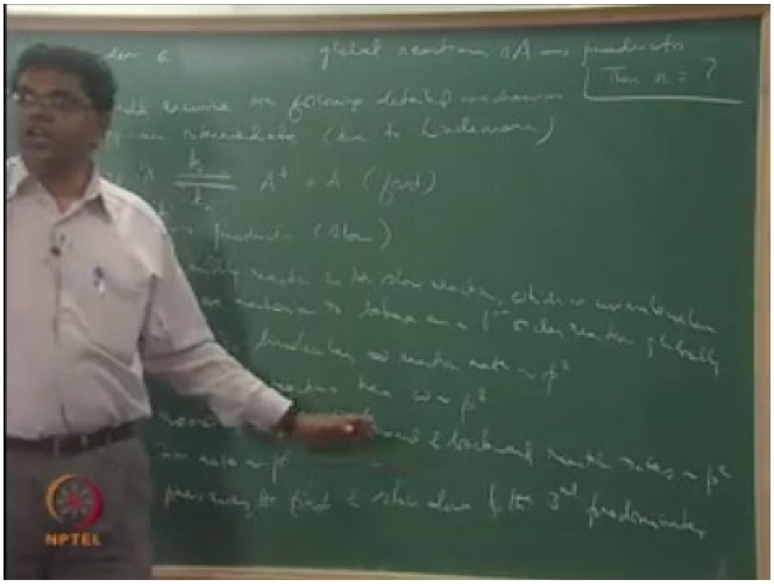

So let us suppose that we consider a first order reaction, first order global reaction I will put this within codes first order global reaction A gives products we do not really worry about what the products are because the law of mass action says that the reaction rate does not depend on the concentration of the products it is only the reactants that we have to worry about not that we are really worrying significantly about the reactants it is just A okay, so it is a, a template reaction right.

Now we could examine the following detail mechanism involving an intermediate, involving an intermediate the means whenever you want to propose a theory the quickest way to publishers to make a number of variables as little as possible right, so just keep it one so you are looking at the role of intermediates just keep an intermediate with you do not get into this soup bowl of intermediates, right so this is due to Lindeman.

So let us suppose that we now have A+A gives and takes A*+A and we denote the forward reaction by the rate constant KF and the backward reaction by the rate constant KB and let us suppose that A* gives words these targets products and let us call this a second reaction rate constant is KF, KF′ I am sorry KF′ this is actually a set of three reactions okay, so A+A gives

A*+A as one reaction, A*+A gives A+A is another reaction okay, each of them having KF + KB as the rate constants respectively and the third one is A* gives products with a A constant KF.

And let us suppose that this is actually this set of reactions is fast and this one is the one that is low that means the moment you have A it produces A* and it now starts getting in equilibrium with us right, the more A* it produces A* combines with A to produce a back therefore there is an equilibrium that can be associated with this okay, so and then these things are happening very fast so it is like you now finally have like a some pool of A*.

Now what is the job of A*, A*s job to actually produce products it is not A job, A job is only to produce A* and get into equilibrium method that is for the first two reactions do, producing A* and getting into equilibrium okay. The third reaction is where the A* is the one that is producing the products and that is slow okay, so now we are beginning to think what would be the order now think about this what would be the order of the global reaction a giving products that is what is supposed to happen okay, and all this is like details that are happening in reality okay.

So let us now think about how to deduce this okay, so the rate controlling reaction is the slow reaction right, so which is uni-molecular, which is uni-molecular A* giving products is a uni-molecular reaction therefore we expect the mechanism to behave as a first order reaction globally right, because it depends only on concentration of one of the species okay, so what is meant by globally like for example if you now think about these things as gases which is what we have been doing all the time right.

The concentration of these is actually directly proportional to pressure right, if you now had a bimolecular reaction then the law of mass action will have a P^2 so the question is essentially are you going to have the reaction, reaction rate for the final global reaction go as linearly SP or P^2 or somewhere in between right order for the global reaction does not have to be an integer right.

So what is it going to be so in fact a way to post the problem a little bit more general is consider a global reaction n A gives products okay, and we basically for the global reaction assign a value of n based on what is the order that is deduced from the detailed reactions the elementary reaction steps right. So question is then n equal to what is it supposed to be first order or second order or somewhere in between or what or anything else, that is exactly what you are thinking about with this being the detailed mechanism in this case okay.

So but you see the first reaction is bimolecular, bimolecular which implies reaction rate goes as P^2 and that is important for us to think about because what is ultimately going to affect is as far as a reaction rate is concerned is the concentration of A raise to whatever the exponent is and the concentration of A shows up in the first reaction which is bimolecular okay, even though the second reaction is the slowest and therefore the rate determining step it is actually in A* so it is reaction rate is going to actually depend on the concentration of A* rather than A.

You look at the reaction that is actually depending on the concentration of a the first reaction tells you it is bimolecular right, which means it has to go as square of pressure okay and recall or note, a note that tell molecular reactions to molecule reactions have ω goes P^3 okay, it is kind of like extending from bimolecular if you have P^2 inter molecular reactions of course you are not looking at your molecule reactions here just mentioning this because what we have to consider is it is going to go as P or P^2, P^3 okay.

Then what happens is if you now or working at a high pressure then P^2 is going to be log sensitive and compared to P okay, or P^3 is going to be a lot more sensitive to pressure than P^2 and then P. But if you are working a low pressure with the predators are low P^2 will be lower than P and P^3 will be still lower than P you see that it becomes like anti-sensitive there is a P^3 by the intermolecular reactions now become lot more sluggish when compared to al the sensitive in that sense that as you now decrease the pressure they suddenly become or very drastically become less important right and it is the P^2 ones are less important when compared to the P reactions.

So here at normal pressures, normal pressures the forward and backward or reverse reactions okay, or reaction rates goes P^2 and the third reaction rate goes P but at very low pressures but very low pressures then the first one actually becomes slow the first two reactions become slow right, the first two slow down and the third who predominates right, that is what we expect that means we cannot put a number to n for all pressures depending upon the mechanism which we have which in this case we have considered a particular mechanism we can see that the number for the order could be anywhere between one and two okay. So normally it could be like a second order reaction at low pressures it could actually behave more like a first order reaction okay, so you are now beginning to look at this disposability so how do you demonstrate this the answer is we now try to adopt to study the steady-state approximation.

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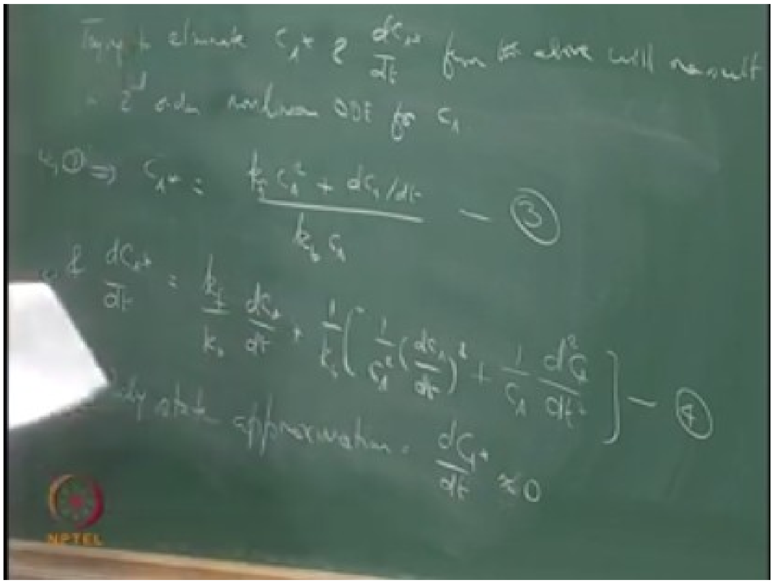

Trying to eliminate c_{A*} & $\frac{dc_{A*}}{dt}$ from the above will result in 2nd order nonlinear ODE for c_A

$$① \Rightarrow c_{A*} = \frac{k_f c_A^2 + dc_A/dt}{k_b c_A} \quad — ③$$

$$\& \quad \frac{dc_{A*}}{dt} = \frac{k_f}{k_b}\frac{dc_A}{dt} + \frac{1}{k_b}\left(-\frac{1}{c_A^2}\left(\frac{dc_A}{dt}\right)^2 + \frac{1}{c_A}\frac{d^2c_A}{dt^2}\right] \quad — ④$$

Steady state approximation: $\frac{dc_{A*}}{dt} \approx 0$

So when you write $dc/dt=-kfc^2+kbcA\ cA*$ so this is for the depletion of A, this is for the production of A okay, A is being depleted because of the first reaction what is being produced by the second reaction okay, this negative sign with the coefficient one takes care of the fact that we have two molecules of a consumed versus one molecule of a being produced even in the first reaction. So it is taking into account the fact that there is some partial production of A there all right, and still there is like a net depletion that is the reason why you have a negative sign.

And so let us so now say this is one and $dcA*/dt=kfcA^2$- now A*is actually being is participating in three reactions okay, it is being produced in the first reaction and is getting consumed in the second there is a reverse reaction there and the third right, so kfc is C^2 is actually the production rate for A* but it is also getting depleted twice which is kbcA cA*- kf ′CA* let us call this 2 right.

Our goal is to actually solve for cA and cA* that is what we supposed to do okay, and this is as I said a system of two simultaneous or E’s and we have to supply initial conditions and of course I can gladly tell you that cA* initially is equal to 0 okay, so I got it and then I will supply some number for cA and starting from there you want to now march in time and then see how these things grow and then try to fill up this graph essentially right that is what you are supposed to do.

So what you could do is you know in the in this equation you could try to eliminate cA* let us say you are not you are not interested in cA*at all case we can eliminate your CA*from these two equations and then you can also try to get your dcA*/dt which will involve dcA/dt when you try to eliminate cA*and then plug for cA*and dcA*/dt and you now get like a humongous looking non linear second order or e for dc cA that means you will have a d^{2}cA/dt^2 term you can also potentially have because you are showing up these squares and so on it could also have some (dcA/dt)^2 terms and then dcA/dt and so on.

So you now have like 1ODE which is like second order nonlinear in dcA/dt okay, and then you can if you can you can solve that okay. So trying to eliminate cA*and dcA*/dt from the above will result in a second order ODE non-linear ODE or for cA right, that is cA= kfc2+dcA/dt kbcA that is something that you can get from 1 okay, let us call this 3 and dcA*/ dt = kf / kb dcA/dt+1/kb(1/cA2 dcA/dt)2 + 1/cA d^{2}cA/dt^2 okay, and then you now try to put 3 and 4 back in 2 and then you will now get an equation that involves only cA and its derivatives okay, but it is going to look so ugly that we do want to consider it at all.

Instead what we want to do is steady state approximation, approximation means that we now say dcA* / dt is approximately equal to 0 that is exactly what we started out with to consider right, so do this and then we will try to take it up from here and see what we get next class.

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