Indian Institute of Technology Madras

NPTEL

National Programme on Technology Enhanced Learning

COMBUSTION

Lecture 10
Partial Equilibrium Approximation
Chemical Explosions

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So we have been looking at the approach of partial equilibrium approximation and as a template set of equations or reactions I am sorry we could let us look at about three forward and reverse reaction pairs are leading up to a fourth reaction which we deliberately take as a intermolecular reaction so that it is slow the idea being that if you now have these bimolecular reactions happening relatively faster and they are forward and reverse reaction pairs then we can assume that because they are happening quite fast they could stay in equilibrium with each other which means their respective forward and reverse reaction rates would match.

And therefore the ratio of the rate constants of the forward and reverse reactions in each case would turn out to be the equilibrium constant based on pressure right, and so we can write these equilibrium equations for each of those reactions and therefore we now are rewriting these and numbering them as 1,2,3 so what is going on with this here is here we are saying.

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We recognize A2, B2 and A2B as a stable species and AB and AB as a intermediates right. We are interested in d/dt of concentration of A2B that is the final product whose rate of production we are interested in right. Now looking at the fourth reaction where this is being produced we could write this as concentration of A times concentration of I am sorry equals KF4 times concentration of A times concentration of AB times concentration of M right, but we need to know what these are.

The concentration of A and concentration of B which are intermediates okay, in terms of concentrations of the stable species in the system namely A2B2 and A2B if we were to suppose that we do not have all these things right, these are all too much detail all I want to think about is A2+B2 gives you A2B or maybe A2+1/2 B2 gives A2B right, I would like to write the rate equation as dcA2B/dt= k times small k times concentration of A2 times concentration of $B2^{1/2}$.

But they the powers that we are looking at 1 and 1/2 should really be orders and not molecularity because that is like the global reaction and we are not sure that we can actually use these parametric coefficients in the global reaction for the orders right, that means we empirically found and that is what we are trying to do with the detailed reaction and here the detailed reactions tell us that this actually in terms of the intermediates which we do not want to deal with we want to now express the concentrations of the intermediates in terms of the concentrations of these tables species.

When we say stable species we mean both reactants and products because it is possible that the concentrations of these intermediates depend on the concentrations of products stable products as well as concentrations of stable reactants so we should not distinguish between products and reactants of a stable level we should simply say stable species right. So how do we find these is how is why we write out these three equilibrium equations and you see what happens here the intermediates are AB and A B and we have three equations.

So we strictly speaking if as assuming that we are okay with dealing with A2 B2 and A2B right, is it possible for us to write AB and AB in terms of those though the stable concentrations right, that is what we want to do having said that we are interested only these two we are not really interested in concentration of B because that is not part of the final answer. So is it possible for us to eliminate concentration of B in these equations and look for only expressions for concentrations of A and AB in terms of A2B2 and A2B is it easy rigmarole we have to go through it you know.

So eliminating CB from equations 1 and 2 you can do this so you can now write this with in terms of concentrations of A and B as if you are now looking at only a and B do not worry about AB let it be there and then we have A and did I make a mistake, I might have made a mistake let me just check this AB+A2 yeah sure yes, okay, okay I understand what you mean yes you are right okay, so you are right, so strictly speaking what I need to do is to factor in okay, let us do that thanks. +kf3 it is being produced in the forward reaction CAB CA2 – kf kb3 CA CA2B CA yeah.

I was wondering about it myself because it is not so simple that is not strictly speaking so simple you could do this but what you would find is this is equal to this, because we are assuming equilibrium all right. Therefore it gets canceled right, so it is always good to go through the details in yeah, therefore we are stuck with only this right if this were not to be canceled then we understand that this is unknown but this is to be treated as known and this is to be treated as unknown and this is unknown and still we would be requiring concentration of AB and A to be expressed in terms of A to B21 A to B this is the procedure that we are looking for so if you now eliminate C be from equations 1 & 2 I am sorry here yes that is what I was searching for right so yeah so we now have this so you know so you can rearrange these things do not worry about AB showing up it is an unknown right.

But you try to eliminate CB what you get here is then CAB equal to KP_1 KP_2 CA_2 CB_2 half you can work out the mathematics and you will you should, you should be able to find that this is the case then using, using three right so we have used one and two equations let us go to the third equation we should be able to find there is a CA sitting there and AB is something there so we can plug this expression there and so you can find in C_{CA} equal to I am just giving the final answer KP_3 KP_1 KP_{23} ½ CA_3 ½ CB to the ½ divided by CA_2B therefore right.

If you now use if you now write this equation as for right that means we are primarily interested in this expression because those two terms got cancelled so what happens is in, in 4 $dC_{AB}/DT=kf$ for coming in and therefore start with a small K_{F4} then you have everything else showing up kp3, KP_2, KP_1, CA_2^2 , C_{B2} C_M there is still there we will just let me just write this in the same line divided by CA_2B.

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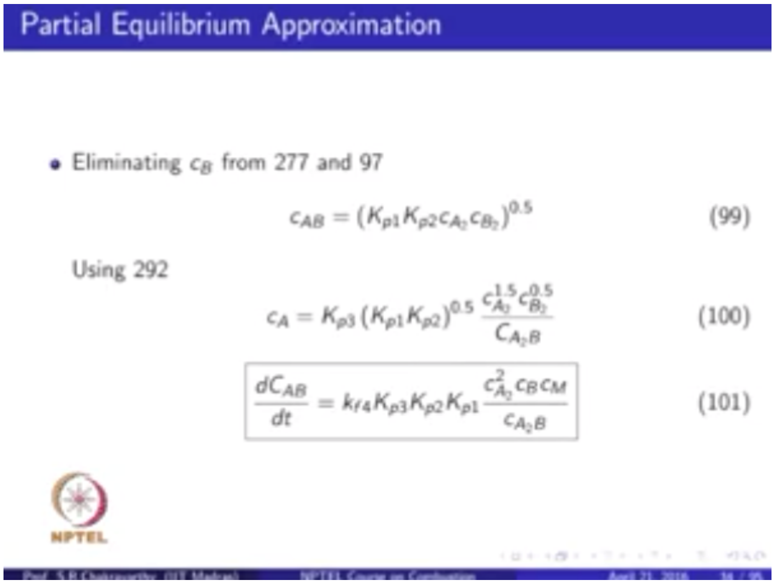

Partial Equilibrium Approximation

- Eliminating c_B from 277 and 97

$$c_{AB} = (K_{p1} K_{p2} c_{A_2} c_{B_2})^{0.5} \tag{99}$$

Using 292

$$c_A = K_{p3} (K_{p1} K_{p2})^{0.5} \frac{c_{A_2}^{1.5} c_{B_2}^{0.5}}{C_{A_2B}} \tag{100}$$

$$\boxed{\frac{dC_{AB}}{dt} = k_{f4} K_{p3} K_{p2} K_{p1} \frac{c_{A_2}^2 c_B c_M}{c_{A_2B}}} \tag{101}$$

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So that is the answer for you I just worked it out for you so you know you know you are not suppose to look at what has happened we now got an answer based on these table species which is a little bit more surprising than what you would have expected for a global reaction alright which is first of all it is going square of A2 so you might argue let me write the global reaction as instead of A2+1/2 V2B I might write this as twice A2+ B2gives twice A2B alright.

But then that would have meant that I need to have a to hear which I do not okay and then you would be able to say I can put a square here and a power one there but the other two are extra that would have that you would have never figured outright unless you went through the details and if you went through the details as it is without the partial equilibrium approximation it would be more horrendous when compared to having these algebraic equations replace here what E is called the rates of the intermediates right.

So, so you now have a CM which is sort of like saying it depends on the container what is the total number of moles that is there in the entire container because as the pressure increases this now goes as the whole thing will now go as P2 PPP to the P to the three because this is now going to have a contribution to the pressure this is going to have a corresponding contribution to the pressure and finally all the four of them should hang up and say it is going to go as P power P P^3 right.

So this acts in bringing that up number on the one hand second what is the A_2B showing up in the denominator remind you of something that we went through last class self inhibiting reaction right the more A_2B that you produce the less the rate at which you're producing it is what this really means and that is because A_2B is actually participating in the reverse reaction as well so more it is getting produced it is also getting depleted all right so all these things kind of come up in these expressions based on the approximations that we do.

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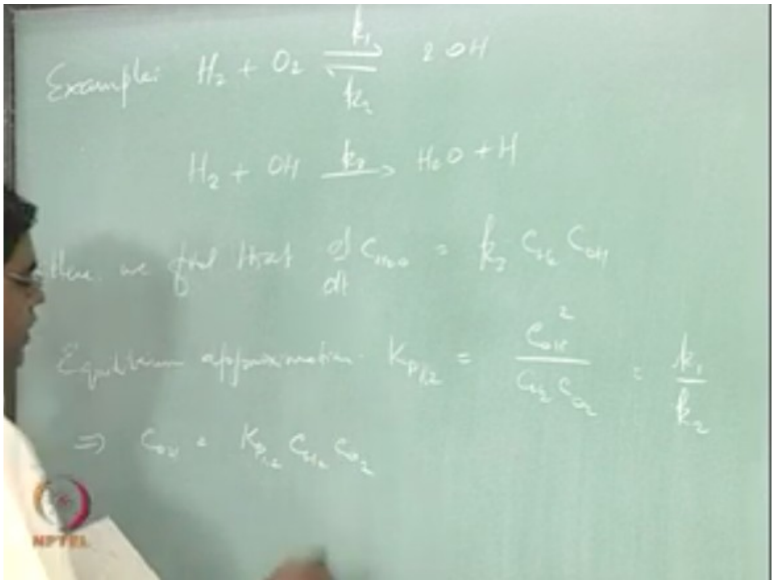

Example: $H_2 + O_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2OH$

$H_2 + OH \xrightarrow{k_2} H_2O + H$

Here we find that $\frac{d C_{H_2O}}{dt} = k_2 C_{H_2} C_{OH}$

Equilibrium approximation: $K_{p_{1,2}} = \frac{C_{OH}^2}{C_{H_2} C_{O_2}} = \frac{k_1}{k_2}$

$\Rightarrow C_{OH} = K_{p_{1,2}} C_{H_2} C_{O_2}$

So let me also give you a simple example which is which is a little bit more realistic here so example just like how we had the what should I say the hydrogen bromide example for the steady state approximation here that are suppose that we have H2 +O_2 gives and takes with the k1 here k2 for the rivers two ways OH on the other hand and $2H_2$ + O_H gives k3 h_2O + H okay so here we find that D over DT of CH_2O equal to K3 CH_2 COH and I do not like COH sitting there in this I would like to actually have a H2 is already there I would like to express COH in terms of H_2O_2 and maybe H_2O that is permissible right.

That is what I want to do so I use the equilibrium approximation, I use the equilibrium approximation and say KP2 I should KP1 let me use a notation KP1, 2 are equal to C_OH_2/CH_2 C_O2 right all right that is equal to k1/ k2 all right now keep in mind when you write KP strictly speaking we should be writing P_OH^2 / PH_2 PO_2 okay it just turns out that the molecularity is the same for both the forward and the reverse reaction and therefore the, the total pressure gets cancelled out.

And you can write in terms of concentrations directly if the molecular entities are not the same for both the sides then you will get into trouble so a more direct thing to do is to probably right KC instead of KP but if you are insisting on KP then there is a conversion between KP and KC that we have gone through that is that you need to factor then yeah so if you now use this then what happens is from here you try to evaluate what your C_OH is so C_OH then is $KP_{1,2}$ CH_2 CO_2 boldly half is what we have.

And therefore the CH_2O is k3 let us, let us now get rid of KP 1 to use k1 and k 2 because they are like given information in the reaction scheme and you can say this is k 1 divided by k 2to the ½ CH_2 to the 1/2 goes with CH_2 there and so it Is like CH_2 to the three halves and CO_2 the half remains so you have CO_2 half right so that is that see that is the final answer what it means is if you were having this as the reaction scheme like a three-step reaction scheme for production of the water right.

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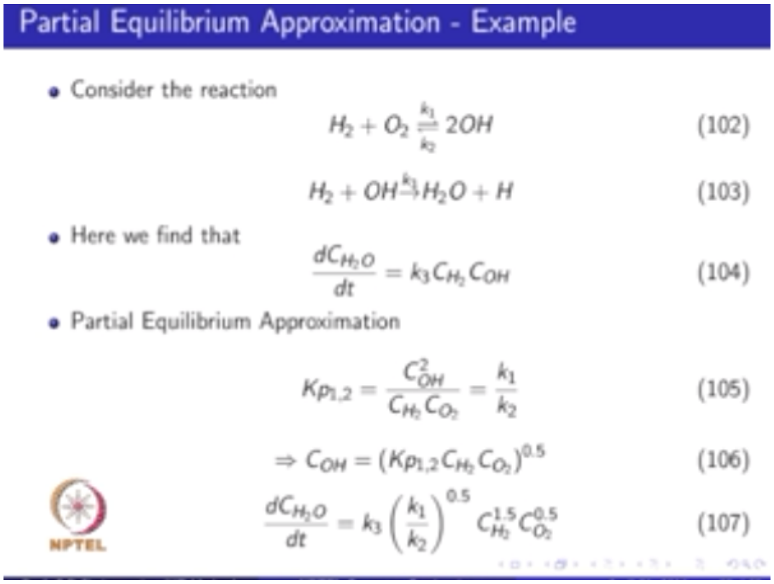

Partial Equilibrium Approximation - Example

- Consider the reaction

$$H_2 + O_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2OH \qquad (102)$$

$$H_2 + OH \xrightarrow{k_3} H_2O + H \qquad (103)$$

- Here we find that

$$\frac{dC_{H_2O}}{dt} = k_3 C_{H_2} C_{OH} \qquad (104)$$

- Partial Equilibrium Approximation

$$Kp_{1,2} = \frac{C_{OH}^2}{C_{H_2} C_{O_2}} = \frac{k_1}{k_2} \qquad (105)$$

$$\Rightarrow C_{OH} = (Kp_{1,2} C_{H_2} C_{O_2})^{0.5} \qquad (106)$$

$$\frac{dC_{H_2O}}{dt} = k_3 \left(\frac{k_1}{k_2}\right)^{0.5} C_{H_2}^{1.5} C_{O_2}^{0.5} \qquad (107)$$

Then the partial equilibrium approximation tells you that this is partially tells you that the rate of production of water actually depends 2 3 half the power of CH_2 and one-half the power of O_2 okay these are now the orders with respect to H 2 and O2 respectively together if you now look at the total order right three 1/2 one half is 2 so again you can easily see that this is like a second order reaction that we are looking at all right but the, the division between the fuel and oxidizer is not equal let us see that is a lesson that we learned from these, these, things all right.

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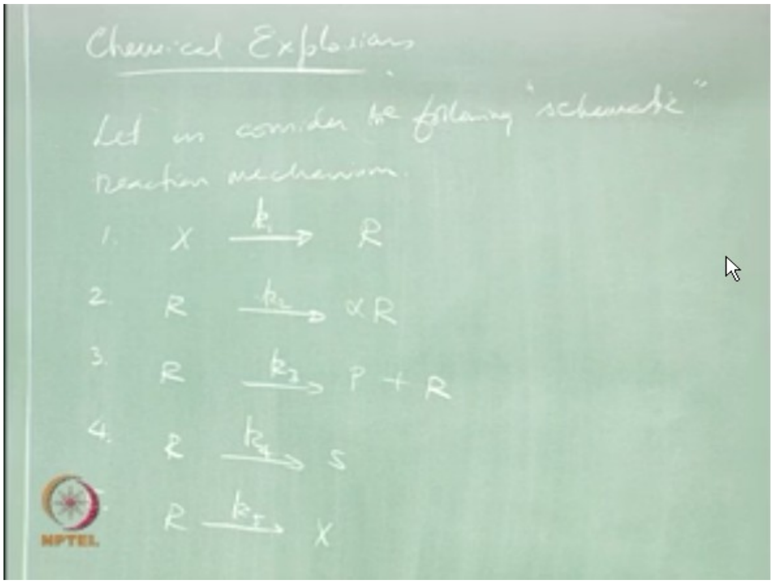

Chemical Explosions

Let us consider the following "schematic" reaction mechanism.

1. $X \xrightarrow{k_1} R$
2. $R \xrightarrow{k_2} \alpha R$
3. $R \xrightarrow{k_3} P + R$
4. $R \xrightarrow{k_4} S$
5. $R \xrightarrow{k_5} X$

Let us now do some chemical explosions based on what we have learnt okay so this is the last topic that we would like to cover under chemical kinetics before we proceed on further with other things in combustions so let us let us consider the following schematic reaction mechanism right 1 x gives you or with reaction rate constant K 1, 2 R gives you α R with a rate constant K 2, 3 R gives you k 3 p +R, 4 R goes to S and 5 R K 5 goes to X now this is obviously looking a bit strange if it not looking strange then you must be a genius right what we mean by a schematic reaction mechanism.

Here is this reaction scheme is focusing only on the intermediates that means there are hidden stuff around there are stable on either side which you are not worried about okay why so because you can now clearly see that this is a chain in this initiation step right because this is the birth of an intermediate or is the intermediate to be looking at R becoming α R for α greater than 1 means we are now branching more and more okay.

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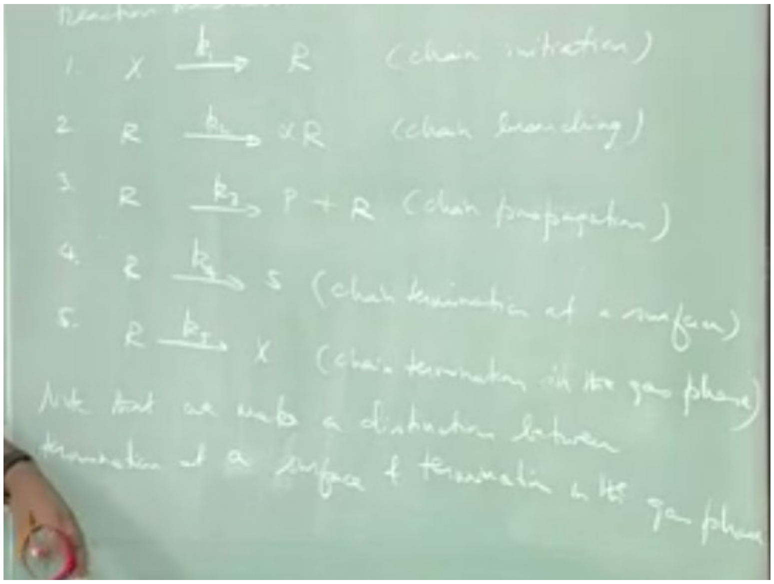

Reaction

1. $X \xrightarrow{k_1} R$ (chain initiation)
2. $R \xrightarrow{k_2} \alpha R$ (chain branching)
3. $R \xrightarrow{k_3} P + R$ (chain propagation)
4. $R \xrightarrow{k_4} S$ (chain termination at a surface)
5. $R \xrightarrow{k_5} X$ (chain termination in the gas phase)

Note that we make a distinction between termination at a surface & termination in the gas phase

So this is like some intermediate giving rise to more intermediate right so this is chain branching of course α less than one would mean chain termination kind of reactions right but they do not they do not really show up like high up in the list k they are kind of the end and R gives p + RP is like a stable product like let us say we are interested in this finally okay but then what is what is happening you start with our you have something else and then you also have our so as far as intermediates is concerned it is neutral.

That means it is a chain propagation yeah so you have a chain, chain propagation step in reality you would have a bunch of steps like this okay so each of these kinds of things could be like a bunch it is not just one okay R to going S is schematically representing chain termination at our take surface whereas R going to X means chain termination at in the gas phase in the gas phase X is any molecule right So you could have started with any X giving rise to intermediates and R could go back to any X okay so in that sense this is not strictly like a reverse of that because X could be anything.

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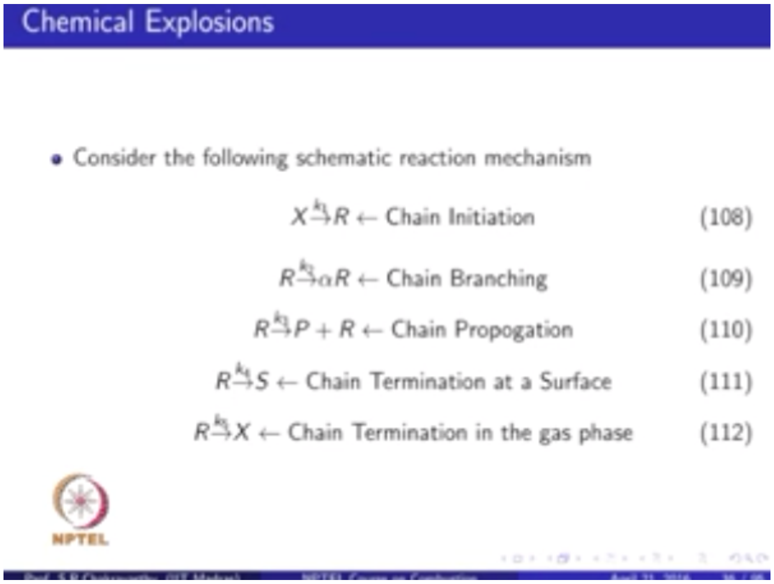

Chemical Explosions

- Consider the following schematic reaction mechanism

$$X \xrightarrow{k_1} R \leftarrow \text{Chain Initiation} \qquad (108)$$

$$R \xrightarrow{k_2} \alpha R \leftarrow \text{Chain Branching} \qquad (109)$$

$$R \xrightarrow{k_3} P + R \leftarrow \text{Chain Propogation} \qquad (110)$$

$$R \xrightarrow{k_4} S \leftarrow \text{Chain Termination at a Surface} \qquad (111)$$

$$R \xrightarrow{k_5} X \leftarrow \text{Chain Termination in the gas phase} \qquad (112)$$

But we are, we are we are making a distinction on the way the intermediates are getting terminated either wrote the surface around anywhere or in the gas phase by colliding with other molecules around and disappearing and becoming some stable, stable species so note that we make a distinction but between termination or the surface at a surface it can resurface and termination in the gas phase why, why would you want to make the distinction how does not matter a termination means the intermediates disappear right.

How does it matter which way they disappear what are we looking, looking at so whenever we were doing things in the past I asked you to keep an eye out on distinctions between uni-molecular reactions to bio molecular reactions in a scheme or by molecular to term auricular reactions in a scheme and so on and the reason was to look at the pressure dependence of the rates of these reactions okay or the differences in the pressure difference dependence of the rates of these reactions.

And so as you change the pressure from low pressure tome intermediate pressure too high pressure the importance of these different reactions becomes different right so effectively we were looking at what is what is it going to be in terms of pressure similarly looking at the termination either a surface or in the gas phase is going to be dependent upon pressure because a surface termination is relatively independent of pressure I surfaces a hard surface it is not going to change its packing depending upon the pressure okay.

Whereas a gas phase is going to actually get more and more packed give it less and less mean free paths for the collision between the molecules as you as you increase the pressure so what you would expect is as you increase the pressure determination via the gas phase is going to be more and more predominant when compared to the termination via the surface okay so this is this distinction is going to enable us to tell us how things are going to change with pressure right and as the reason why we want to make this distinction.

So there is another way of distinguishing things as well as particularly intermediates is concerned okay so this term molecular bio-molecular and so on is for any species it does not have to be intermediates but here we speak specifically talking about termination for intermediates in two different parts and they are dependent pressured in different ways okay that is what we want to try to explore okay.

So then let us look at how to write the reaction rates for these now I am going to write these things in such a way that we care only about concentrations of the intermediates we will not worry about concentrations of stable species okay they are not showing up in the schematic reaction, reaction mechanism anyway there are stable reactive species around which are which we are not simply bothered about because when we look at a reaction mechanism before to characterize it as a chain initiation branching or propagation or termination.

We were primarily looking only at the intermediates ok we just disregarded the presence of these stable species they are always looking for our intermediate is being created more of them created then what, what is being consumed or the same amount is created and we did not even distinguish but between the intermediates like it could be OH one side and H and the other side does not matter they are all very active radicals anyway right.

So they are going to kind of propagate the reactions if one of them got killed and the other one got produced right so this is the way we were looking at it and obviously they were reacting with stable things like H2 O2 and so on we should interview which we did not really worry about and these are all there so since they are they are hidden we cannot write rate equations exactly depending upon their concentrations so we are going to write equations that are sort of functionally correct but not accurate right.

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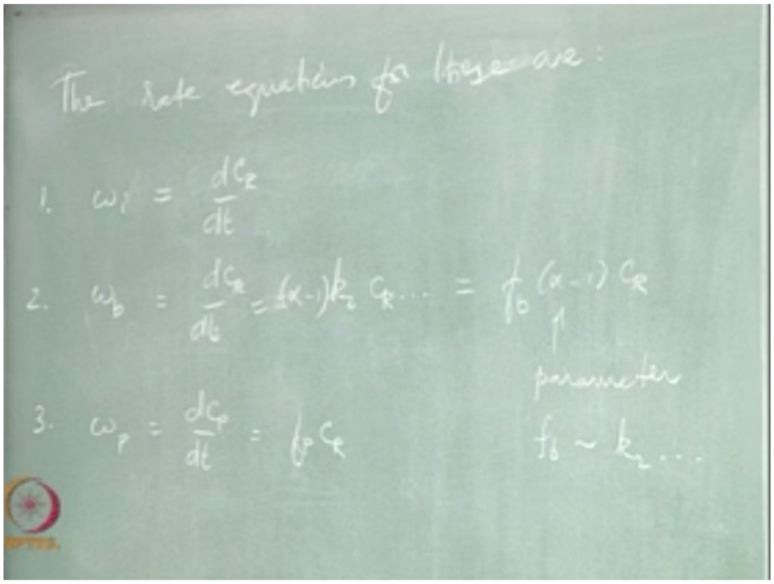

The rate equations for these are:

1. $\omega_i = \frac{dC_R}{dt}$

2. $\omega_b = \frac{dC_R}{dt} = (\alpha-1)k_2 C_R \ldots = \underset{\substack{\uparrow \\ \text{parameter}}}{f_b}(\alpha-1)C_R$

3. $\omega_p = \frac{dC_p}{dt} = f_p C_R$

$f_b \sim k_2 \ldots$

So that is what we will end up doing so let us say the first equation so the, the rate equations for these, these R 1 let us say we call this ω_I for the chain initiation step all we are going to write is DC all over DT because we do not want to be worrying about the fact that it depends on the concentration of X okay we could write k1 CX for example okay let me not worry about it okay I am just going to keep this ω_i right second ω.

Let us now call this chain branching so we will call this ω_B that is equal to DCR over DT as well for this reaction here this, this would be written as K2 strictly speaking I should write α- 1 k2 CR times other things which are hidden right so I since I do not know what those are I am simply going to write this as equal to FB times α-1 CR α the parameter here parameter FB is like it is going to take care of k2………. is like concentrations of stable species okay which, which does not enter the picture.

So essentially what you are saying is let us deal with FS rather than case because the F will couch things that are not really important what we got we want to explicitly keep a C or ok and so this is a production step so we will call this as ω_P the third step this is DCP over DT this is equal to FPC are okay here the intermediates are neither getting produced nor consumed on the whole but so if you could say that this is this is basically k FP is of the order of the same as k3 you do not but you could have something hidden right.

So we just write F instead of k & 4 let us call the surface termination reaction rate so we have a negative DC all over DT there and that is FS CR we do not know what else is there other than or on the left hand side so we just write FS instead of K4 and similarly let us call this ω_G for gas phase termination reaction rate this is again -VC all over DT equal to f g CR all right okay so we have explained what the f are there and I also told you what the wide, wide this is a schematic here.

So are the rate of production of the intermediates then the net rate of production of intermediates, intermediates DC or over DT from all the reactions equal to ω_i + FV times α -1 CR - F F scr - f g CR the third reaction did not have a net rate of production of intermediates at all because it is a propagation reaction yeah therefore we have only four reactions that are contributing here two of them where things are produced if α is greater than 1 that is if α is less than 1this would mean consumption anyway and obviously here the radicals are getting consumed yeah and keep noting that these things depend on concentration of CR.

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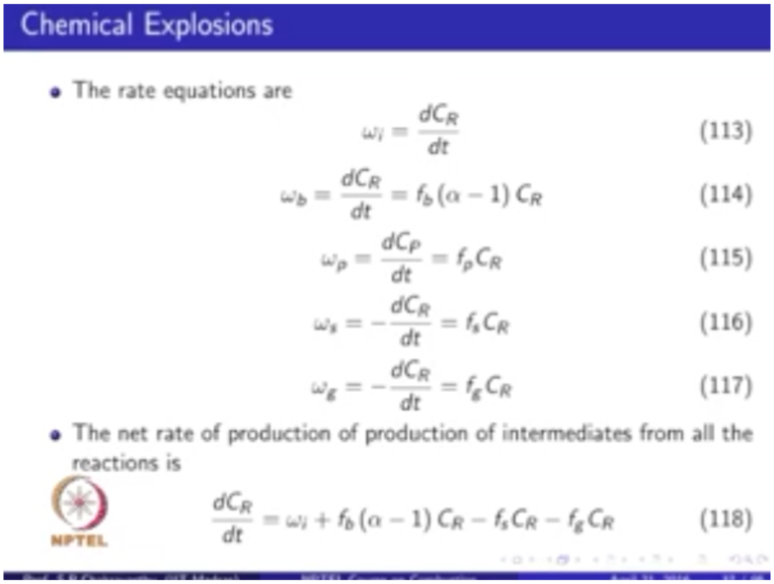

Chemical Explosions

- The rate equations are

$$\omega_i = \frac{dC_R}{dt} \qquad (113)$$

$$\omega_b = \frac{dC_R}{dt} = f_b\left(\alpha - 1\right) C_R \qquad (114)$$

$$\omega_p = \frac{dC_P}{dt} = f_p C_R \qquad (115)$$

$$\omega_s = -\frac{dC_R}{dt} = f_s C_R \qquad (116)$$

$$\omega_g = -\frac{dC_R}{dt} = f_g C_R \qquad (117)$$

- The net rate of production of production of intermediates from all the reactions is

$$\frac{dC_R}{dt} = \omega_i + f_b\left(\alpha - 1\right) C_R - f_s C_R - f_g C_R \qquad (118)$$

Because it is like chain branching or termination but ω_I does not depend on concentration of CR because it is starting from things that are pre-existing there is there not intermediates fine we now apply the steady state approximation right.

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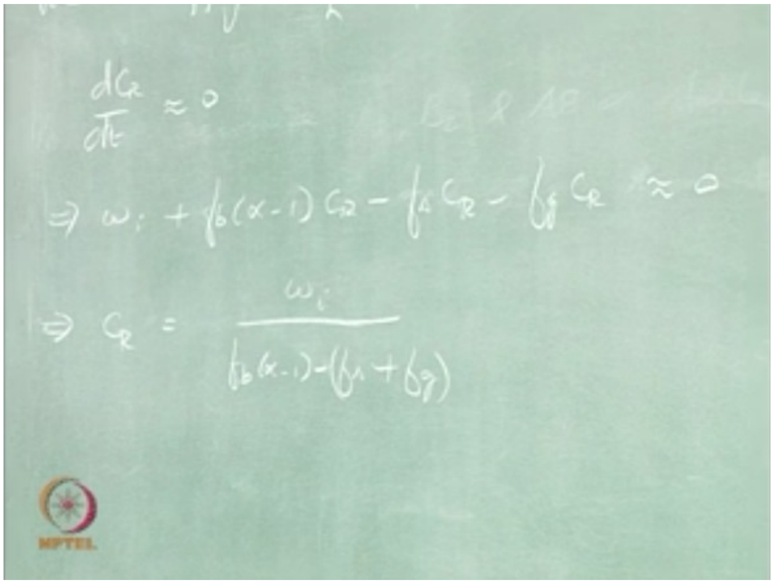

$$\frac{dC_R}{dt} \approx 0$$

$$\Rightarrow \omega_i + f_b(\alpha-1)C_R - f_s C_R - f_g C_R \approx 0$$

$$\Rightarrow C_R = \frac{\omega_i}{f_b(\alpha-1)-(f_s+f_g)}$$

If you want to be quite precise which is a quasi steady state approximation that means Dcr over DT the net rate of production is approximately equal to zero for bulk of the time when reactions are proceeding right so this implies we now say that ω_I plus FB α-1 CR -FS CR- FG CR is approximately equal to zero from which we can try to find out the concentration of the intermediate.

So this implies CR is equal to ω_I / FB α-1 minus FS+ FG okay so the steady-state approximation did this for us you go back and think about what we did what it means is we want to get algebraic equations that govern the concentrations of intermediates right so that we can evaluate the concentrations of the intermediates in terms of the concentrations of the stable species and then plug those expressions in the raid equation for the production of products that is our we are finally interested in right.

So what we should then say then we are interested in DCP/DT that is a products it is kind of like this kind of like life you know we should be interested in the in producing products but we keep going, going talking about intermediates like in most of our lives that we just got a get caught up in intermediates right so let us not lose sight of our goal our goal is actually DCP over DT right

FP XCR of course in life money is one of the biggest intermediates the distractors right yeah we are losing see right here because let us admit that by swapping the nominator I do not like negative signs for concentrations right.

So we say FS+ FD-FB times α -1 happy you need to keep me happy as well do not get negative concentrations Yeah right your-your-your advisors are not going to like you when you get them right so if they want to you all have a positive quantity that okay so FF pcr then is a FB ω_I /FS+F G -FB times α-1okay I pointed out this for you earlier in the context of let us say the hbr reaction or example or I do not remember what but let me do this once again and, and this, this becomes very intuitive for us what is happening in this expression for you is these are this is a this, this division it is also this difference here is basically telling you the competition between termination and production okay.

Which is being compared with ω_I that is the initiation okay in other words the rate of production of your final products depends on what is the interplay between the rate of production and rate of consumption of the intermediates for a given rate of initiation of the intermediates once you have intermediates initiated and left into the pool then the dynamics of how they produced further by chain propagation a chain branching steps versus chain termination steps okay.

That ratio is what determines your rate of production of products you see so it is sort of like telling us the entire physics of what is going on right just the expression like looking at the expression fine if you did not worry about all that stuff and you now said this is the expression when you look at it what would you worry about again I am trying to kind of ingrained certain traits in you.

You now look at an expression and, and the moment you have a square root there you should be worried about whether the stuff inside the square root is going to become negative right so similarly when you see logarithm, logarithmic expression you have to look at whether the argument is going to actually become negative or zero and so on so these are all like things that got to be wired in your head.

Similarly and do these are like the square roots and logarithms do not happen all the time but ratios do happen most many times right and the moment you see a ratio and you see the denominator you have to start looking at is this denominator going to become zero right we are always afraid of infinity okay so we have to start looking at when would this denominator ever become zero yeah so for as the less than one the denominator is always positive right and what is meant by α less than one when you now have α less than 1.

I first of all told you that this reaction should not belong in that place there it should be somewhere bar in below because it is beginning to actually only he'll eat itself the inhibiting the intermediates are actually consuming themselves right but that is not what we are talking about for the reactions being up there we are now talking about the α typically greater than one that's what chain branching is all about right.

So when you know I have α greater than 1 okay for α greater than 1then you have a positive quantity here and a positive quantity there and it is possible that they become equal oh ho we have a problem right so fs+FG equal to FB times α - 1 implies denominator, denominator goes to zero and DCP over DT goes to infinity right this is what we are talking about as chemical explosion it is basically saying that once you have produced your intermediates okay.

At whatever finite nonzero rate so long as the intermediates are producing themselves more and more and consuming themselves at the surface or in the gas phase in such a way that the rate of production rate of their production match is the rate of the consumption right you are now going to be continuing to produce products like crazy the rate of production of flawed is just going to go, go on and on very high.

So that means you are going to produce a lot of products so the intermediates are actually playing a sustained role in a continuous production of products at a very infinite level infinite rate right so this is essentially the basis of chemical explosion and then what you are going to do is to say well let me begin to distinguish between FS and FG as we change the pressure okay so at low pressure we now expect that FS should predominate over FD and at high pressure.

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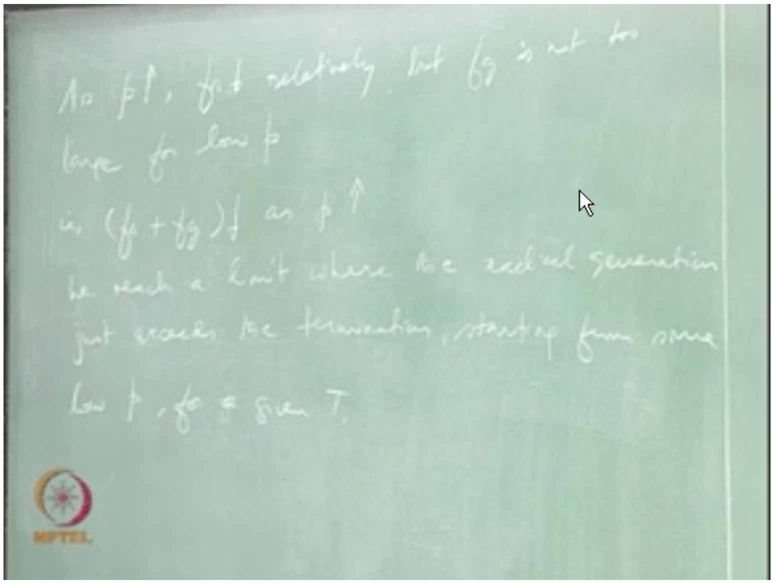

As $p\uparrow$, $f_s\downarrow$ relatively. But f_g is not too large for low p

i.e. $(f_s + f_g)\downarrow$ as $p\uparrow$

We reach a limit where the radical generation just exceeds the termination, starting from some low p, for a given T.

We expect that FG should predominate over FS all right so this is what we are going to be doing as SP increases SP increases FS decreases are relatively politically right but FG is not too large right at 44 loopy because you do not you do not have a rigorous gas-phase termination at low pressure that is together FS plus FG decreases as P increase okay so you now have a limit you now reach a limit okay.

So we reach a limit that means we are looking for as you change the pressure how is this going to change relative to this such that at some limit you might equate, equate right so we reach a limit where the radical generation just exceeds determination right so let us suppose we start out with a very, very low pressure alright and we now found that from there as you increase the p okay the termination actually comes down and in this low pressure range because FG is not very active yet because if the pressure is not increased a lot but FG is something very, very small at this at this pressure.

So you are now actually having a situation where the termination is coming down but the generation is going up and therefore you now reach a point where the generation just exceeds determination and the moment when you say just that means this is just beginning to equal that so far this is higher this was lower this is now increased so it is getting to this and therefore you know have an explosion limit okay. For starting sets a termination starting from starting from some low p for a given T you fix the other thermodynamic variable and you get this so this is this is what you would call as a first explosion limit okay and then as you now look at this dynamics we do not care which is higher which is lower all we are looking for is when things match all right.

So when this keeps on going as you change your pressure if this catches up again then you again have any quality which is bad right so a special pressure increases further right ft increases ft increases okay which implies F s + FD increases okay and here the termination catches up with the generation right then this distress this is what will lead to the second explosion limited right.

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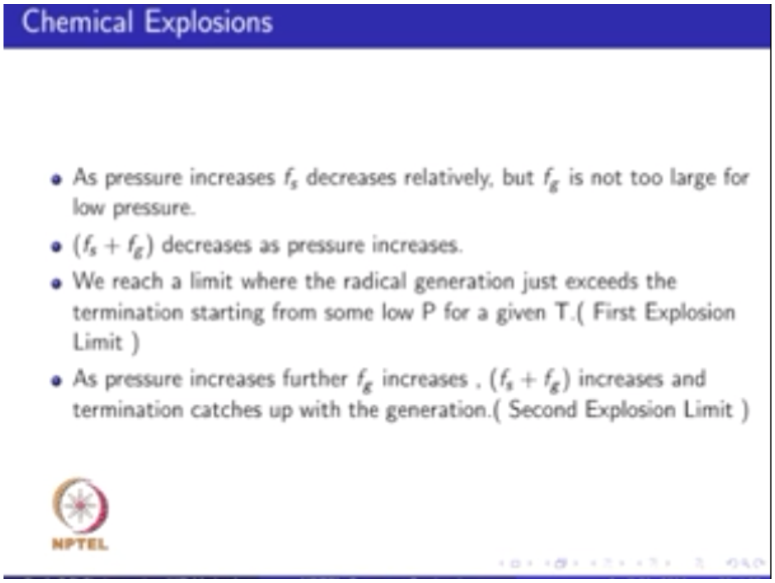

Chemical Explosions

- As pressure increases f_s decreases relatively, but f_g is not too large for low pressure.
- $(f_s + f_g)$ decreases as pressure increases.
- We reach a limit where the radical generation just exceeds the termination starting from some low P for a given T.(First Explosion Limit)
- As pressure increases further f_g increases , $(f_s + f_g)$ increases and termination catches up with the generation.(Second Explosion Limit)

We will stop here and pick up from here in the next class you.

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