Indian Institute of Technology Madras

NPTEL

National Programme on Technology Enhanced Learning

COMBUSTION

Lecture 7
Equilibrium Reactions, Global Kinetic, Order of Reaction

Prof. S R Chakravarthy
Dept. of Aerospace Engineering IIT Madras

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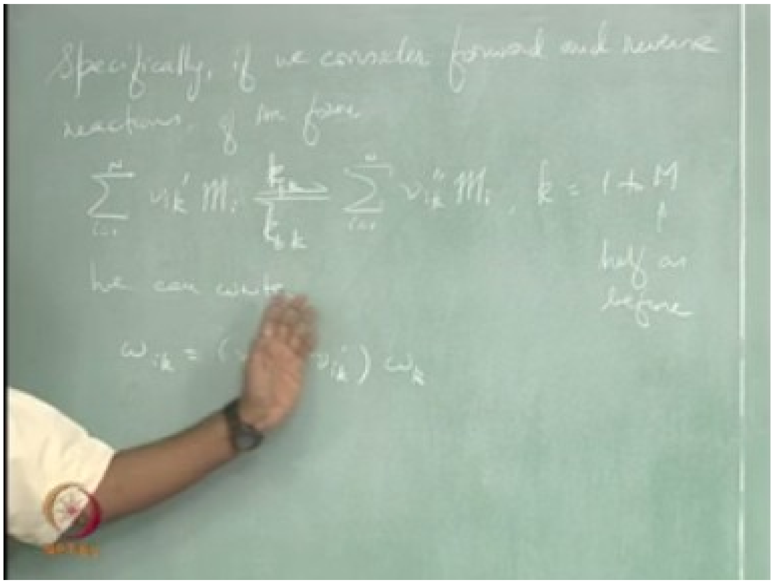

Specifically, if we consider forward and reverse reactions, of the form

$$\sum_{i=1}^{N} \nu'_{ik} M_i \underset{k_{bk}}{\overset{k_{fk}}{\rightleftharpoons}} \sum_{i=1}^{N} \nu''_{ik} M_i, \quad k = 1 \text{ to } M$$

half as before

we can write

$$\omega_{ik} = ([illegible] \nu'_{ik})\, \omega_k$$

So now we had this template notation for a reaction earlier but now let us suppose that we consider that we have forward and reverse reactions all right that means we are saying that we have one set of reactions that are going the forward direction another set of reactions that are going the backward direction, now we could have actually written this as two sets of reactions all right all of them going in the forward direction he says essentially that means like for example if you know went from k equals 1 to M.

You can now write these as two sets and some $K = M + 1$ to $2M$ you will now have the other set of reactions okay, so if you now write it this way then this M is half as before that is what it amounts to okay if it is possible that in the previous set some of them were not going through reverse reactions then those reactions will have new ik single prime as well as new a k double prime equal to 0, and in the previous set all right so let us suppose that in the previous set we had a full set of which some of them.

Were actually reverse of the other but some of them were not okay the new ik single Prime a new I k double prime for them both will be 0 for a hypothetical reaction that is a reverse which does not really happen at all so it is possible for you to write this interms of what we did before also that is what I am saying so we can write $\omega ik = \mu ik$ double prime – μik single prime ωk keep in mind we had this yesterday and we are using the symbol ω right and this is for a particular species ωik I is for the a species in k is for the Kth reaction right, so when you when you are able to actually write it for a particular species you might be able to go from a molar reaction rate to amass mass based reaction rate okay.

So this from moles per second per meter cubed to kilograms per me second per meter cube by multiplying by the molecular weight all right.

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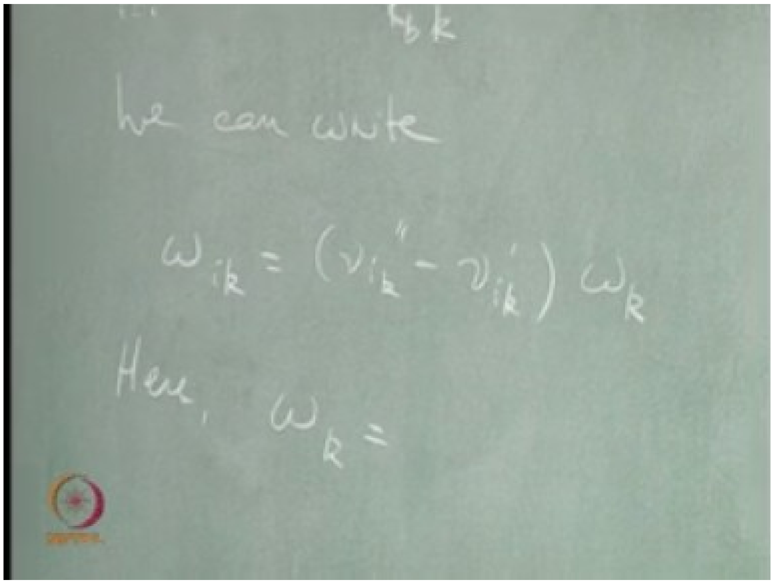

We can write

$$\omega_{ik} = (\nu''_{ik} - \nu'_{ik})\,\omega_k$$

Here, $\omega_k =$

So we could do that and that is what will actually be used in the mass balance because the mass balance is looking for number of the amount of mass that is produced to consume rather the number of moles that are produced to consume we will go through a molar conservation equation also okay at that at that time we will try to use number of moles but when you try to use mass we will change from Greek to just English alphabets from ω will become w small w so those are things that we will talk about which is something that we did yesterday you know so here ωk is now this is for the Kth reaction out of 1 to m.

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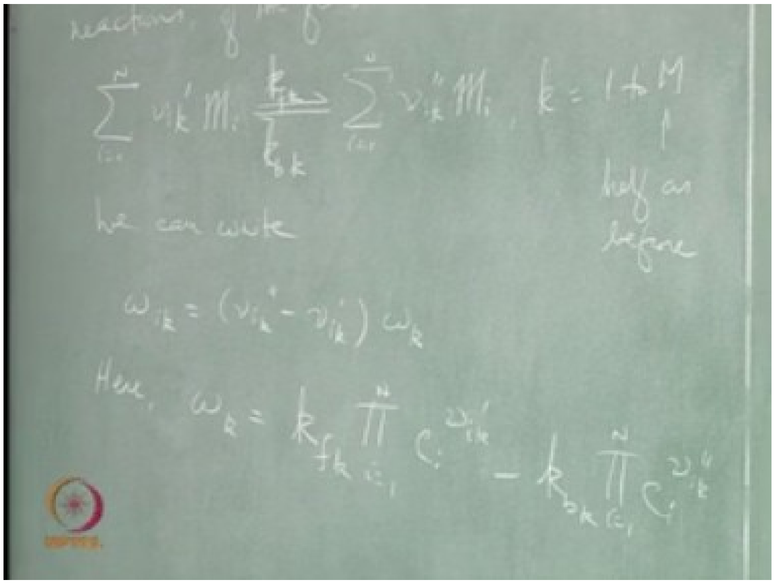

reactions, of the

$$\sum_{i=1}^{N} \nu'_{ik} M_i \underset{k_{bk}}{\overset{k_{fk}}{\rightleftharpoons}} \sum_{i=1}^{N} \nu''_{ik} M_i, \quad k = 1 \text{ to } M$$

↑ hold as before

we can write

$$\omega_{ik} = (\nu''_{ik} - \nu'_{ik})\,\omega_k$$

Here, $\omega_k = k_{fk} \prod_{i=1}^{N} C_i^{\nu'_{ik}} - k_{bk} \prod_{i=1}^{N} C_i^{\nu''_{ik}}$

You see therefore there is like a forward reaction rate and a backward reaction rate right so that is like something that is going forward and then some of it is getting consumed therefore it has to actually be subtracted out yeah, so then we can say this is a $_{kF}$K πi =1 to N and ci µk single prime - k B_K πi = 1 to n ci to the µ ik double prime right by the way it is customary to actually indicate the specific reaction rate of the rate constant on top of the arrow for a given reaction to indicate that that is the kinetic data.

That we are looking for okay pretty much k contains the kinetic data your A and E or B mn and what we saw yesterday all that stuff is contained in this, so to say that you have this means that you are supplying the kinetic data for this particular reaction rate specific reaction rate constant here what would we see that is this like ci to the µik single prime means you are looking at the forward reaction having the µik single prime digit species as reactants with the µik single time as the coefficients you say cik.

C_i to the µik double prime we are now looking at the reactants over here as the reactants for the backward reaction that the reason why you using make a double right.

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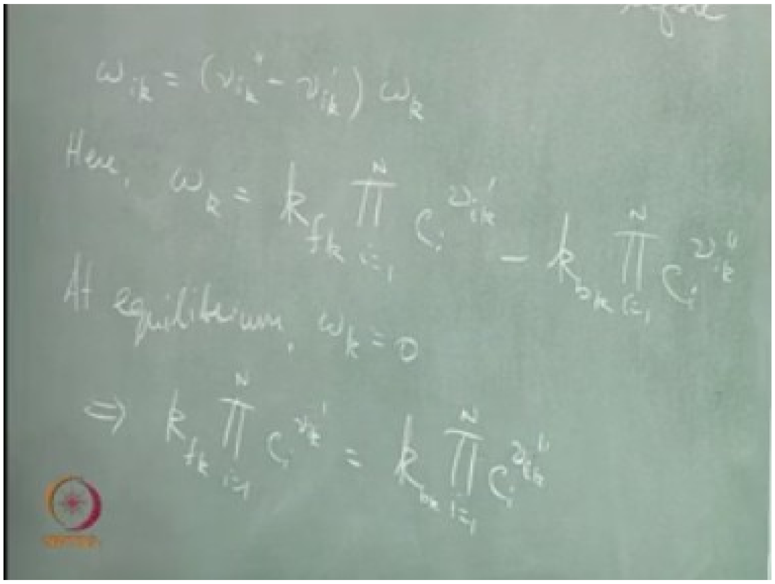

$$\omega_{ik} = (\nu''_{ik} - \nu'_{ik})\,\omega_k$$

Here, $$\omega_k = k_{f_k} \prod_{i=1}^{N} c_i^{\nu'_{ik}} - k_{b_k} \prod_{i=1}^{N} c_i^{\nu''_{ik}}$$

At equilibrium, $\omega_k = 0$

$$\Rightarrow k_{f_k} \prod_{i=1}^{N} c_i^{\nu'_{ik}} = k_{b_k} \prod_{i=1}^{N} c_i^{\nu''_{ik}}$$

Then at equilibrium at equilibrium ωk = 0 that means the rate at which the forward reaction takes place should be equal to the rate at which the backward reaction takes place then you have a equilibrium it is a dynamic equilibrium, okay that is it does not mean that the reactions are not taking place the reactions are taking place you have a forward reaction going on you have a backward reaction going on but the rate at which the forward reaction is going on is the same as the rate at which the backward reaction is going on okay.

So it is a dynamic equilibrium react reactants are being produced and consumed all the time in the in that situation, so we then say k KF k π i = 1 to n ci to the μik single prime equal to K_Bk πi = 1 to n ci to the μik double prime right.

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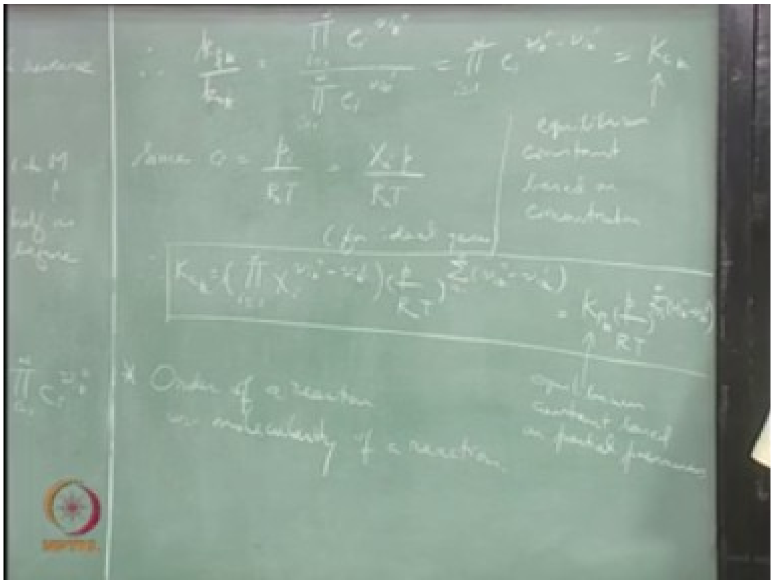

There for k_FK / k_BK = πi = 1 to n ci to the new I k double prime divided by πi = 1n ci to the μik single prime which is nothing but πi = 1 to n ci to the μik double prime - μ ik single prime, now what does this look like we have seen this a little bit before maybe about a couple of classes back except we did it for like let us say hydrogen oxygen reaction specifically or something like that anybody what is it, k_KP capital KP, so this is actually not KP here because this is actually based on concentrations whereas we wrote this in terms of partial pressures.

Earlier case when you had partial pressures we had like partial pressure of a product raised to its stoichiometric coefficient times partial product pressure of another product ratio documentary coefficient if you had two products / partial pressure of reactant to its documented coefficient times partially / another reactant if you had no one will react to the is so committed coefficient and so on so behind this before that is what it is what you are going through but in terms of partial pressures we call it KP which is exact which is basically the capital KP which is the equilibrium constant based on pressure.

Or partial pressures here you are writing in terms of concentrations therefore this actually is K_CK which is the equilibrium constant based on concentration.

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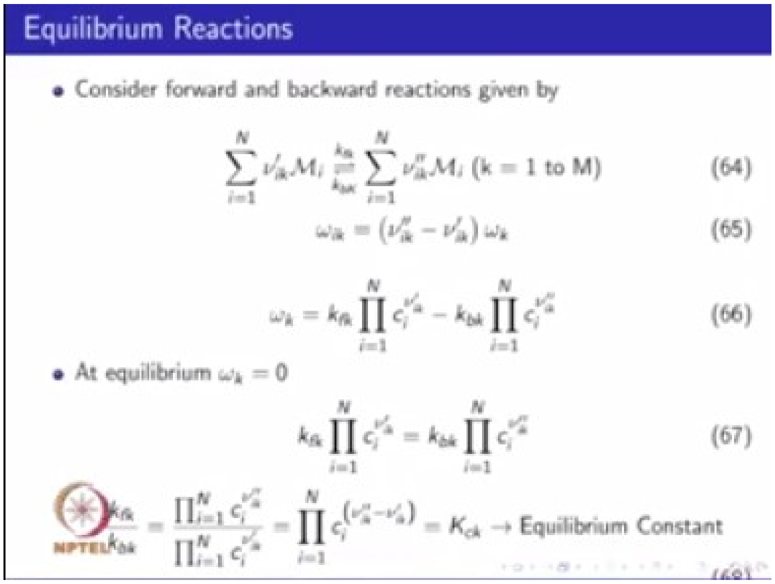

Equilibrium Reactions

- Consider forward and backward reactions given by

$$\sum_{i=1}^{N} \nu'_{ik}\mathcal{M}_i \underset{k_{bk}}{\overset{k_{fk}}{\rightleftharpoons}} \sum_{i=1}^{N} \nu''_{ik}\mathcal{M}_i \text{ (k = 1 to M)} \quad (64)$$

$$\omega_{ik} = (\nu''_{ik} - \nu'_{ik})\,\omega_k \quad (65)$$

$$\omega_k = k_{fk}\prod_{i=1}^{N} c_i^{\nu'_{ik}} - k_{bk}\prod_{i=1}^{N} c_i^{\nu''_{ik}} \quad (66)$$

- At equilibrium $\omega_k = 0$

$$k_{fk}\prod_{i=1}^{N} c_i^{\nu'_{ik}} = k_{bk}\prod_{i=1}^{N} c_i^{\nu''_{ik}} \quad (67)$$

$$\frac{k_{fk}}{k_{bk}} = \frac{\prod_{i=1}^{N} c_i^{\nu''_{ik}}}{\prod_{i=1}^{N} c_i^{\nu'_{ik}}} = \prod_{i=1}^{N} c_i^{(\nu''_{ik}-\nu'_{ik})} = K_{ck} \rightarrow \text{Equilibrium Constant}$$

Okay fine since ci is equal to Pi / RT how do you get this number of moles per unit volume is essentially molar concentration number of moles of species I divided by the volume is the molar concentration of species I, so if the ideal gas equation of state is valid for each species therefore ni /V = Π/RT right therefore we can write ni / Ci we can relate the partial pressure to the concentration and further we did not like partial pressures even last time you want to get the total pressure therefore we use the mole fraction.

Which is being defined now properly for us divided by RT in fact this is this is our you we are talking in terms of number of moles molar concentration and so on this is our you for ideal gases right, therefore $K_CK = \pi$ can just plug this in there and then say I = 1 to n Xi to the μik double prime – μik single prime p over R_UT to the this p / or U_TC is going to be constant you should be like a common factor for each of those excise right, so xi_I goes through this the fate of what see I went through.

But then when you now have the P_i /RT that is common for all of them then it gets summed over all the species right, so you now have I = 1 to n μik double prime means μ ik single prime, so in fact this is nothing but K_PK which we were familiar with to begin with times P / RT to the power σi = 1 to n σuik double prime - σik single prime trying to squeeze there okay, so from here you can see that the kinetics is related to equilibrium.

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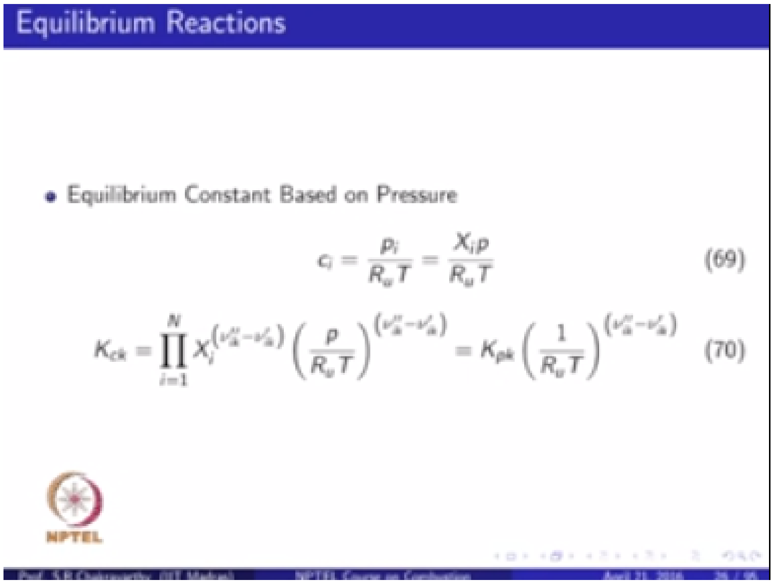

Equilibrium Reactions

- Equilibrium Constant Based on Pressure

$$c_i = \frac{p_i}{R_u T} = \frac{X_i p}{R_u T} \quad (69)$$

$$K_{ck} = \prod_{i=1}^{N} X_i^{\left(\nu''_{ik}-\nu'_{ik}\right)} \left(\frac{p}{R_u T}\right)^{\left(\nu''_{ik}-\nu'_{ik}\right)} = K_{pk} \left(\frac{1}{R_u T}\right)^{\left(\nu''_{ik}-\nu'_{ik}\right)} \quad (70)$$

And this is something that you are not unfamiliar with you must have gone through this in your high school for regular reactions and so on, but here we are trying to put all of them together in the algebraic notation that we are coming up with for a general set of forward and reverse reactions and that is a relationship between equilibrium constant based on concentration and equilibrium constant based on this is equilibrium constant based on, now partial pressures okay before we proceed from here the next thing that I would like to discuss here is order of a reaction.

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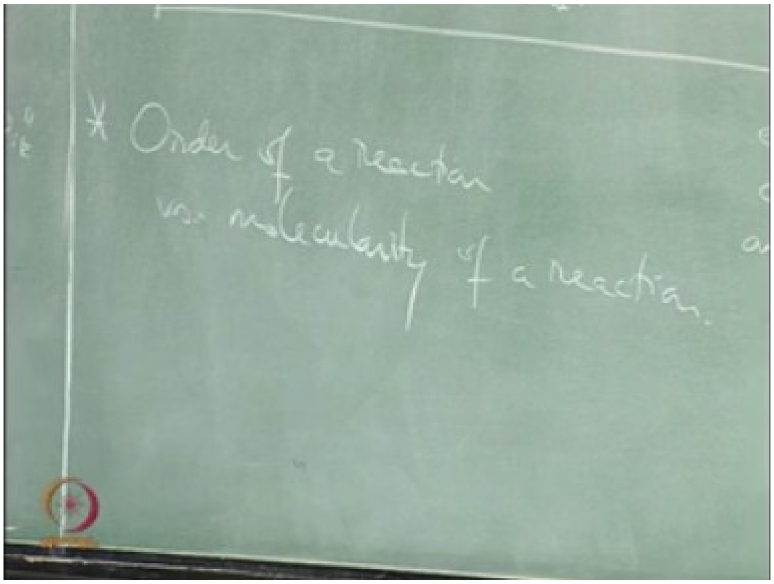

* Order of a Reaction
vs. molecularity of a reaction.

Molecularity okay molecularity of a reaction order the order of reaction vs. molecularity of reaction so many times we come across we come across these things like we have a first order reaction of a second order reaction okay and sometimes, we also hear this thing like we have a uni molecular reaction or a by molecular reaction or a terror molecular reaction and so on okay so what are we talking about any feel for this we have to try to sort of anglicized is right, so that means we have to say what we are what we are hearing in English in typical sentence.

It sound very difficult to think about for example what is a by molecular reaction the means we are looking at a reaction where you have two molecules that are colliding with each other to react the pins as first the reactants are concerned we want to have two molecules of different species one molecule each one molecule each of two different species have to collide with each of them can we say that or could it be like two molecules of the same species have to collide with each other yes or no obviously.

If you want to have a species react molecules have to collide there is something that we started talking about it as an axiom, so even if one particular species just disintegrates why would the disintegrate it would disintegrate because molecules of itself start colliding with each other right and then you could think well maybe I need two molecules to collide instead of just one molecule design disintegrating by itself without any collision huh would that be bio molecular okay so let us have this thing in our minds okay of course , now if you can extend this confusion to let us say tell molecular which of it is pretty easy.

You can now say I want to have three molecules of different three different species each it will three molecules each of three different species in a tear molecular reaction or a try molecular reaction or I could have like two from one and one from the other and so on, right okay so we have that situation so what would you do for example let us suppose that you had a reactant a and I say that I want to have to a gives products how do I write the reaction rate we will I now say that the reaction rate for this reaction.

Is equal to K times concentration of a squared or can I say now let me divide it by half I mean do I divide the whole thing by 2and then say a gives half products yeah and therefore the reaction rate should be equal to K times concentration of a raise to the power 1 there is a big difference you cannot have a rate either depend linearly on the concentration of a or a square of the concentration they are vastly different, so which one would you do right and then let us suppose so you have something like $2H_2 + O_2$ gives products.

Let us not worry about the products because the law of mass action is only depending upon the reactant concentrations right so $2H_2 + O_2$ gives products versus $H_2+1/2\ O_2$ gives products how would you write your reaction rates would you like this as K times concentration of H_2 to the power 2 times concentration of CO_2 or would you write it as K times concentration of H_2 times concentration of what would be half the two expressions are vastly different right, so what is the reality will which is the right answer could you just recklessly divide the reaction by whatever number you want like I just say / 2.

And then I now come up with a new reaction rate constant expression I do not know which is right then until now we did not care we could we could divide and save okay a half a mole here one mole there does not matter but now we have an implication these things are now going to show up as exponents of the concentrations of the reactants in the reaction rate expression we cannot be fiddling around with this, so what is going on right the answer is if you now look at a reaction where you are talking about like let us say H2 + 1/2O 2 gives H2O you know that it is not really happening that way.

Because you cannot have half a molecule of oxygen react with one molecule of hydrogen okay it is not like oxygen is half-heartedly reacting with hydrogen right, so we are always been saying it should be half amole and half a mole contains a large number of molecules, so any now look at the actually the molecules what are they doing obviously you need to have them react one on one you cannot have half a molecule do with another one or another half right, so if you now have anything that has like a half you know that it is not a molecular level reaction.

That we are talking about it is it is what is called as a global reaction okay and for a global reaction you could, now write the law of mass action globally and there you could have the exponents to the concentrations raise to whatever value it does not have to be integers you get the point, so let us try to write this.

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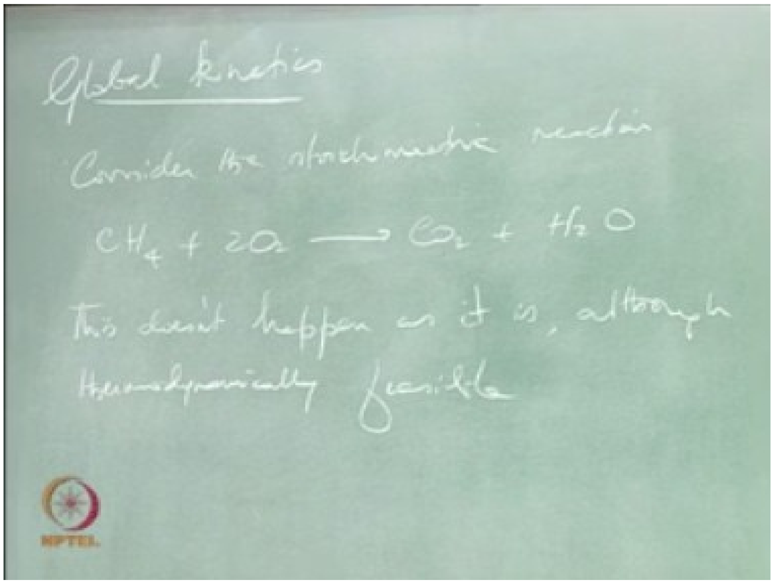

Global kinetics

Consider the stoichiometric reaction

$CH_4 + 2O_2 \longrightarrow CO_2 + H_2O$

This doesn't happen as it is, although thermodynamically feasible

We have something called Global kinetics right so consider the stoichiometric reaction does not have to be a stoichiometric reaction, but let us consider this reaction not happen as it is although thermodynamically feasible thermodynamically feasible okay does not happen in reality yes going back to this.

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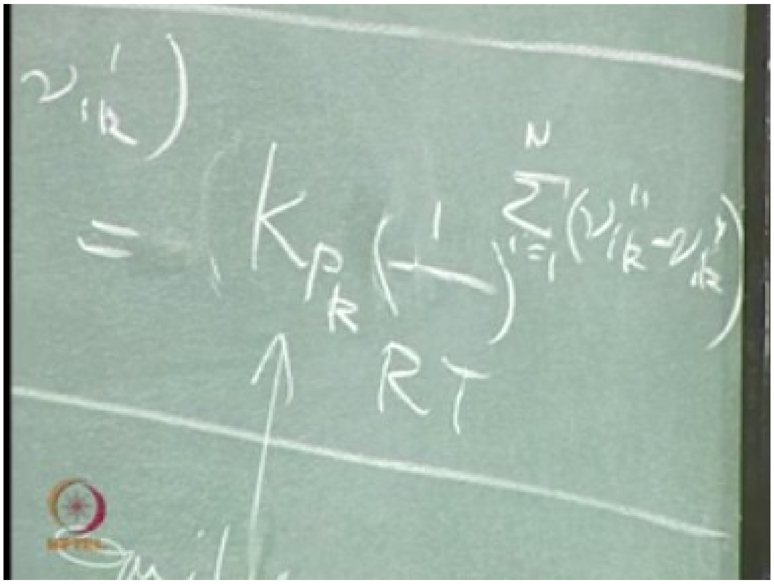

Can you say what you are asking that is fine, but oh did I make a mistake should we have this no let us just keep it this way no I think I made a mistake you are right you do not have the P here that is what you mean yeah correct thank you right because which what she is saying is this pressure should actually go along with this for you to have a p is mall pi yeah okay fine you go back to what we were talking about fine, so what I am saying is this reaction actually does not happen the way it is written here.

That means it is not like CH for a molecule of CH_4 reacts with two molecules of oxygen that is not what is going on in reality, when you now get methane and oxygen together okay what else is going whatever what happens in reality in reality unfortunately for you now have a huge set of reactions that are that kick in the moment you get this to go okay, so the first thing that happens is like you now have methane breakdown intimate I will like CH_3 CH_2 CH those kinds of radicals and also release some H radicals, okay and then you now have a put of these radicals right oxygen could split it to 0 and 0 can actually get together with H to form OH lots of such things lots of such things such things are happening similarly H2 + ½ O2 gives H_2O does not happen as it is and we saw this we cannot we said that we cannot have half an oxygen molecule get together with hydrogen molecule.

You are okay with half a mole of oxygen getting reacting with on the whole okay but essentially when you say on the whole then these reactions are now representing what is called as global reactions that are representative of a huge set of reactions that kick in at the molecular level, so those reactions that are happening at the molecular level or what is called as elementary reaction steps in a reaction scheme, so this is the terminology that is typically used so you have a reaction scheme the means.

You have scheme of lots of reactions going on and each of those reactions if you talk about in reality would be like an elementary reaction step that is happening at the molecular level right, but all of it together could be represented by a global reaction if you now have this kind of a global reaction then, so let us now go back to this example right then if you want to now write the let us say the production rate of CO_2 concentration right, so this is dc CO_2 / dt that is like saying dci / dt where I is for CO_2okay.

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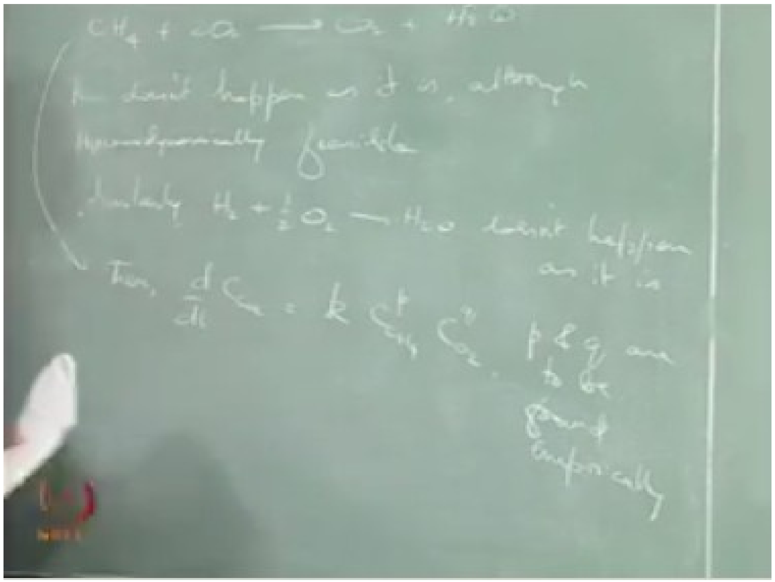

$CH_4 + 2O_2 \longrightarrow CO_2 + H_2O$

This doesn't happen as it is, although thermodynamically feasible

Similarly $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$ doesn't happen as it is

Then, $\frac{d}{dt} C_{CH_4} = k\, C_{CH_4}^{p}\, C_{O_2}^{q}$. p & q are to be found empirically

You can now write this as K CH_4 power P and C subscript O2 power Q we would not write for this reaction P = 1 and Q = 2 now okay because P and Q are to be found empirically.

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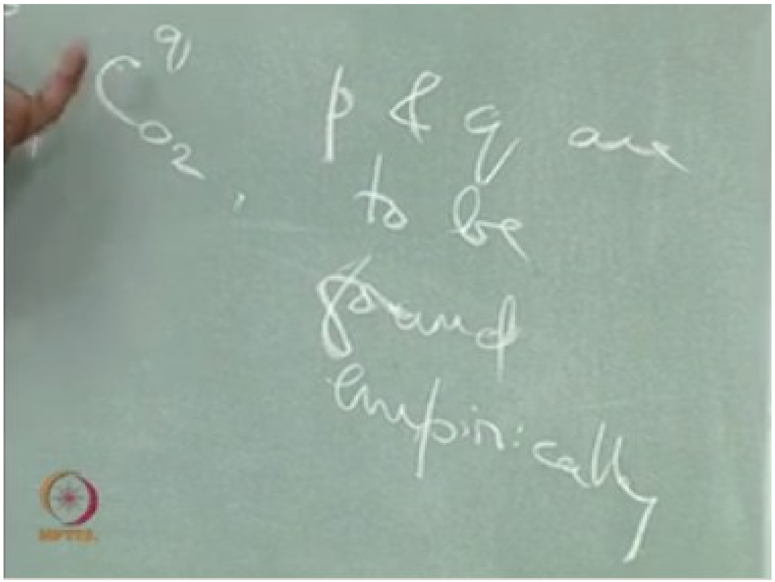

Many times in many applications you will find that these values are more like p is of the order of like point 15.15 and curious like about 1.65, so you see that first of all they are not integers number one number two it is got nothing to do with the coefficients of these reactants that are appearing in the global reaction because the global reaction is like a representation of what is happening in reality through a huge number of elementary reaction steps in a reaction scheme and to give you an idea of what the what is how huge it is for the methane oxidation you could be thinking about like at least about hundred reactions 100 reactions minimum okay.

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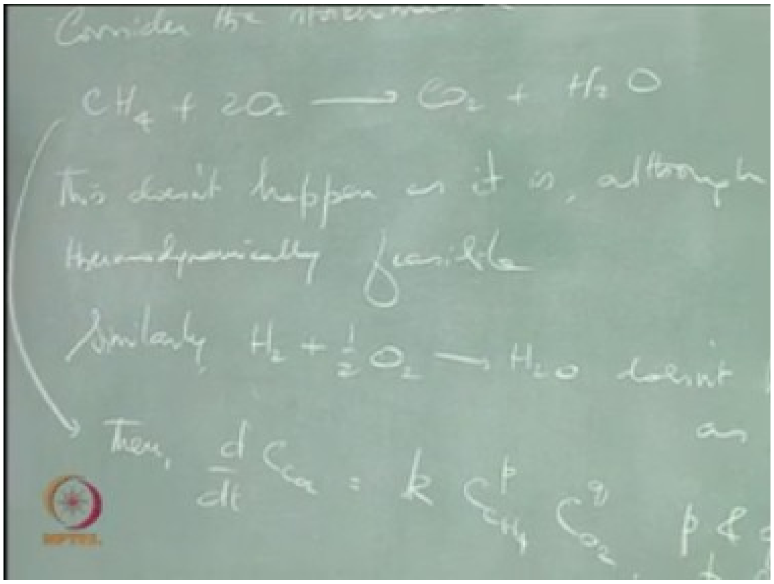

Consider the

$CH_4 + 2O_2 \longrightarrow CO_2 + H_2O$

This doesn't happen as it is, although

thermodynamically feasible

Similarly $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$ doesn't

as

Then, $\frac{d}{dt} C_{CO_2} = k\, C_{CH_4}^{p}\, C_{O_2}^{q}$ p &

And the number of species that it produces because it is now splitting into CH_3 CH_2 CH, HOH and call those kinds of things it could be as many as about 40 species okay we are now looking at fairly large number of reactions and not so hope mostly not so large number of species but relatively large for this right game here you will be thinking about like a few tens of reactions that are really happening and a that is a handful of species at least okay five to ten species that are involved he add a molecular level you can go back and write the law of mass action.

As it is looking at a reaction and figuring out the coefficients there and then plugging it in here only for the molecular level reactions okay, so if you now do that if you now assure that a reaction is actually a molecular level reaction and not a global reaction then you look at the reaction we can write the law of mass action the rate of production of a particular species all the reaction rate as K times concentration of the reactants raised to the respective coefficients that are seen in the reaction.

Those will typically be integers because we have to have integral number of molecules of each reactant react right, and then we can say you have a molecularity of the reaction is essentially the number of molecules of reactants that are participating there, so there if you now add up those exponents that are happening at the molecular level that gives you the molecularity of the reaction okay, so if you cannot a tear molecular reaction where you are now saying 2H + O gives you H_2O that is like that is one molecular level reaction that is happening then you can say it is a tear molecule reaction that because that is because you need to have two hydrogen atoms collide with one oxygen atom to form.

A water molecule but you could also now distinguish and say the reactions molecularity is to in hydrogen atom and one in oxygen the means you should not be able to say what is the molecularity in each of the reactants that is the next level of refinement in trying to identify the molecularity right, it is also possible for you to say this for what is called as a order of reaction and order of reaction is typically like what we are talking about for a global reaction in a global reaction p + q will now give you the order of the reaction.

Which are empirical constants right and then you can further say the reaction is of P^{th} order relative term attained and q^{th} order in oxygen you see you can say that there is all common practice to identify what is the reactions order in each of those species each of those reactants for a global reaction, okay of course for a elemental reaction step that is happening at the molecular level the molecularity and the order are the same, but the order is not the same as the molecularity when I am looking at a global reaction and it is got nothing to do with the stoichiometric coefficients.

That are obtained for mass balance essentially when you are trying to do a balancing the reaction you are essentially doing a mass balance okay you want to balance the same number of nuclei and each of those nuclei have some mass right that is what you are trying to do good.

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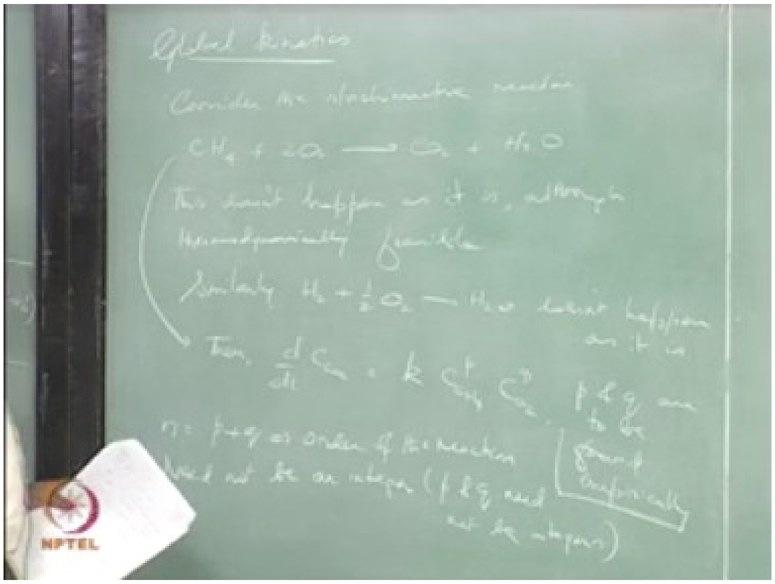

So n + n we now say n = p + q is the out of reaction and need not be need not be a integer you need not be an integer okay, so p and q need not be integers okay can they be negative what does that mean, if you now throw in a reactant the reaction rate actually comes down and why would I would I would you have the reaction in the first place yeah it is possible under some circumstances and I think we will we will proceed further and I will try to explain that to you because we are trying to sort of globalize a series of reactions.

That are happening and under different conditions you can now have different emphasis for the role of each of those reactants sometimes it is also possible for the reaction rate or the rate of production of your product so rate of depletion of your reactants whatever to be depending globally, globally speaking depending on product concentrations also, so that looks like a violation of the law of mass action okay and many times under those circumstances the exponent for the concentration.

Of product dependence on the reaction rate will be negative which is what is called as a self inhibiting reaction okay that is more the product is formed the less and less the reaction is going to happen because as the concentration of the product increases the body the reaction gets inhibited, because there is like a self inhibition mechanism okay we will also look at some examples for that as we go along, but these are basically looking at the global reactions at the molecular level.

We do not have any problem we can just go ahead and do whatever we did with the law of mass action the previous class right fine. Can we do we have to have a global reaction that is only one step can we have like multi-step groups reaction yes or no why not while we are having fun might as well have more from this is not fun at all right.

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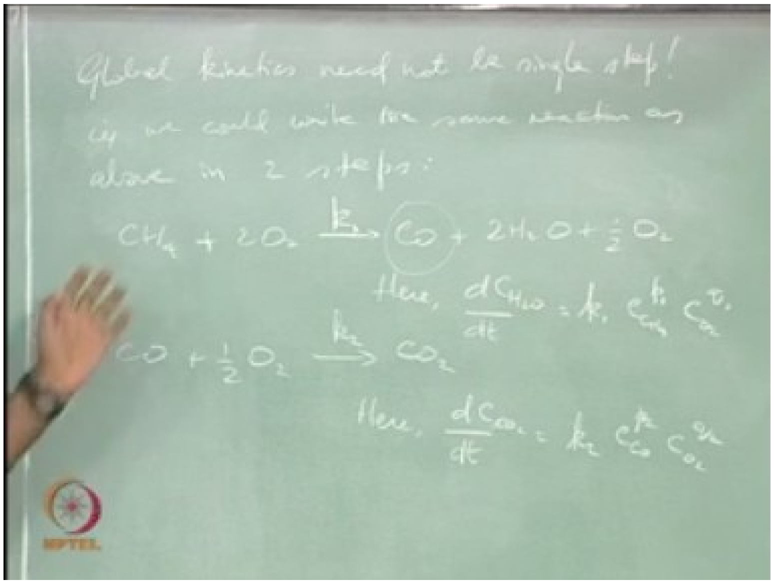

Global kinetics need not be single step!

i.e. we could write the same reaction as above in 2 steps:

$$CH_4 + 2O_2 \xrightarrow{k_1} \boxed{CO} + 2H_2O + \frac{1}{2}O_2$$

Here, $\frac{dC_{H_2O}}{dt} = k_1 C_{CH_4}^{b_1} C_{O_2}^{a_1}$

$$CO + \frac{1}{2}O_2 \xrightarrow{k_2} CO_2$$

Here, $\frac{dC_{CO_2}}{dt} = k_2 C_{CO}^{b_2} C_{O_2}^{a_2}$

So Global kinetics need not be single step right that is we could write the same reaction as above in two steps okay CH_4 + $2O_2$ and then let us say that this has a rate constant k1 CO + $2H_2O$ + $1/2O_2$ right, and then you have CO + ½ O2 gives k_2 with the rate constant K_2 it gives you a CO_2 right keep in mind I have a gap here, so I am going to fill it in with something right question is why would you do this why would what we do we understand why we want to have a global reaction right that means we do not want to go through the details we do not want to go through what is happening in the molecular level.

We do not want to burden ourselves with those hundred reactions and 40 species and all those things we can I get a David chemistry no I cannot that is combustion well you can it is possible if you now instead of thinking about global kinetics we now have something called infinite trade chemistry there is something that I will talk about in the context of diffusion flames as we go along we try to try to side step chemistry completely, okay but shut off side stepping chemistry the best we can do is to globalize.

Means you just have one single step that represents all the details unfortunately the K will still be represented as an Arrhenius reaction and the A and the E that we have with a B m and E that we have as well as the p and q all have to be obtained empirically because it does not happen in reality right we do not do quantum mechanical calculations to obtain those not that we do that for all the other molecular level reactions, but it can be done it is tedious but it can be done okay but we do not do it for global reactions.

So the means we have to get numbers from literature for global reactions which are empirically obtained but while you are there why would you want to do like a two-step global reaction and of course when you do two step you could do three step you can do five step not 100 step and so on right why would you do that why would you want to, now split the global reaction which was convenient nice reaction and then have a splitting headache over it right, any ideas in this case we are not just interested in this reaction going on we would like to see if we can track how much CH_O is being produced.

So if you are particularly interested in a intermediate right I would like to now write my global reactions in such a way as to include that species showing up as a product and one reaction and a reactant another reaction possibly the two rates are not going to be the same right, so you are now going to have a CO that is being formed as an intermediate and I would like to know how much it is I like to see if it is actually going to be completely consumed as much as it is getting produced which means I now start looking at what is my k_1 what is my $k_2$right.

So I can then right here so we will try to fill the gap here dc, dcH_2O for example over dt equals you could write divide this first CO as well maybe yeah okay let us just do this k_1 C, CH_4 to the p1 CO_2 to the q_1 and here we say dc CO_2 /dt equals k_2 to C_CO p_2 to the p_2 CO_2 to the q_2 right and then we will have to empirically find out what is your k1 and k2 which in turn means we have to now know what is or a_1 and e $_1$ or b_1 m_1 and e 1 a $_2$ 1 m_2 or b1 mb_2 m_2 1 t 2for these are the kinetic constants and then you have these p_1 and q_1 here.

P_2 and q_2 to here which all have to be empirically supply but provided we can actually try to get those empirical relationships what this tells you is if you were to have this situation it is pretty much like the rate of production of water and rate of production of carbon dioxide are actually the same, but here we will now be able to distinguish that the rates of production of water and related rate of production of carbon dioxide are different depending upon the individual rates at which these things happen.

And look at something very interesting that is going on, you see that in this reaction the first reaction carbon monoxide has to be produced before the second reaction can happen, so the second reaction rate will depend on the concentration of carbon monoxide which is produced in the first reaction if you the first reaction did not happen the second reaction cannot happen right and when the second reaction happens it competes for the same oxygen as the first reaction they are happening simultaneously right, so you have methane getting oxidized carbon monoxide also is getting oxidized but the same oxygen in the pool.

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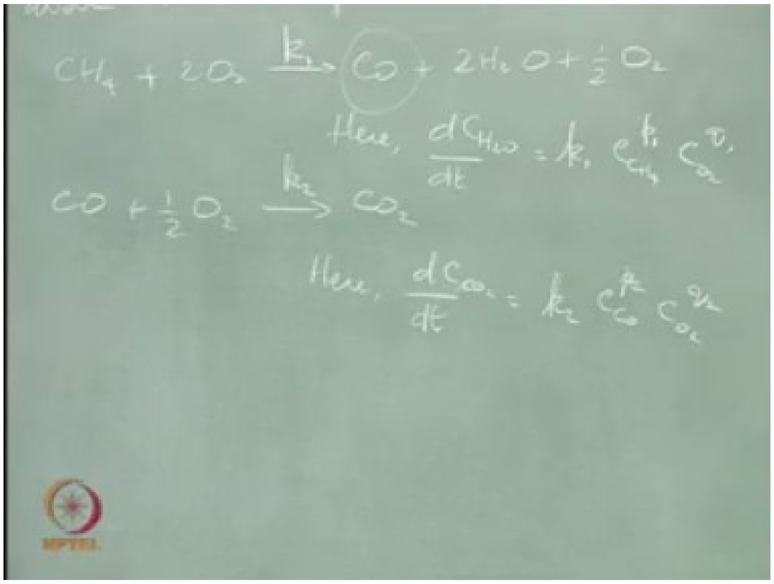

$$CH_4 + 2O_2 \xrightarrow{k_1} CO + 2H_2O + \frac{1}{2}O_2$$

Here, $\frac{dC_{H_2O}}{dt} = k_1 C_{CH_4}^{p_1} C_{O_2}^{q_1}$

$$CO + \frac{1}{2}O_2 \xrightarrow{k_2} CO_2$$

Here, $\frac{dC_{CO_2}}{dt} = k_2 C_{CO}^{p_2} C_{O_2}^{q_2}$

So it is as if like within was trying to get oxidized it produced some carbon monoxide the carbon monoxide now begins to actually eat up the oxygen that is trying to oxidize the methane and then reduces the rate of that reaction because it is consuming some oxygen, but if it reduces the rate of that reaction it cannot get oxidized so it reduced see what is going on there is a competition between these two but it has to be sequential it is sort of like mother and daughter competing with each other.

Yeah one of them gives rise to the other but then they compete right so this is pretty interesting dynamics here and it will depend on what your key one is what your k_2 is there, so think about k_1 being much lower when compared to K to see what happens then you have like it takes forever to get this going but the moment this happens it is immediately formed the next reaction the moment the next reaction immediately tries to happen it tries to rub O2 and then flows that down that means this also has to slow down.

Because $C_{C}O$ has to come down you see so there is a nice my dynamics that you can think about in these things which will finally fetch you a certain carbon monoxide that may be remaining that means you are trying to track carbon monoxide and that means you have to bring that in as part of your global reaction set now we are now beginning to talk about global reaction set rather than just one global reaction.

There is a reason why we are thinking about a two-step global reaction there are much more complicated systems that are there, so typically in chemistry or that that you want to encounter like hydrocarbon oxidation methane is like the simplest hydrocarbon okay one carbonate then you get into step into things like methane and ethane and all those things right, and then you have acetylene sorry not easy acetylene and propane and propane and butane all those things so keep on going and then you get into heavier hydro carbons heptanes and so on.

Then you now go to do decane know those things that is like you would now begin to get into things like petrol diesel those kinds of enzyme it is like somewhere in between there and so on so keep on growing and growing this number of the elemental reaction steps becomes longer and longer right, but we are still talking about a carbon hydrogen oxygen system, if you want to now use air to oxidize and then you are interested in Knox that means you have to now factor in oxides of nitrogen being formed okay.

Then you are now throwing in one more atom type into the pool and the set of reactions that you have to consider there at the molecular level becomes a lot more you certainly are looking at about 500 reactions happening okay, so I used to be working with ammonium per chlorate reacting with poly butadiene right, so the poly butadiene is like a polymer that is based on like a butadiene as a monomer and soon you are looking at about four carbon atoms in a monomer but you now have a change.

It is about having a molecular weight of about 22,000 k which has to break down and then react with ammonium per chlorate and then there you have ammonia and per chloric acid that are formed and then you have a chlorine that is coming up as a new atom type and apparently ammonium per chlorate can actually react by itself it is like a monopropellant and it is estimated that there are like about thousand reactions that are actually happening in a very thin layer of about five to ten microns thick.

Which we cannot even see for most part because the temperature gradients are so steep right and typically it is approximated by five global reactions, so it is like the typical number we are looking at okay so from thousand.

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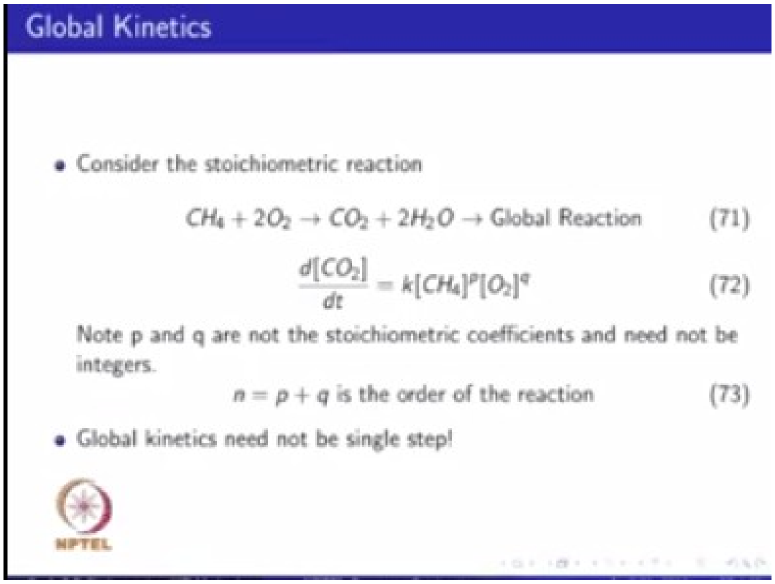

Global Kinetics

- Consider the stoichiometric reaction

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \rightarrow \text{Global Reaction} \qquad (71)$$

$$\frac{d[CO_2]}{dt} = k[CH_4]^p[O_2]^q \qquad (72)$$

Note p and q are not the stoichiometric coefficients and need not be integers.

$$n = p + q \text{ is the order of the reaction} \qquad (73)$$

- Global kinetics need not be single step!

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We try to reduce it down to something like five so that we can handle it okay are there better ways of handling it in a more realistic manner we will wait and watch Monday.

Production and Post Production

M V Ramchandran
G Ramesh
K R Mahendra Babu
Soju Francis
S Subash
R Selvam
S Pradeepa
Ram Kumar

Ram Ganesh
Udaya Sankar
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Karthi

Studio Assistants
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Saranraj

NPTEL Web & Faculty
Assistance Team

Allen Jacob Dinesh
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K S Janakrishman

Principal Project Officer
Usha Nagarajan

Video Producers
K R Ravindranath
Kannan Krishnamurthy

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