Chemical Reaction Engineering
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Lecture No. # 16
Monomolecular Reaction Network and Lumping Analysis

Friends, let us consider the example of a complex reaction by looking at one specific network, which is both important practically, as well as gives an elegant way of analyzing the chemical reactions. So, what we are going to do today is look at monomolecular reversible reaction network.

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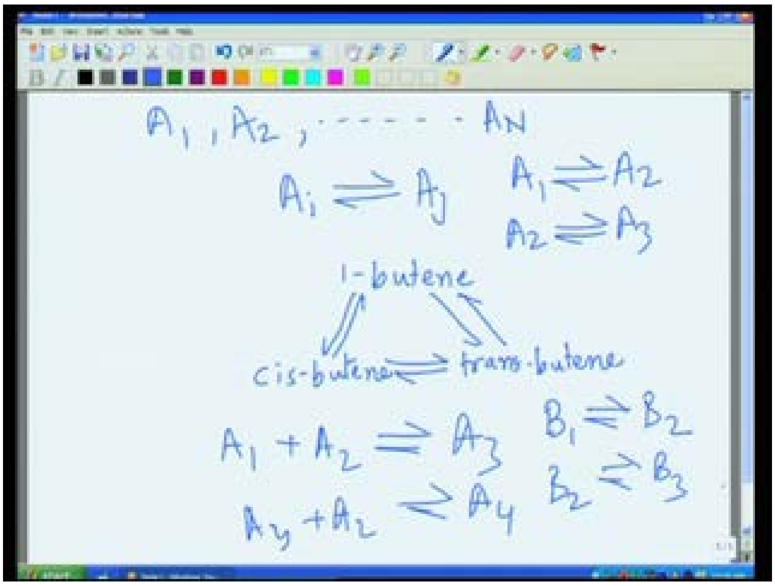

$A_1, A_2, \ldots\ldots A_N$

$A_i \rightleftharpoons A_j$

$A_1 \rightleftharpoons A_2$

$A_2 \rightleftharpoons A_3$

$A_1 + A_2 \rightleftharpoons A_3$

$A_3 + A_2 \rightleftharpoons A_4$

$B_1 \rightleftharpoons B_2$

$B_2 \rightleftharpoons B_3$

So, what is monomolecular reaction reversible reaction network? Let us say that we have N chemical reacting species. So, these are our chemical reacting species, N species. and there are reactions between this species, which can be represented by A i going to A j. i and j are anything between 1 to n, of course, they cannot be equal, because A 1 going to A 1 does not make any sense. So, we are looking for example, reaction networks which are A 1 going to A 2, A 2 going to A 3 and so on. These are called monomolecular reaction networks, because both reactant side and product side the molecularity is one. They are reversible reactions, so we have monomolecular reversible reaction network. Now, one may ask what is importance of this kind of networks.

Number 1, there are certain reactions which actually follow this monomolecular reaction network. For example, 1-butene, cis-butene and its isomers and trans-butene. So, we have three species and this three and there are reactions of this kind between this three species. And monomolecular reaction network which is actually a real reaction. But also, it is important, because many times we can take this monomolecular reaction network this monomolecular reaction network, as a typical example of a simplified complex network. So, let us say that we have a reaction real reaction something like this A 1 plus A 2 going to A 3, A 3 plus A 2 going to A 4 and so on.

we will see in the next example, that we can actually write this reaction network represent this in an hypothetical reaction or simplified reaction network like B 1 going to B 2, B 2 going B 3 and so on. B 1, B 2, B 3 is not real species. They are hypothetical species, but they contain all the information. That is there for the real network that is in the species A. So, from that point of view, analyzing these networks is important. So, let us take a simplest type of this reversible monomolecular reaction network and see what kind of results we get for this network. And then we will generalize those researches.

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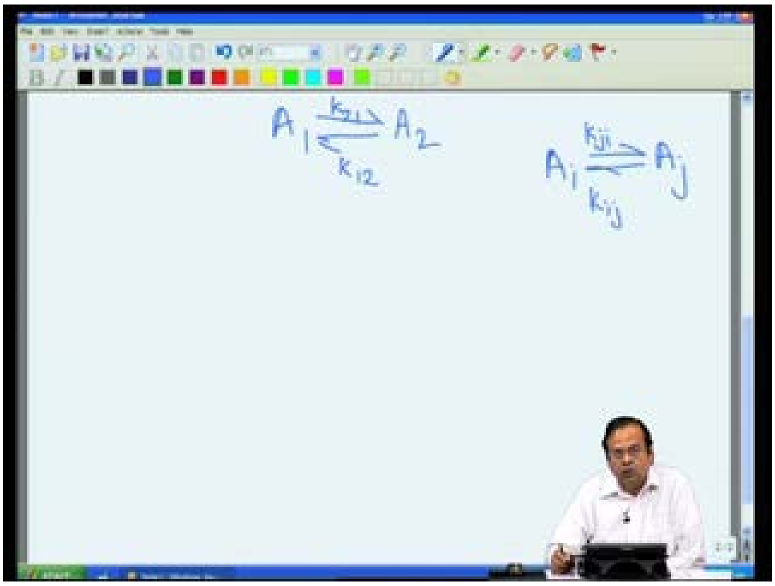

$$A_1 \underset{k_{12}}{\overset{k_{21}}{\rightleftharpoons}} A_2 \qquad A_i \underset{k_{ij}}{\overset{k_{ji}}{\rightleftharpoons}} A_j$$

So, let us start with what is the simplest network possible. There has to be minimum two species nothing can be simpler than that. So for a reaction, A 1 going to A 2, this is simplest kind of monomolecular reversible reaction network that one can think of. So, we will write this reaction network and kinetic rate constants for this forward and backward reaction, using the following location. Since, we are getting 2 from 1 in the forward reaction. Let us call this reaction rate constant as k 2 1. and the backward reaction we are getting 1 from 2. So, let us call this backward reaction rate as k 1 2.

Let me also simultaneously generalize this, so that we need not come back to the notation, once again. If we have a reaction A i going to A j, let me write it down. If I have reaction A i going to A j, formation of j from species i the reaction rate constant is k j i. Formation of species i from species j reaction rate constant is k i j. So, that is our reaction network, in general. If I have this reaction network, so let's go back to this, is the general case, we will come back to that little later on. So, if I have a reaction network and let me rewrite this.

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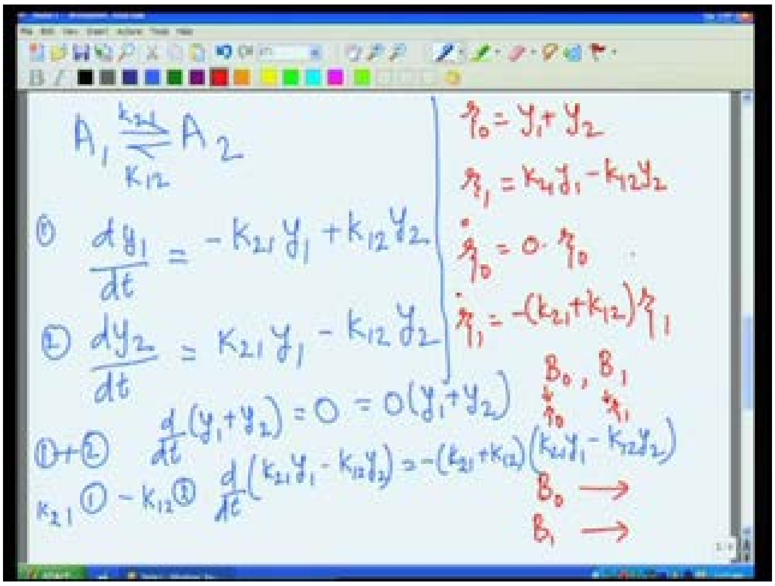

$$A_1 \underset{k_{12}}{\overset{k_{21}}{\rightleftharpoons}} A_2$$

① $\dfrac{dy_1}{dt} = -k_{21} y_1 + k_{12} y_2$

② $\dfrac{dy_2}{dt} = k_{21} y_1 - k_{12} y_2$

①+② $\dfrac{d}{dt}(y_1 + y_2) = 0 = 0(y_1 + y_2)$

k_{21} ① $- k_{12}$ ② $\dfrac{d}{dt}(k_{21} y_1 - k_{12} y_2) = -(k_{21} + k_{12})(k_{21} y_1 - k_{12} y_2)$

$\eta_0 = y_1 + y_2$

$\eta_1 = k_{21} y_1 - k_{12} y_2$

$\dot{\eta}_0 = 0 \cdot \eta_0$

$\dot{\eta}_1 = -(k_{21} + k_{12}) \eta_1$

B_0, B_1

$\eta_0 \quad \eta_1$

$B_0 \longrightarrow$

$B_1 \longrightarrow$

So, that we have enough space to write things. let us say my reaction network is A 1 going to A 2, I am calling the forward reaction as k 2 1, the reverse reaction rate as k 1 2. So now, let us try to work around the kinetics of this process, but this time instead using concentration, we will use mole fractions. It is one and the same thing, because concentrations by taking the individual concentration and dividing it by the total concentration, we will get the mole fraction. So, we will this kinetics in terms of mole fraction. Let us write d y 1 d t, again a close system d y 1 d t that is y 1 is the mole fraction of species A 1, will be minus k 2 1 y 1, the forward reaction plus its generation k

1 2 y 2. Similarly, we can write d y 2 d t as k 2 1 y 1 its generation from species 1 minus k 1 2 y 2. So, we have these two reactions, two mass balances 1 and 2. And let us play around with this mass balance little bit.

We will say that we will add 1 and 2. If you add 1 and 2, what do we get? We get d d t of y 1 plus y 2 equal to 0. Because, we know the mole fractions cannot change and indeed, if we add this two equations we will get 0. But this 0, I am going to write it as y 1 plus y 2. Why? Reason will become clear in a minute. Let us also do another manipulation. let us multiply the first equation by k 2 1 and subtract it by multiplying second equation by k 1 2. So, we are multiplying this term by k 2 1 and then subtracting minus k 1 2 from this term. Now, if you do that and little bit of rearrangement. We will get d d t of k 2 1 y 1 minus k 1 2 y 2 that is the left hand side. And the right hand side, if we manipulate little bit we will get k 2 1 plus k 1 2 into k 2 1 y 1 minus k 1 2 y 2.

So we have chemical species A 1 and A 2. Its dynamics being represented by mass balances 1 and 2. And we have manipulated this mass balances 1 and 2. Let me now, re look at this equations this two equations. And let us say that I define zeta naught as y 1 plus y 2 and zeta 1 as k 2 1 y 1 minus k 1 2 y 2.

if I do this and I also now call, if I do this, let if you go back to our equations of this two equations and defining zeta naught and zeta 1 in this manner. We see that the dynamics is represented by zeta 1. So, we have two equations zeta naught and zeta 1 dynamics, which is represented in this manner. Now, what is the motivation for doing this? The motivation for doing this is that, I am now going to say that I have two hypothetical species B naught and B 1, whose compositions are zeta naught and zeta 1. These are hypothetical species these are not real species. My real species are over here and the real reaction. These are my hypothetical species. Now, what why do we need to this? We need to do this for the following reason, if you look at the mass balances of the real system they are coupled y 1 y 2 y 1 y 2 and so on.

So, the original species dynamics is coupled and it is not very easy to see what is happening there. But the same dynamics for hypothetical species is completely decoupled. Zeta naught equation has only zeta naught, zeta 1 dot equation has only zeta 1 and if there are many more species, you will always find that will be the case. Or in other words, what we have done is we have uncoupled the original dynamics uncoupled it, but not for the real system, but for the hypothetical system.

So now, what is the reaction involving this hypothetical species? If you look at this we can write this reaction, as simply B naught going to something, B 1 going to something. What is that something? I do not care, because if I had told that my system reactions are B naught going to something, B 1 going to something. Its concentrations are zeta 0 and zeta 1. then you would have written its kinetics zeta naught, as some kinetic rate constant some kinetic rate constant times zeta 0 zeta 1 dot another kinetic rate constant times zeta 1. And the solution of this is listed forward. How do we solve this? So, what I am going to do, let me see.

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Let me go back.

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What I am going to now do is, I am going to now look at this hypothetical system. Although, I have my original system, but what is this hypothetical system? What is the solution of this hypothetical system? This one particular over here, that is very easy.

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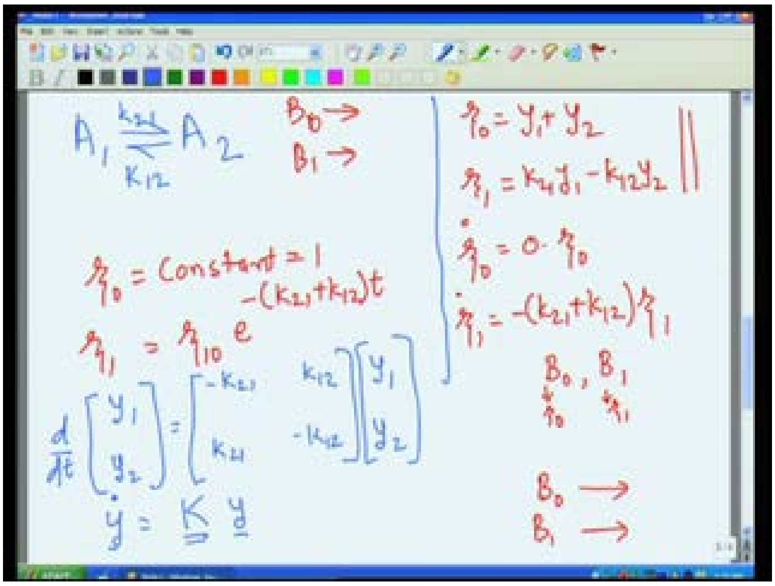

$A_1 \underset{k_{12}}{\overset{k_{21}}{\rightleftharpoons}} A_2$

$B_0 \rightarrow$

$B_1 \rightarrow$

$\zeta_0 = \text{Constant} = 1$

$\zeta_1 = \zeta_{10} e^{-(k_{21}+k_{12})t}$

$$\frac{d}{dt}\begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \begin{bmatrix} -k_{21} & k_{12} \\ k_{21} & -k_{12} \end{bmatrix}\begin{bmatrix} y_1 \\ y_2 \end{bmatrix}$$

$\dot{y} = \underset{=}{K}\, \underset{-}{y}$

$\zeta_0 = y_1 + y_2$

$\zeta_1 = k_{21} y_1 - k_{12} y_2$

$\dot{\zeta}_0 = 0 \cdot \zeta_0$

$\dot{\zeta}_1 = -(k_{21}+k_{12})\zeta_1$

$\underset{\zeta_0}{B_0}, \underset{\zeta_1}{B_1}$

$B_0 \longrightarrow$

$B_1 \longrightarrow$

So, my reaction for hypothetical is B naught going to something, B 1 going to something. Its solution is zeta naught is constant. And if you look at the definition of zeta naught that constant mole fractions must add up to 1. And zeta 1 is zeta 1 0 e raise to minus k 2 1 plus k 1 2 into t, because this is simply zeta 1 dot equal to some rate constant minus some rate constant times zeta 1.

Now, if we know zeta naught and zeta 1, we can always regenerate our original system by inverting this relationships. That is, if I know zeta naught as a function of time, zeta 1 as a function of time, I can always find y 1 as a function of a time, y 2 as a function of time. So, even though my original system is coupled, by decoupling the system in term of hypothetical species, I am able to get complete the solution of y 1 and y 2. These are simple linear relationship y 1 plus y 2 is zeta naught, you know what is zeta naught 1, this A 2 1 y 1 minus A 1 y 2 is zeta 1. We know what it is as a function of time. So, let us see what we did, now in a more general sense.

So, let us go back to our original system. And we could have written the dynamics, in a compact form y 1 y 2 as minus k 2 1 k 1 2 k 2 1 minus k 1 2 into y 1 y 2. The same the same mass balances written in a more compact form. This can be alternately written, y dot equal to reaction rate coefficient matrix K times y, this particular mass balance equations. Now, what is a link? Why we are doing this? we are doing this, to find out how do we get this rate constants of this, what are this 0 minus k 1 2 k 1 uh plus k 2 1, what are they. it turns out that the eigen value of this matrix K, eigen value of this matrix is K is nothing but 0 and k 1 2 plus k 2 1, this number over here or the eigen values of matrix K. So, eigen values is 1 is 0 other one is k 2 1 plus k 1 2.

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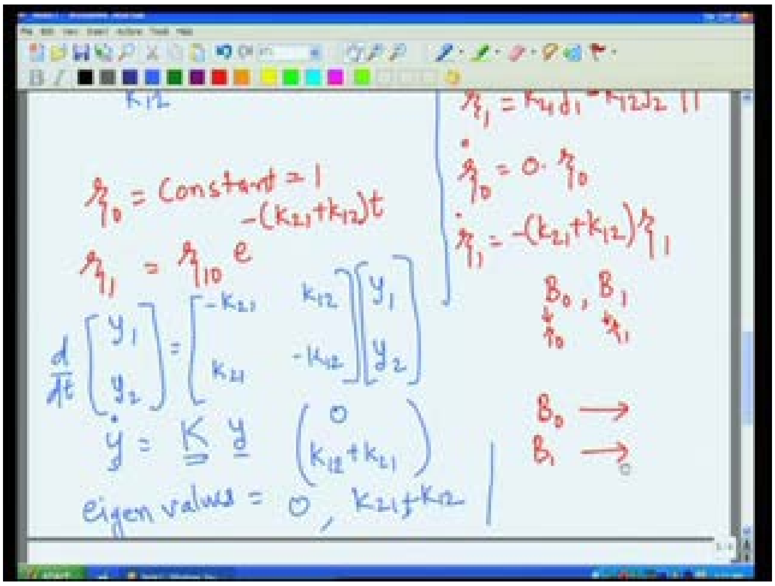

K_{12}

$\zeta_1 = k_{21}d_1 - k_{12}d_2$

$\dot{\zeta}_0 = 0 \cdot \zeta_0$

$\dot{\zeta}_1 = -(k_{21}+k_{12})\zeta_1$

$\zeta_0 = \text{Constant} = 1$

$\zeta_1 = \zeta_{10} e^{-(k_{21}+k_{12})t}$

$$\frac{d}{dt}\begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \begin{bmatrix} -k_{21} & k_{12} \\ k_{21} & -k_{12} \end{bmatrix}\begin{bmatrix} y_1 \\ y_2 \end{bmatrix}$$

$\dot{y} = \underline{\underline{K}}\, \underline{y}$

$\begin{pmatrix} 0 \\ k_{12}+k_{21} \end{pmatrix}$

eigen values = 0, $k_{21}+k_{12}$

B_0, B_1

ζ_0 ζ_1

$B_0 \rightarrow$

$B_1 \rightarrow$

So now, let us see what happens? So, these are my eigen values for y dot equal to. And these eigen values over here are nothing but the rate constants of this hypothetical species.

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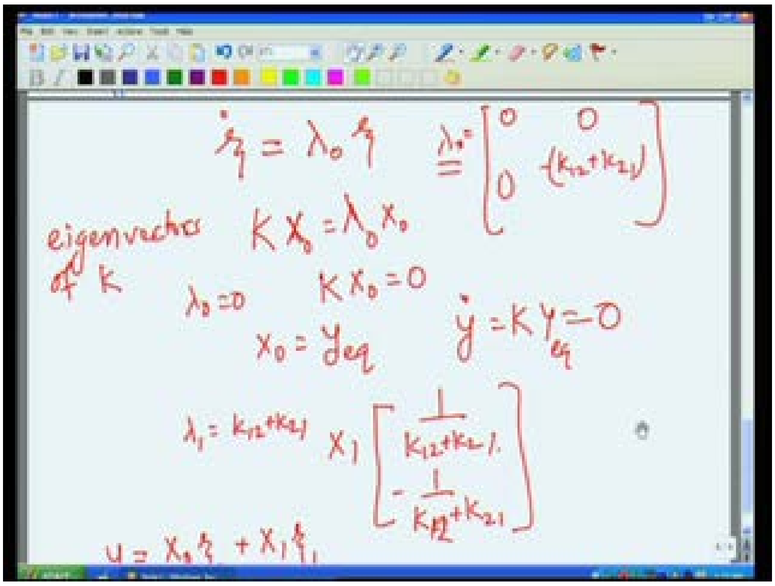

$\dot{\zeta} = \lambda_0 \zeta$

$$\underline{\underline{\lambda_0}} = \begin{bmatrix} 0 & 0 \\ 0 & -(k_{12}+k_{21}) \end{bmatrix}$$

eigenvectors of K

$K X_0 = \lambda_0 X_0$

$\lambda_0 = 0$ $K X_0 = 0$

$X_0 = y_{eq}$ $\dot{y} = K y_{eq} = 0$

$$\lambda_1 = k_{12}+k_{21} \quad X_1 \begin{bmatrix} \frac{1}{k_{12}+k_{21}} \\ -\frac{1}{k_{12}+k_{21}} \end{bmatrix}$$

$y = X_0 \zeta + X_1 \zeta_1$

So, we can write for my hypothetical species, zeta dot just as we wrote y dot equal to KY. We can write zeta dot equal to lambda 0 times zeta. Where, what is lambda 0? Lambda 0 is a matrix, consisting of eigen values negative of eigen values of that is 0 minus k 1 2 plus k 2 1, for this particular example 0 0. So, diagonal elements are the eigen values. This is as far as the eigen values are concerned, what are the eigen vectors? We can find the eigen vectors of K eigen vectors of K eigen vectors of K with lambda value equal to 0. What are the eigen vectors? Eigen vectors must satisfy the relationships K X, whatever is that eigen value must be lambda 0 X 0. Now, for lambda 0 equal to 0, this tells K X 0 equal to 0. And when does K X 0 become 0, when does K into y become 0. K into y equal to 0 means system has reached equilibrium.

So, first eigen value X 0, eigen vector is nothing but the equilibrium value obtain from the dynamics y dot equal to K Y equal to 0. So, the solution of this is y equilibrium. So, that is my first eigen value. And it turns out, if we take the second eigen value the that is lambda 1 as k 1 2 plus k 2 1. Then corresponding eigen vector works out to be 1 by k 1 2 plus k 2 1 minus 1 by k k 2 1 plus or k 1 2 plus k 2 1. So this is X naught, this is X 1 and my y, I talked about getting that y from zeta. It turns out is nothing but X naught zeta naught plus X 1 zeta 1, for this particular case. So, what has happen? If we look at my dynamics, this is my original dynamics, the eigen values of this strychometric matrix is 0 and k 2 1 and k 1 2. And zeta 1 dot is given, as we saw here 0 into zeta 0 zeta 1 dot minus k 2 1 plus k 1 2 zeta 1. So, knowing zeta naught value as a function of time. And zeta naught we know, what is zeta naught? Zeta naught is 1.

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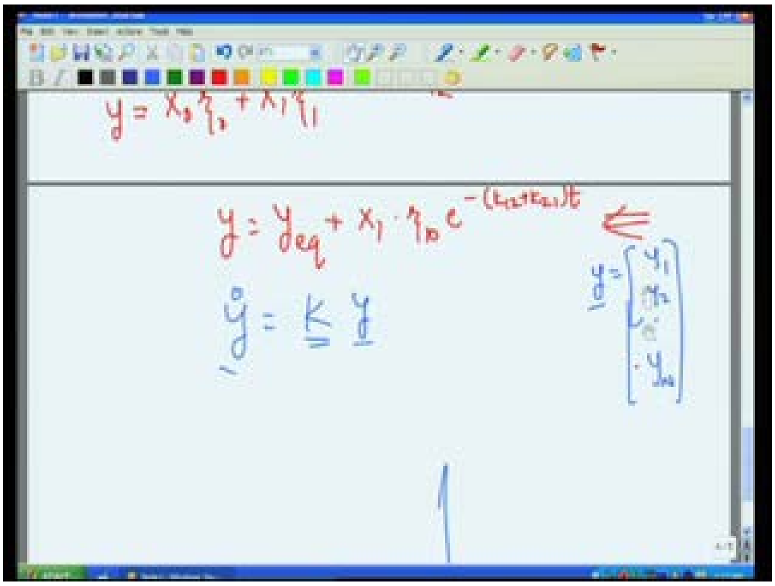

$y = X_0 \zeta_0 + X_1 \zeta_1$

$y = y_{eq} + X_1 \cdot \zeta_{10} e^{-(k_{12}+k_{21})t} \Leftarrow$

$\mathring{\underset{\sim}{y}} = \underline{\underline{K}}\, \underline{y}$

$\underline{y} = \begin{bmatrix} y_1 \\ y_2 \\ \vdots \\ y_n \end{bmatrix}$

So, we can write y as an X naught y equilibrium plus, whatever is this X 1 into zeta 1 0 e raise to minus k 1 2 plus k 2 1 into t. So, we are in a position now, to find y from this particular relationship. So, the original dynamics which was coupled by decoupling it and writing it as hypothetical species. We are now able to find the solution of the complete reaction network in a much simplified form. So, let us generalize this result now. Let us generalize this result, for a general system given by y dot equal to K y. So, I have N species now. So, y vector is nothing, but y 1 y 2 y N. And what is K? K is the reaction rate matrix as we define earlier. But this is for a 2 into 1 system, now looking at more general results.

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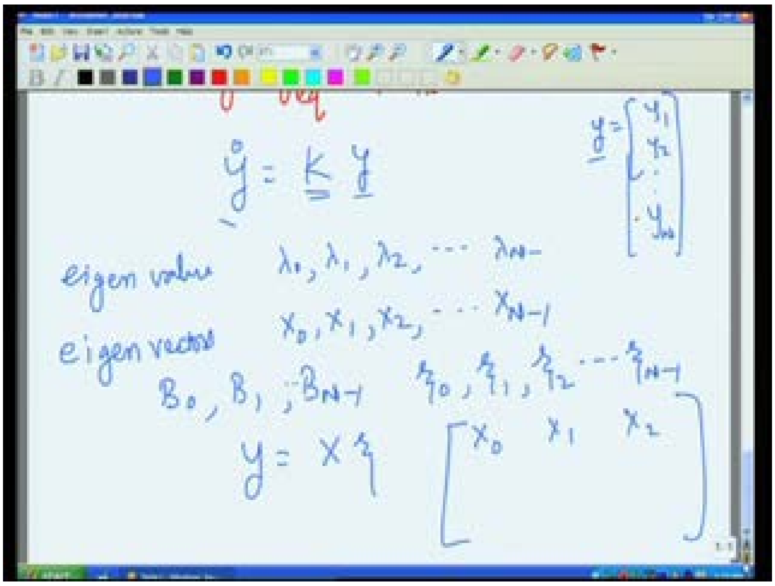

So, what are those generalized results? We say that eigen values of this K are lambda 0, lambda 1, lambda 2, lambda N minus 1. One of that eigen value is 0, we know that. An eigen vectors, let us say X 0, X 1, X 2, X N minus 1. We have hypothetical species B naught, B 1, B N minus 1, whose concentrations are zeta 0, zeta 1, and zeta 2, zeta N minus 1. Now, if we know this, we can write y as X into zeta. That is, the generalized form of this particular relationship. X is the vector X naught X 1, X 2. So if I write my X vector, whose X naught vector, X 1 vector, x 2 vector and so on. Then my y is given by this particular relationship, so this is my X.

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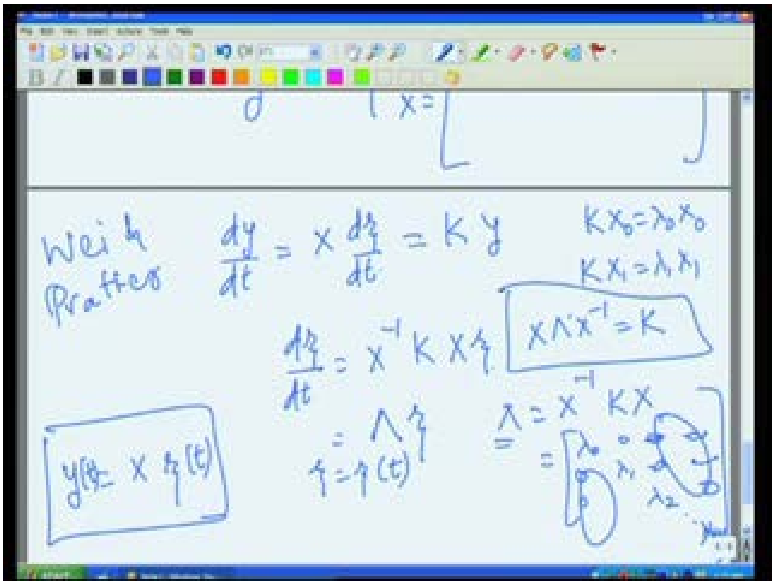

Now, let us take d y d t is nothing but X into d zeta d t. And this is nothing but K y from our original dynamics. So now, let us write zeta, what is d zeta d t? d zeta d t is, so let me. What is d zeta d t? d zeta d t is nothing but this, X is nothing but my diagonal matrix. Let us do it other way. So, from this relationship, I can also pre multiply both sides by X inverse and I will get d zeta d t is X inverse K and for y, I am going to write X into zeta. So, the dynamics is now given by,

Where lambda is X inverse K X. what is lambda? Remember what is our definition of definition of eigen vector? eigen vector is K into X naught is lambda naught into X naught, K into X 1 is lambda 1 into X 1 and so on. So now, by taking this relationship, I can now get what is to therefore? Lambda is nothing but lambda 0 0 0 0, 0 lambda 1 0 0 0 and so on. Only diagonal elements are non zero, everything else is 0. So 0 here 0 here and up to lambda n minus 1. So, that is my lambda vector.

We now get from this. So, we know the solution of this now, solution of this is straight forward, zeta naught is e raise to minus lambda naught zeta naught zeta 1 dot is minus lambda 1 zeta 1 and so on. So once we know zeta, as zeta of t. we can go back and calculate y which we did here, as X into zeta. So, this gives me now, y as a function of t in a completely decoupled manner. Elegant use of mathematics and chemical reactions, this analysis is known as wei and prater analysis, done in late 60s or early 70s during that period. So this in fact, can be also used to calculate the kinetic rate constants of such system. What we need to find to get the kinetic rate constant is, we that is if you want to find K if you want to find K. So, K is nothing but X lambda X inverse. So, from this relationship, I can also write X lambda X inverse equal to K. To find kinetic rate constant K, I need to know X, I need to know lambda and I need to know X inverse. If I know that I can find the kinetic rate constant.

Let’s look at this kind of reaction networks and it is use for another class of examples. This is an example, where we do not know what our reactants and our products are? But how do we do then lumping analysis and using this monomolecular reaction network idea.

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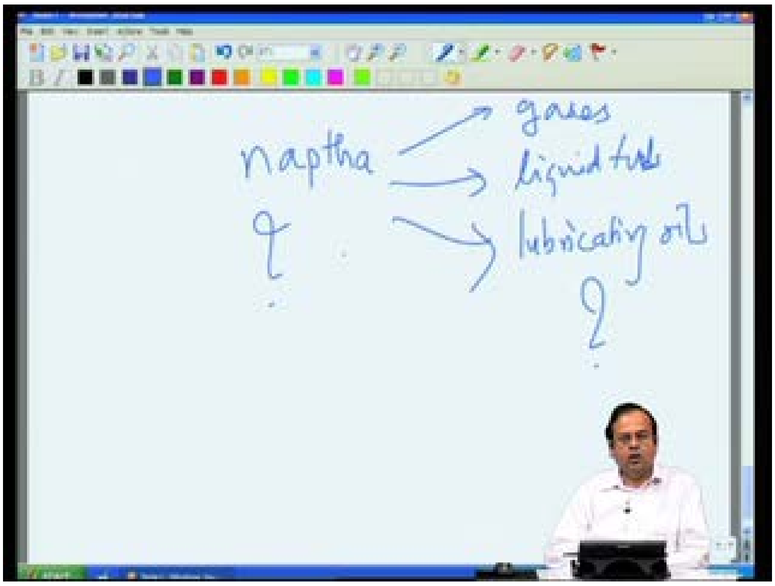

Let me give you an idea. As you are aware, if you do cracking of naptha, you get wide variety of product gases, liquefied, liquid fuels, lubricating oils and so on. So we get all this kind of products. Now, the problem here is, chemically we do not know what is naptha? What is its exact composition? We do not know that we cannot define naptha as C 20 h 25 or blah blah blah, we cannot do that. Neither can we define what these products are? Liquid fuels, petrol. For example, what is petrol? we know what petrol does, but we do not know what chemically petrol is. In fact, it is a mixture, it is not single species.

So, we do not know what these reactants are, we do not know what these products are. So, let alone the reactions between them. We cannot even know about what reactions are there, because we do not know what reactants and are and products are. So, how do we go about kinetic modeling of such reactions? Why do we need kinetic modeling? We need, because we want to design reactors and you cannot always do experimentation at uh 1000 or million ton per annum plant and hope that you get good results. What if you do not entire investment will go to waste. So, we need modeling, we need kinetics to get some reasonable estimate. It may not be accurate; it is not likely to be accurate, because we when we do not know what reactants and products are, how we can expect very accurate reaction network, but as accurate as possible.

So to do that, let us start with lumping all this chemicals that make naptha as single species. And say that my reaction is naptha going to products. What does products are? I do not know. So, that is a simplest kind of lumping that you can think of the entire crude is one chemical species. Naturally, you do not expect modeling or kinetics of this to be reasonably accurate. Then, let us make another simplification. let us say that my naptha consist of aliphatics plus aromatics.

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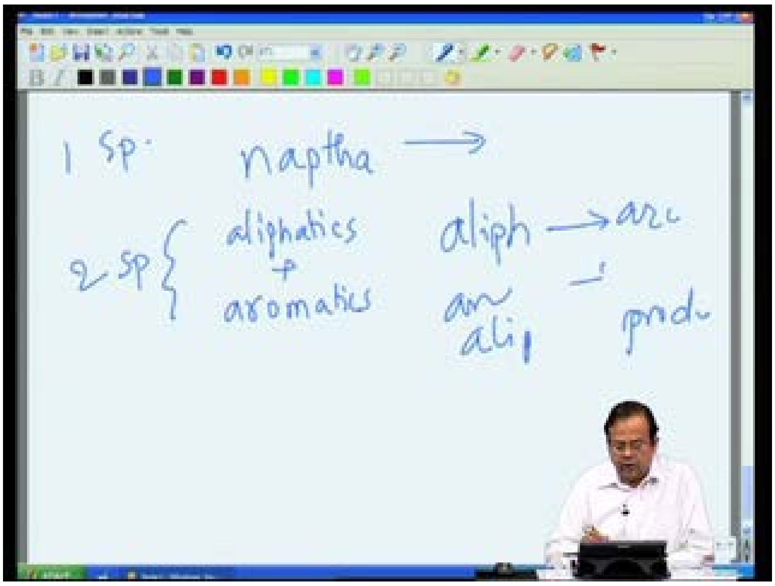

So two species, this is one species, this is two species. And then I am going to say, I am going to model my naptha reaction as something like aliphatic going to aromatic, aromatic going to aliphatic, aliphatic going to products and so on. So some network of reaction. So, this going to something, my intuition tells me that my results are with this approximation, aliphatic plus aromatic are certainly going to be better than assuming naptha as a single species. What about three species?

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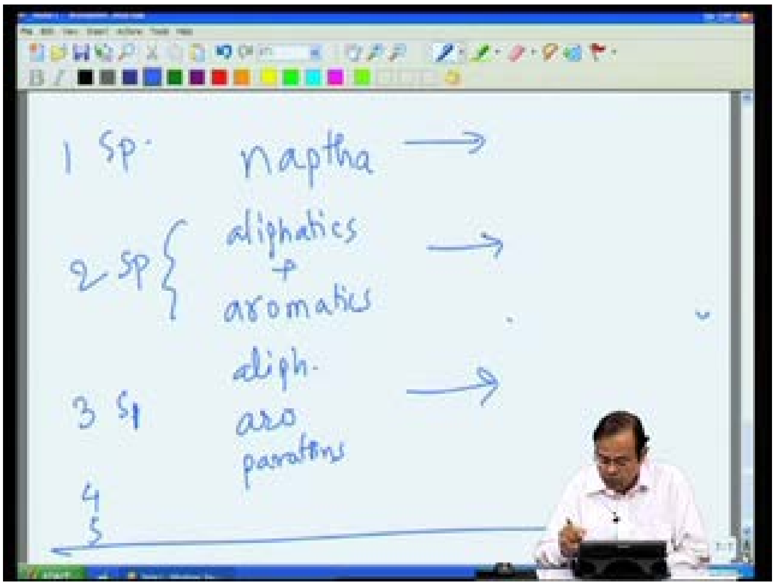

Let’s say aliphatics, aromatics, paraffins. That is arbitrary; this is going to be better. My intuition tells me and intuitions are always intuitions, the probability that they are right is very high. That is why call it intuition. What if I do 4 species, 5 species, 10 species, 100 species, and 10000 species? If I do that, I certainly can expect better and better results. But the problem is, how do I define this 10000 species and so on and so forth. So, I am back to square 1. So, where to stop? Do I go 3, 4, 5, where do I draw line? How do I know, my results are accurate. To know that, let us try to see how lumping analysis will help us arriving at this problem.

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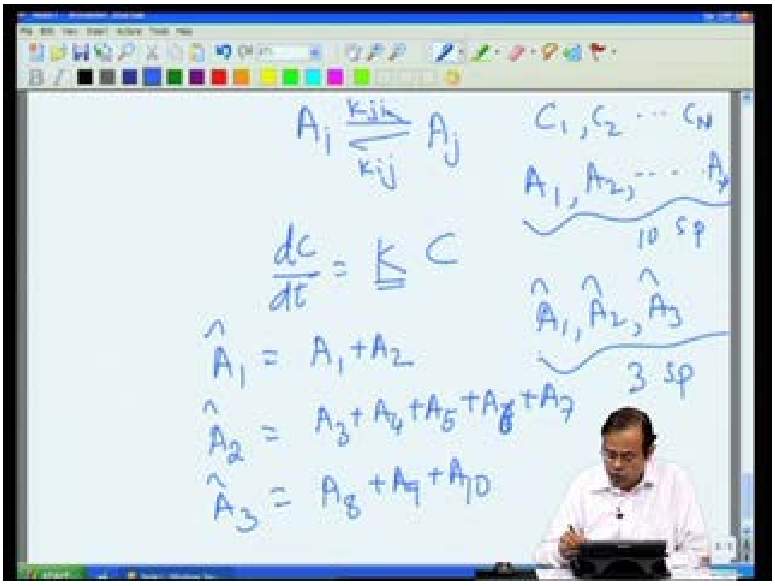

$$A_i \underset{K_{ij}}{\overset{K_{ji}}{\rightleftharpoons}} A_j$$

$$C_1, C_2 \cdots C_N$$

$$\underbrace{A_1, A_2, \cdots A_N}_{10\ sp}$$

$$\frac{dc}{dt} = \underline{\underline{K}}\, C$$

$$\underbrace{\hat{A}_1, \hat{A}_2, \hat{A}_3}_{3\ sp}$$

$$\hat{A}_1 = A_1 + A_2$$

$$\hat{A}_2 = A_3 + A_4 + A_5 + A_6 + A_7$$

$$\hat{A}_3 = A_8 + A_9 + A_{10}$$

So, let us go back to our monomolecular re reversible reaction network. And say that my reactions are A 1 or A i going to A j with kinetic rate constant K j i and K i j. I know that, I can write define the species concentrations as C 1, C 2, C N and write d c d t in the vector form, as strychometric matrix, reaction rate matrix, constant matrix K and C. We just now saw, what is this reaction rate constant matrix. We do not spend time on that. Now, what am I trying to do? So, I have species A 1, A 2, A 3, A n. I am trying to see whether can I lump some of the species into an hypothetical species A 1 hat. So, can I write for example, A 1 hat equal to A 1 plus A 2.

Then suppose, I had 10 species to began with, then can I write A 2 hat as A 3 plus A 4 plus A 5 plus A 7 or A 6 plus A 7. And then A 3 hat as A 8, A 9, A 10. So original ten species, can I lump them to hypothetical species A 1 hat, A 2 hat and A 3 hat lump species. And still say that the dynamics represented for this lump species is fairly a good representation of the original dynamics. What is a connection to naptha problem? Let us say my naptha is N species problem, can I represent naptha as A 3 hypothetical species aliphatic, aromatics and paraffin. So, that we can look at the dynamics of this three species and still say something about cracking of naptha. If you want to say something about original system, by looking at the simplified system, we can at least consider the limiting cases. When will it be exactly same that is when is lumping exact. When does my 10 species are exactly represented by three species. Is it possible at all? Indeed, it is possible and let us try to see how do we achieve that. So let's go back, on one hand, we have A 1, A 2, An species which I want to write as A 1 hat, A 2 hat, A p hat.

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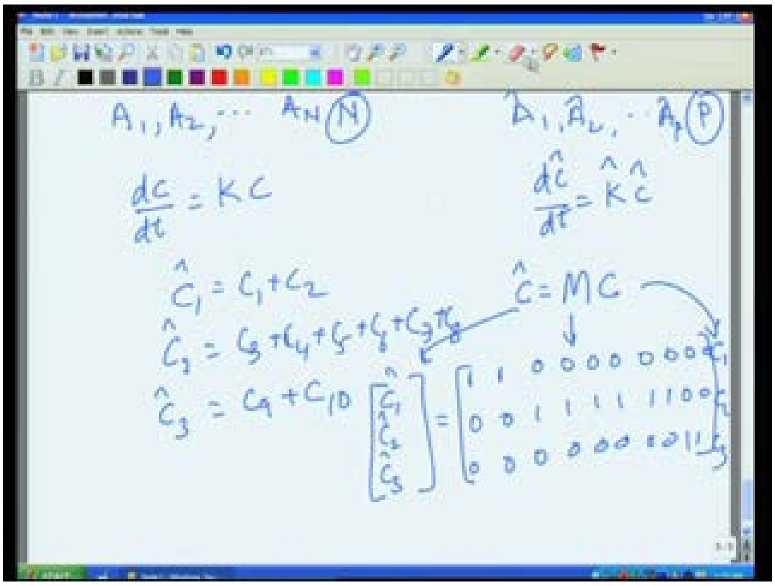

$A_1, A_2, \cdots A_N \; \textcircled{N}$ $\qquad$ $\hat{A}_1, \hat{A}_2, \cdots \hat{A}_p \; \textcircled{P}$

$$\frac{dC}{dt} = KC \qquad \frac{d\hat{C}}{dt} = \hat{K}\hat{C}$$

$$\hat{C}_1 = C_1 + C_2$$

$$\hat{C}_2 = C_3 + C_4 + C_5 + C_6 + C_7 + C_8$$

$$\hat{C}_3 = C_9 + C_{10}$$

$$\hat{C} = MC$$

$$\begin{bmatrix} \hat{C}_1 \\ \hat{C}_2 \\ \hat{C}_3 \end{bmatrix} = \begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 1 & 1 & 1 & 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \\ C_3 \end{bmatrix}$$

So, original N species lumped P species. My original dynamics is d c d t equal to K C, I want my lump species dynamics dc hat dt equal to K hat sorry K hat C hat, and when I am try to see, when this lumping exact. Now, when I wrote something like this, we actually defined a matrix from this lumping. What was that matrix? if I were to write like this, then I also know that I can write C 1 hat as C 1 plus C 2, C 2 hat as C 3 plus C 4 plus C 5 plus C 6 plus C 7 plus C 8, C 3 hat as C 9 plus C 10 5, 6 ,7, 8. So, I want to write C hat equal to M C, M is lumping matrix. If you look at this relationship, what do we have here? We have C 1 hat, C 2 hat, C 3 hat. For this equal to, what is this equal to this is equal to 1 1 0 0 0 0, then 0 0 0 0 0 1 2 3 4 5, where did I 3 4 5 6 7 8. So, one more 0 0 0 0 0, 9 10, 0 0 0 0 1 1 and this multiplied by C 1, C 2, C 3. So, this is my matrix M, this is my vector C, this is my vector C hat.

So, can I define this lumping matrix M. When is that lumping exact? That is original system exactly represented in this particular form. So, let us look at that and try to simplify these two dynamics and connect this two pieces.

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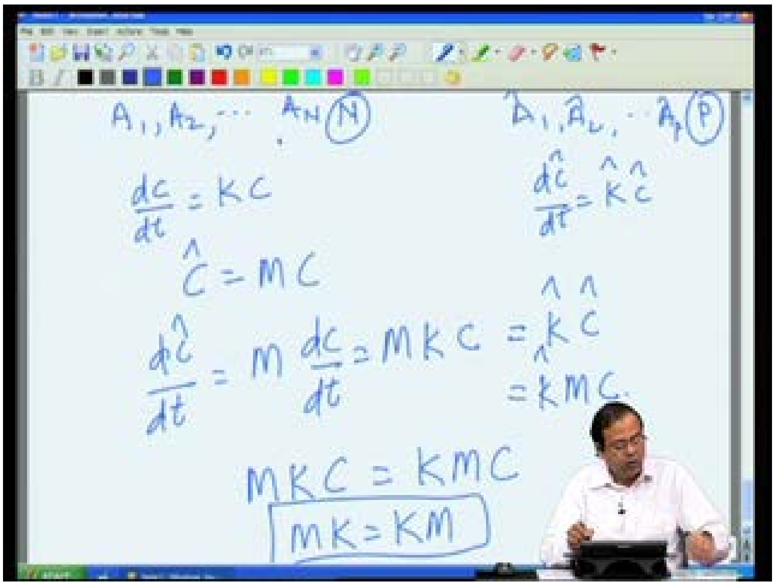

$A_1, A_2, \cdots A_N$ Ⓝ

$\hat{A}_1, \hat{A}_2, \cdots \hat{A}_P$ Ⓟ

$\frac{dc}{dt} = KC$

$\frac{d\hat{c}}{dt} = \hat{K}\hat{C}$

$\hat{C} = MC$

$\frac{d\hat{c}}{dt} = M\frac{dc}{dt} = MKC = \hat{K}\hat{C} = \hat{K}MC$

$MKC = KMC$

$\boxed{MK = KM}$

So let us write down d c d t, which is our K C. d c hat d t is K hat into C. and we are trying to write, C hat equal to M C. So, what is d c hat d t, is M d c d t, which is M into matrix K C which we want as K hat C hat, which we want as K hat M into C. Or in other words, M into K into C is K into M into C. So, what is our lumping condition then? Our lumping condition is M K must be same as K M. this if this condition is satisfies, and then I can represent my original N species system in terms of P species. Let us take an example and things will be more clear.

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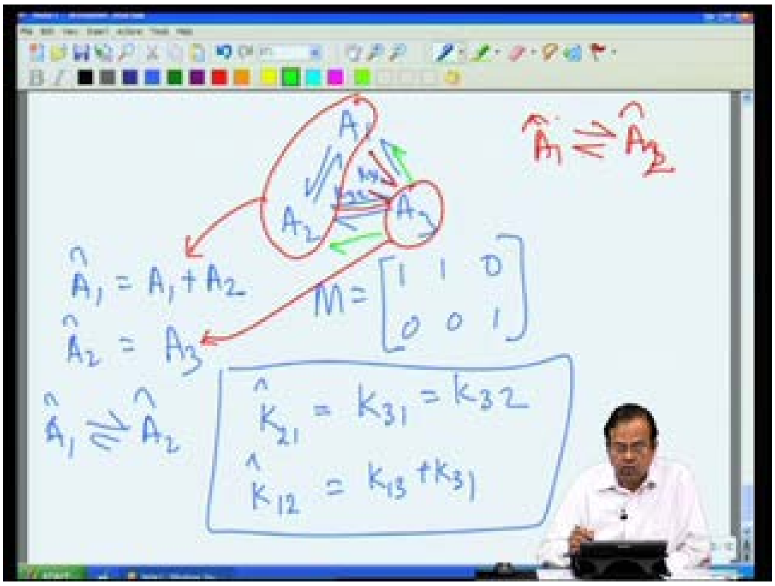

$\hat{A}_1 \rightleftharpoons \hat{A}_2$

$\hat{A}_1 = A_1 + A_2$

$\hat{A}_2 = A_3$

$M = \begin{bmatrix} 1 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

$\hat{A}_1 \rightleftharpoons \hat{A}_2$

$$\boxed{\begin{aligned} \hat{k}_{21} &= k_{31} = k_{32} \\ \hat{k}_{12} &= k_{13} + k_{31} \end{aligned}}$$

So, let us say that we have A 1, this reaction network A 2, A 3 with corresponding reaction network, reaction rate constants. And let us say that I want to define A 1 hat as A 1 plus A 2 and A 2 hat as A 3. So, two species A 1, A 2 lumped into single species and A 3. So, my matrix M here is 1 1 0 0 0 1. And if we use this if we use this if we use this lumping condition, we get the following.

We get my reaction rate constant K 2 hat 1 and what is our reaction now? A 1 hat going to A 2 hat, much simplified reaction compared to this triangular reaction network. We have just two species one reaction. So, if I satisfy this condition, this is my lumping condition that I get and if I satisfy this lumping condition, my results are exact. What is this lumping condition? That is what we are saying is this rate constant K 3 1, the rate at which you get 3 from 1, is same as the rate at which you get 3 from 2, so this particular reaction parts.

That is the rates at which both A 1 and A 2 are giving going to A 3 are same. Then, I can write these reaction network by combining A 1 and A 2 as a hypothetical species, A 1 hat and write these reaction as and this as another species. And write this reaction as A 1 hat going to A 2 hat. Notice here, that it does not matter, how is A 3 at what rate is A 3 split into A 1 or A 2. Then no condition on that it can be anything, but as long as A 2 goes to A 3, as well as A 1 goes to A 3, at the same rate this system and this system are identical they indeed. Let just look at the results of some simulations and convince ourselves that they are indeed exactly identical.

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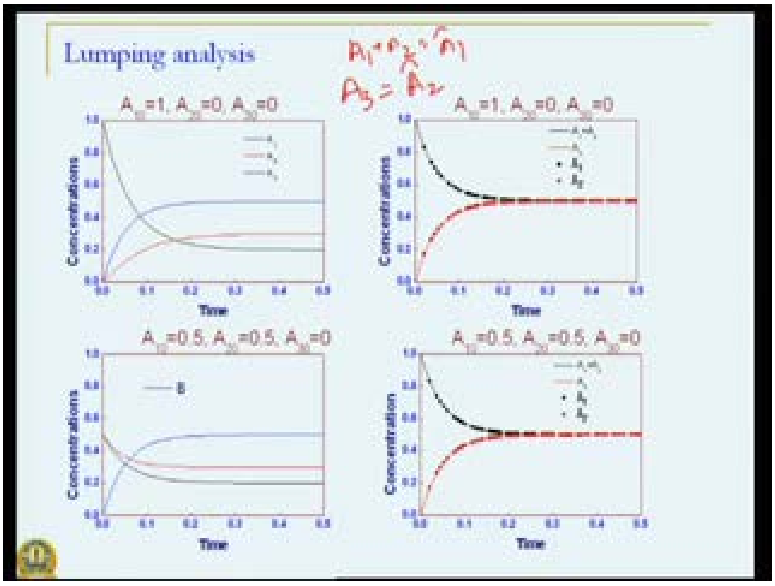

Lumping analysis

$A_1+A_2=\hat{A}_1$

$A_3=\hat{A}_2$

So, what we are looking here, looking at is the following. It is my same example that is provided my, what I am doing is, I am writing A 1 plus A 2 as A 1 hat and A 3 as A 2 hat and let us say that my lumping is exact. So, what does it mean? it means the following. Let us take a case that we had C 1 0 or concentration of one is one, second and third is 0. We have that reaction network. What we have seen here? On the first slide is time and concentrations for 3 species A 1, A 2, A and A 3. Now, I choose to represent A 1 and A 2 as single species. A 1 hat and what we see here is A 1 hat as a function of time and A 2 hat function of a time. A 2 hat is nothing but A 3 and A 1 plus A 2 is 1. So, if our lumping is exact, then what do we get? that A 1 A 2 put together, individual concentrations of A 1 and A 2 may be different, but their addition is same.

So, if you look at this 0.5 0.5 1 1 0 1. So, as long as this condition is satisfied, we get. So, here if you start with different initial condition in original species, we have different behavior compare to this. But look at the combined species A 1 hat and A 2 hat. This two are exactly identical this two are exactly identical, because we have satisfied the lumping condition. So, my three species original could be lumped into two species. My infinitely large number of species in naptha, if the lumping condition is satisfied exactly can be lumped into fewer species 5 species, 6 species, and 10 species.

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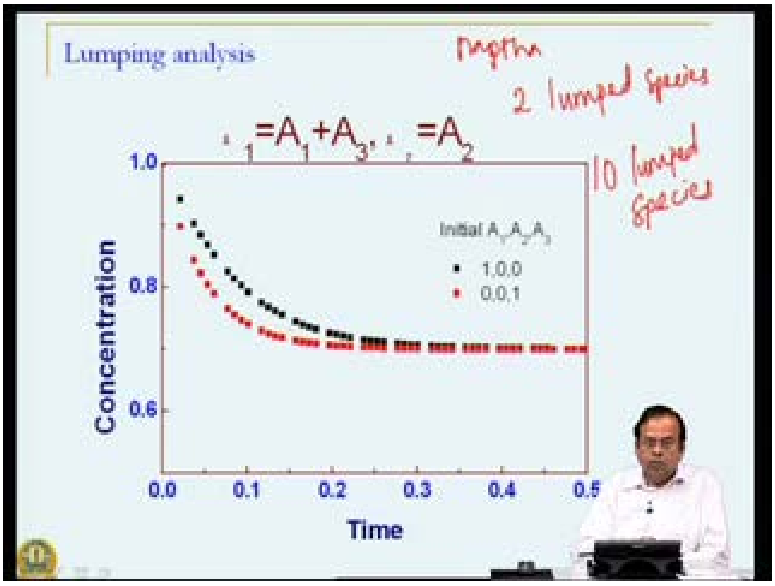

Lumping analysis

naptha

2 lumped species

10 lumped species

In fact, mobil ten species model is most common. Now, how do I know that what I am doing is correct? for a given set of rate constant, if my lumping is not exact and if I for example, lump A 1 and A 3 as one lumped species A 1 hat and another lump species A 2 hat. And if I start with different initial concentrations of A 1 and A 3. A 1 and A 3 is still added one, but my lumping condition is not satisfied. I get two different responses, unlike here, whatever may be the initial distribution, and if my lumping condition is precise, I get the same results. if the lumping condition is not satisfied then I get two different results.

Experimentally, how do I know whether my lumping condition is lumping condition is correct? Experimentally, this is how it is found out? So, let us say that I have my naptha. I lumped it as two lump species. if my lumping is not correct and traced the concentration of this lumped species by different sources of naptha. Different source of naptha will give you different distribution of your components. So if I do that, if I get the dynamics which is different for this lumped species then my lumping is not exact. Turns out, that when you do this 10 lumped species, your lumping is more or less exact. You cannot be as exact as in a hypothetical example, because naptha is a real example, but as close as we can get to the real example.

So, with this we will close our discussion for this session. And in the next class, we will start looking at gas solid catalytic as well as non catalytic reactions or in short heterogeneous reactions. What we have done in, what we can say, the first part of this course is we looked at different types of complex reactions and the kinetics resulting from them. Some ways of analyzing this kinetics, assumptions or approaches for example, quasi steady state approach, and quasi equilibrium approach.

And then several example such as chain reactions, polymerization reactions, kinetics of catalytic reactions. And then today, lumped or monomolecular reaction network. What we are going to do in the coming sessions now, is bring in transport phenomenon into the picture, because we are really dealing in a majority of the cases with heterogeneous reactions. So, we will bring in transport phenomenon and put it together with the kinetics and see what kind of results we get. Thank you.