Advanced Process Dynamics

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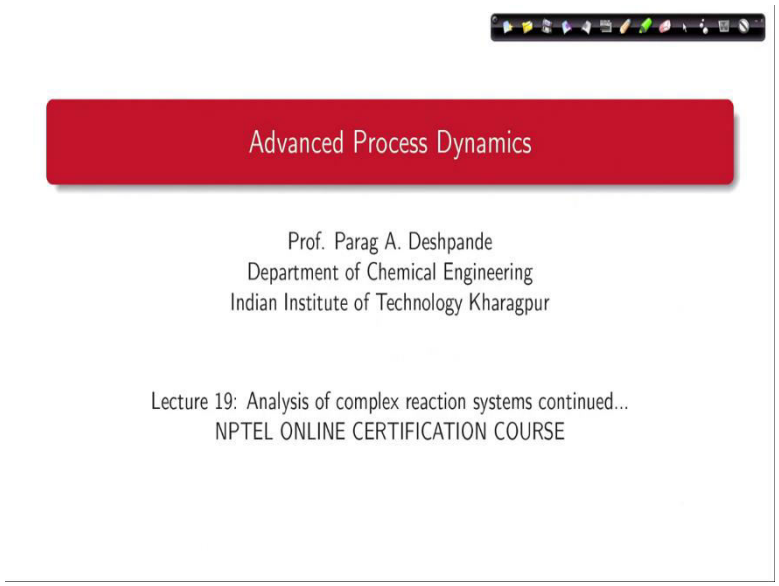
Lecture No 19

Analysis of complex reaction systems continued



A complex reaction system

Consider a system of elementary reaction in series of the type $A \rightarrow B \rightarrow C$. The kinetics of the reaction system is given by the following equations.

$$\frac{dC_A}{dt} = -k_1 C_A \tag{1}$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B \tag{2}$$

$$\frac{dC_C}{dt} = k_2 C_B \tag{3}$$

The reactions are carried out in a batch reactor with the respective initial concentrations as C_{A0}, C_{B0} and C_{C0}, respectively. Analyse the effects of various parameters associated with the system on the time evolution of the concentrations of the chemical species.

A complex reaction system

$$\frac{dC_A}{dt} = -k_1 C_A$$
$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B$$
$$\frac{dC_C}{dt} = k_2 C_B$$

$$\frac{d}{dt}\begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix} = \begin{bmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & 0 \end{bmatrix}\begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix}$$

$$\frac{d\underline{x}}{dt} = \underline{\underline{A}}\,\underline{x} = 0$$

$C_{Ae} = 0$
$C_{Be} = 0$
$C_{Ce} = ?$

$$\begin{bmatrix} C_{Ae} \\ C_{Be} \\ C_{Ce} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ a \end{bmatrix}$$

null space of $\underline{\underline{A}}$

$$\underline{\underline{A}} = \begin{bmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & 0 \end{bmatrix}$$

$-k_1 C_A = 0 \Rightarrow C_{Ae} = 0$

$k_1 C_A - k_2 C_B = 0 \Rightarrow C_{Be} = 0$

$k_2 C_B = 0 \Rightarrow C_{Be} = 0$

$A \longrightarrow B \longrightarrow C$

A complex reaction system

$$\frac{d}{dt}\begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix} = \begin{bmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & 0 \end{bmatrix}\begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix}$$

$\lambda_1 = 0$; $\underline{v}_1 = [0 \quad 0 \quad L]^T$

$\lambda_2 = -k_1$; $\underline{v}_2 = \left[\frac{k_1 - k_2}{k_2} \quad -\frac{k_1}{k_2} \quad L\right]^T$

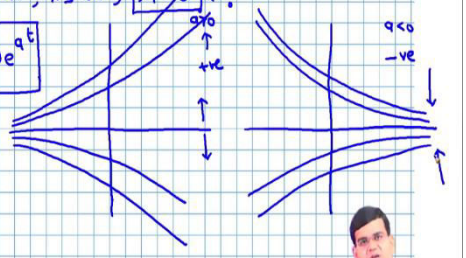
$\lambda_3 = -k_2$; $\underline{v}_3 = [0 \quad -L \quad L]^T$

$k_1 > 0$, $k_2 > 0 \Rightarrow \lambda_2 < 0$, $\lambda_3 < 0$, $\lambda_1 = 0$ ← ?

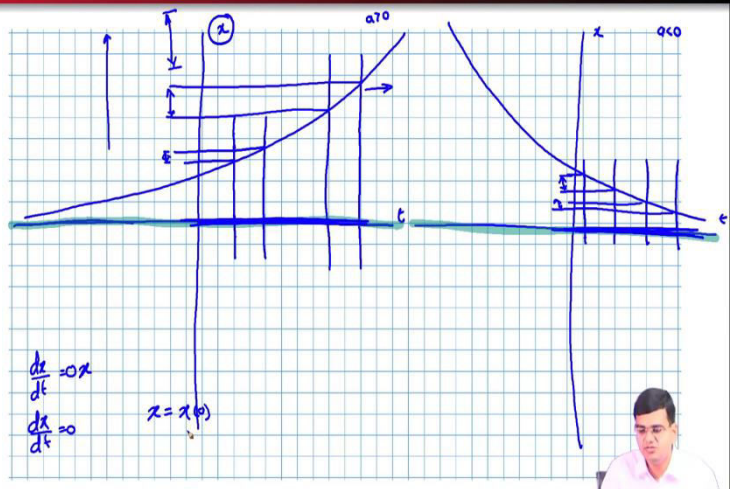
$$\frac{dx}{dt} = qx \Rightarrow \boxed{x(t) = x(0)e^{qt}}$$

eigenvalue of $\hat{L} = \frac{d}{dt}$

$x \rightarrow$ eigenfunction



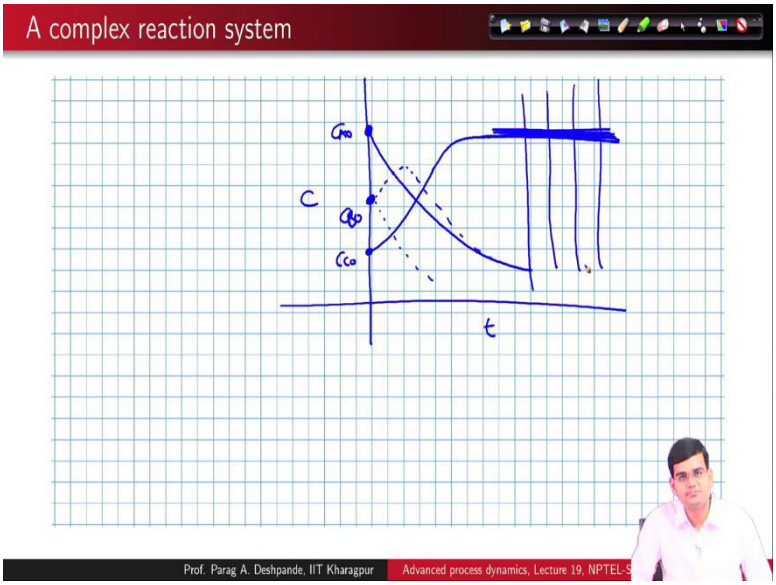
A complex reaction system

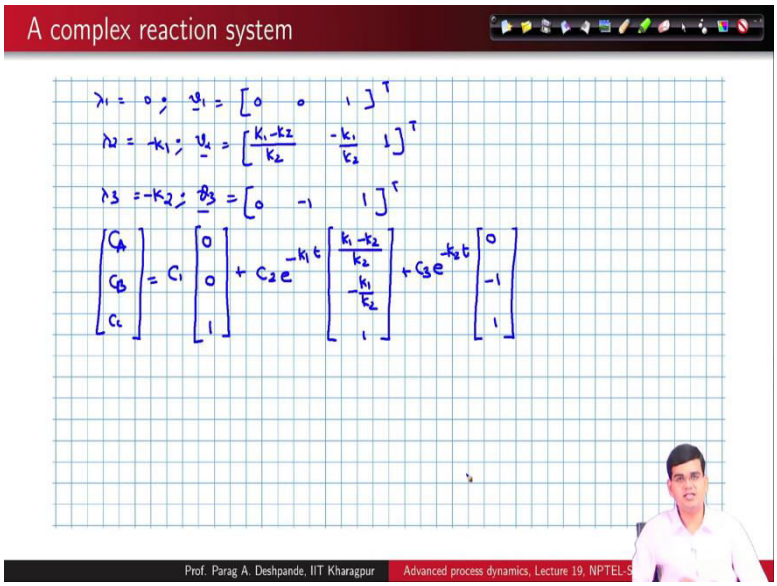


$\frac{dx}{dt} = 0x$

$\frac{dx}{dt} = 0$

$x = x(0)$





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Hello, we are currently analysing a complex reaction network system and we will try to now understand this using the dynamical approach.

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So, what we have in front of us is a system of reactions of the type A going to B going to C and these three equations, we are trying to solve these equations using the matrix approach which we have developed in this course.

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So, let me write it down see

$$\frac{dC_A}{dt} = -k_1 C_A$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B$$

$$\frac{dC_C}{dt} = k_2 C_B$$

As always, we will convert this system of equations to a matrix equation and what we would get is

$$\frac{d}{dt}\begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix} = \begin{bmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & 0 \end{bmatrix}\begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix}$$

Now, we would like to analyse the system by looking at this matrix equation which is nothing but the equation of the form $\frac{d\underline{X}}{dt} = \underline{\underline{A}}\underline{X}$

So, whenever we have a system like this the first thing which we would like to do is to know the equilibrium solutions. So, what are the equilibrium solutions for this kind of system, equilibrium solutions could be obtained by setting this to 0. In other words, we saw in the previous lecture that the equilibrium solutions would be the members of the null space of A, null space of A. So, what is A in the present case? A = $\begin{bmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & 0 \end{bmatrix}$. Ideally what I would have done is I would have row reduced this matrix A and then I would have row reduced matrix to the original equation form and I would have determined the members of the null space.

But in the present case, I already have a matrix which cannot be further reduced in any meaningful manner to give me anything. So, therefore, what I would do is I would write the equations back. So, I would have minus, so from each from the third row let me go step by step from the third row, I would get $k_2C_B = 0$, which means C_{Be} is 0. I have determined one of the components, then from second row, I will get $k_1C_A - k_2C_B = 0$ from where since C_{Be} is 0, I get C_{Ae} is 0. And my first role now is redundant minus k_1C_A is equal to 0, which means I get C_{Ae} as 0.

So, all I know is that C_{Ae} is 0, C_{Be} is 0 even after solving for the null space, I could not have any idea about C_{Ce}. So, C_{Ae} is 0, C_{Be} is 0, but what about C_{Ce}, we have no idea or in other words, in fact, there is no constraint which could be put on Ce. So, C_{Ae}, C_{Be}, C_{Ce} is equal to 0 and there is no constraint which can be put or a no value which can be associated with CCer at this point of time or in other words, you will have to specify certain other things to know the exact value of CC equilibrium.

Let us see, why does that happen? What is the physical meaning behind this particular observation? So, what happens in this reaction system is that you have A which goes to B which goes to C. So, A is your first reactant C is your ultimate product, C never reacts with any species to give you any other species. So, when I say, that, rather when I asked this question that what would what is going to be the ultimate fate of my system as t tends to infinity, I know that A is a reactive species in my system, which is going to react to give me B.

So, what is going to happen at some point of time, all of my A is going to get reacted and therefore, the concentration is going to become 0 and that is precisely the meaning of CAe being equal to 0. Now, what is the fate of B, B react to give you C, so, again although A is reacting to give B which means to you, in principle, the concentration of B can rise, but as t tends to infinity, when you know that all of the A has been consumed, so, that no more B can be available in the system, B will eventually start reducing in concentration because of its reaction following B going to C and what will happen when B when there is no way but the only pathways that B reacts to give C. Well, the concentration of B is going to become 0.

So, this is the meaning of CB equilibrium being 0. But now, the case is interesting with C because C is the ultimate product of your reaction system, it is not getting consumed, but following the mass balance this is a system where all the stoichiometric coefficients are unity, which means one mole of A will react to give one mole of B, one mole of B will react give one mole of C So, there is a perfect one to one match between the number of moles which get reacted and the number of moles which get produced.

So, therefore, if I have an initial quantity $C_{A0} + C_{B0} + C_{C0}$ then this entire number will remain constant at any given moment of time, which means this will be the case even at s time t tends to infinity. So, therefore, C_{Ce} can attain any value subject to this constraint, subject to

the initial amount of A that you have fed to the system, initial amount of B that you are first fed to the system and the initial amount of C which you have fed to the system.

But we have not specified how much of A, B and C have been provided at least from this set of equations alone just these set of equations or the equivalent matrix equation, there is no information which goes in this to tell how much of the total number of moles are present at any given moment that is going to be the ultimate value which would be governing C_{Ce} as time t tends to infinity.

So, therefore, from this analysis by looking at the equilibrium solution, all you can say is that C_{Ae} is 0, C_{Be} is 0 as time t tends to infinity, the system will definitely move such that the convert that the concentrations of A and B are 0 and subject to the mole conservation the equilibrium concentration of C_C would be that value it cannot come from this equation.

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What other information can I get from this system? So, let us see, I have

$$\frac{d}{dt}\begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix} = \begin{bmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & 0 \end{bmatrix}\begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix}$$

This is my equation and whenever I have this autonomous equation, what I do is I solve for the Eigen values and Eigen vectors of A which will ultimately give me the solutions.

So, now, what I have in front of me the Eigen values and Eigen vectors, so, I have λ_1 this is equal to 0, the corresponding Eigen vector is $[0\ 0\ 1]^T$, I have λ_2 this is equal to $-k_1$ the Eigen vector is $[(k_1 - k_2)/k_2\ -k_1/k_2\ 1]^T$ and my final Eigen vector Eigen value is, V_3 would be $[0\ -1\ 1]^T$.

So, now, I can have a look into these Eigen values and Eigen vectors and comment upon the solution I can determine the final expression for this for the solution and in fact I will do that, but before I go into those details, I can have a simple look into the Eigen values and Eigen vectors and comment upon the nature or at least the nature qualitative nature of the system.

So, what did we establish in previous lectures? We basically considered two cases in one case you had a real Eigen values and in the other case you had imaginary Eigen values. In fact, there was a third case where you had complex Eigen values as well. So, let us consider three

cases. So, when the Eigen values were purely imaginary, then you see an oscillatory behaviour in the system.

When the Eigen values are complex numbers such that the real part is greater than 0, then you have an oscillatory behaviour with amplitudes arising in time and conversely, when you have the Eigen value, which is a complex number with a real part less than 0, then you have oscillatory behaviour with magnitude amplitudes reducing with time decreasing with time.

But what about the case of real Eigen values? In case of real Eigen values, we again saw that whenever you have all the Eigen values, which are positive, the system is divergent. So, the system is unstable. You have the solutions which involve exponential with positive powers. And therefore, the system will blow up to infinity. In case where all of the Eigen values are negative, you have a stable system because you will have the equation solutions of the form e to the power minus λ t. So, therefore, as time t tends to infinity, your solutions would decay to 0.

And then you also had stable saddle solutions where some of the Eigen values were positive, some of them were negative. So, what is the case in the current case, now, we have a situation we have we know that the rate constants are always positive. So, I know that $k_1 > 0$ and $k_2 > 0$, which means, that $\lambda_2 < 0$ and $\lambda_3 < 0$, which means, it is a good sign that your reactive system is in fact a stable system as far as only these two Eigen values are concerned the problem is that I have an Eigen value which is 0 and we have in fact not come across such a situation.

So, what is the physical interpretation of λ_1 being 0, what does it tell me? What does it tell me about my system? So, to answer this question, let us first ask ourselves the physical meaning of an Eigen value and the associated importance with infact the importance associated with its signal with each sign.

So, I said that I have if I have the equation of the form $\frac{dx}{dt} = ax$ then the solution is going to be $x(t) = x(0)\, e^{at}$ this is the general solution but what is a, a here is the Eigen value of the operator $\frac{d}{dt}$ and x is the Eigen function all the solutions which satisfy this equation would be the Eigen functions.

So, now, what is the nature of this solution x is equal to $x(t) = x(0)\ e^{at}$. It has two distinct behaviours and we saw the bifurcation in the system for $a > 0$ that behaviour is this and for $a < 0$ the behaviour is this, which means that positive Eigen value diverges the system and negative Eigen value converges the system to one particular value and in fact we saw this in the case of cooling of a sphere example as well.

Now, the question is when I say that the positive Eigen value diverges my system and the negative Eigen value converges my system to a particular value what exactly do I mean by that?

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So, let us quickly redraw this phase portraits t x t x and let me draw just one phase line for the sake of clarity. So, this is the phase line this is $a > 0$ and this is the phase line when $a < 0$. So, what I would do to understand the importance of Eigen value is that I would draw slices of time. So, I draw this first slice and at a later time I draw another slice and I drop these, these corresponding values here and here.

Now we will see what has happened here, this distance and this distance as time t is increasing this distance along my x is increasing with time. So, therefore, if I take a third slice, which is farther here along time this would be even larger. So, a lot along the x direction x means, the dynamical variable my, for the same interval of time for the same interval of time my value of x is the interval is increasing, what about the same analysis for this case, let me do two slices one slice here and the other slice here the slices in time are of equal duration by the way.

So, this is one you can see, this is the distance and this is another one and you will realize that this slice on the dynamical axis has shrunk now. So, if I go farther in time, it would tend to 0, but it would tend to 0, it will not be exactly equal to 0. So, now, I will learn from here that I have the first case when Eigen value is positive, as I go in time the system expands when my Eigen values are negative as I go in time the system shrinks.

So, what would be an intermediate behaviour an intermediate behaviour is that neither expansion takes place, nor does shrinking take place, which means constant behaviour. And that is precisely the meaning of 0 Eigen value. Because if I have this $\frac{dx}{dt} = 0x$, which means what the Eigen value is 0, this is simply what? $\frac{dx}{dt} = 0$, which means this horizontal line this

horizontal line and if I do the same slice analysis along this horizontal line, all I am going to do is I am going to get the same, I am just going to remain there, I am going to get the same value of x which is equal to 0.

So, x will remain as x_0 does not matter which slice of time are you taking, where whether it is it has, which is close to 0 or close to infinity, the corresponding dynamical variable is going to always going to have the same value which means there is a kind of constants in the system.

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So, now, what is the corresponding meaning for our system that when you see that I have the Eigen value one of the Eigen values is 0, then I should imagine that I would have I would somewhere during the dynamics of my system and counter a situation where nothing changes with time not asymptotically. See asymptotically, nothing will change with time for a stable system. That is always true.

But here, you are not asymptotically going to 0 you reach a condition and then system flattens out. Nothing changes with time and what would that condition be? Well, that would be the condition where I can draw this time, this is concentration. So, you may have C_{A0} from our reaction engineering analysis, we know that this is going to go down you have some value of C_{B0} from reaction engineering analysis, I know that it may come down like this or it may go up and again come like this. And finally, I may as well have a situ finally, for C_{C0}.

For this, I know one thing for sure that you are always going to have the concentrations increasing with time, which means that the concentration would increase but when C_A has been consumed in its totality, when C has been consumed in his totality, there will be not be any reaction. So, therefore, whatever C present in your reaction mixture in your best reactor will just we will remain constant. So, therefore, this constant nature of your system and you can do slicing here is indicated by the Eigen value which is 0.

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So, let us write down the Eigen values λ_1 was 0, V_1 was $[0\ 0\ 1]^T$, λ_2 was $-k_1$, V_2 was $[(k_1-k_2)/k_2\ -k_1 / k_2\ 1]^T$ and $\lambda_3 = -k_2$ and V_3 is equal to $[0\ -1\ 1]^T$. So, following our method of analysing autonomous systems, I can write

$$\begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix} = C_1 \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} + C_2 e^{-k_1 t} \begin{bmatrix} \frac{k_1 - k_2}{k_2} \\ \frac{-k_1}{k_2} \\ 1 \end{bmatrix} + C_3\, e^{-k_2 t} \begin{bmatrix} 0 \\ -1 \\ 1 \end{bmatrix}$$

So, when we did this analysis in the previous lecture using the usual method will sequentially solve for C_A, C_B, C_C now, what you have is, you have in front of you a solution where you solve for the dynamical vector and the components of the vector are C_A, C_B, C_C. So, what you will do is you will expand you will take the constants outside from outside to the inside to the individual vectors you will add them you are going to get a vector again on the right hand side, you will equate the first component of the vector with C_A, you will equate the second component of the vector with C_B and you will equate the third component of the vector with C_C.

We will do this in detail in the next lecture. But what we learned today from the dynamical analysis is that, while it is always possible to solve the equations sequentially to get the time evolution what you actually can also do is write the system of equations as a matrix equation. Look into the Eigen values and Eigen vectors of the matrix and solve for the null space of the matrix to get the equilibrium solution.

When we solve for the null space, we found that the equilibrium solution for C_A was 0. So, when you substitute t tends to infinity in the expressions which we got in the previous lecture, you would in fact, find out that your C_A as t tends to infinity would be 0. Similarly, in case of C_B, you again had the solutions which were in terms of exponential of negative power of ki times t and ki is our positive.

So, again or a period of time as time t tends to infinity, you would have the decaying effect and the concentration of B would go to 0. If you remember the expression that we got for C_C, it involves $C_{A0} + C_{B0} + C_{C0}$ plus the effects of A and B which were exponential decaying in nature. So, therefore, this is the genesis of the observation of not in fact non observation of any entry for the equilibrium solution of C, because, unless you know what is this the initial moles which have been supplied, there is no information which this matrix can give you.

Further by the analysis from the analysis of the Eigen values, we found that when the two Eigen values were negative of k_1 and negative of k_2 and since, k_1 and k_2 are always positive, they are the rate constants for the system you expected some stability in the system. So,

therefore, if you introduce some amount of C_A, C_B, C_C to the system, your concentration in fact cannot go to infinity, but one of the Eigen values when it was 0, and we established the importance of 0 Eigen value, which means that the system would attain some sort of a constancy after a certain period of time and that was nothing but the constant concentration of C_C.

We will solve the equation explicitly using the eigenvalues and eigenvectors in the next lecture. Thank you. a