Advanced Process Dynamics
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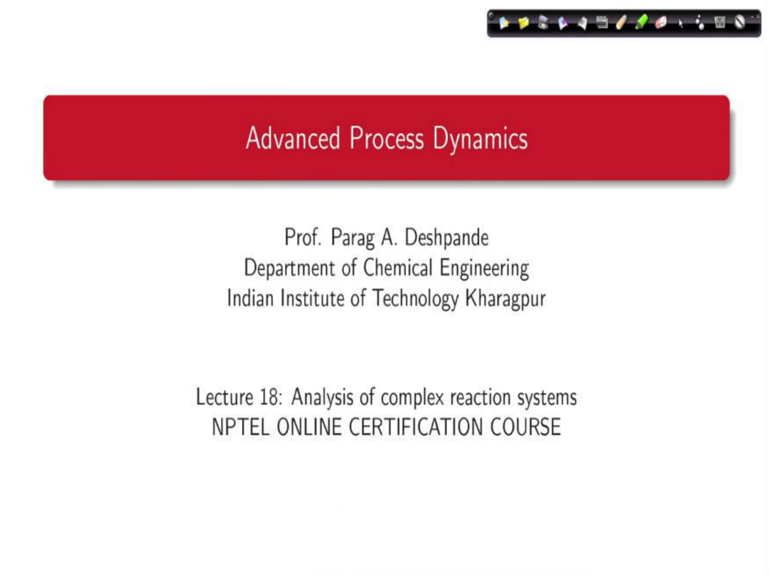
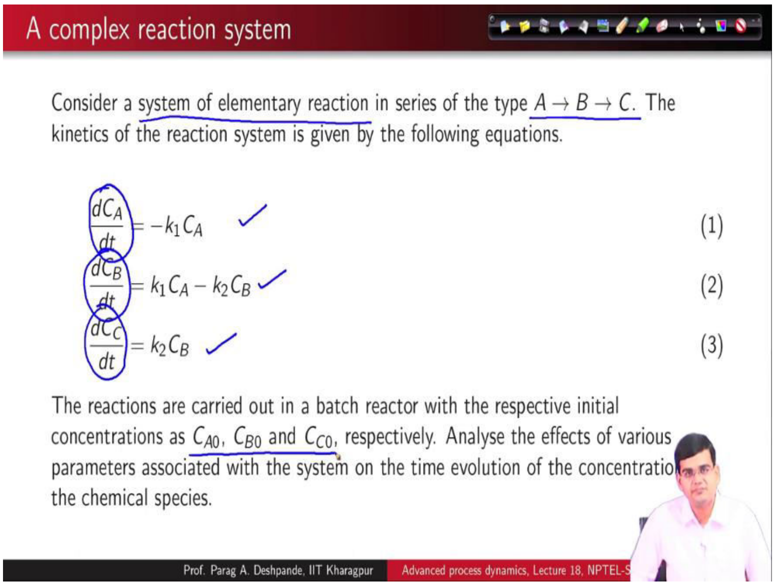
Lecture No 18
Analysis of complex reaction systems





A complex reaction system

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$$\frac{dC_A}{dt} = -k_1 C_A \qquad -(1)$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B \qquad -(2)$$

$$\frac{dC_C}{dt} = k_2 C_B \qquad -(3)$$

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

$$\Rightarrow C_A = C_{A0} e^{-k_1 t}$$

A complex reaction system

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B \; ; \; C_A = C_{A0} e^{-k_1 t}$$

$$\Rightarrow \frac{dC_B}{dt} + k_2 C_B = k_1 C_{A0} e^{-k_1 t}$$

$$\frac{dx}{dt} + f(x) = g(t)$$

$$e^{k_2 t} \frac{dC_B}{dt} + k_2 e^{k_2 t} C_B = k_1 C_{A0} e^{-k_1 t} e^{k_2 t}$$

$$\Rightarrow \frac{d}{dt}\left(e^{k_2 t} C_B\right) = k_1 C_{A0} e^{(k_2 - k_1) t}$$

$$\Rightarrow e^{k_2 t} C_B = \left(\frac{k_1}{k_2 - k_1}\right) C_{A0} e^{(k_2 - k_1) t} + C_1$$

At $t = 0$, $C_B = C_{B0}$

$$C_{B0} = \left(\frac{k_1}{k_2 - k_1}\right) C_{A0} + C_1$$

$$\Rightarrow C_1 = C_{B0} - \left(\frac{k_1}{k_2 - k_1}\right) C_{A0}$$

$$\Rightarrow e^{k_2 t} C_B = \left(\frac{k_1}{k_2 - k_1}\right) C_{A0} e^{(k_2 - k_1) t} + C_{B0} - \left(\frac{k_1}{k_2 - k_1}\right) C_{A0}$$

$$\Rightarrow e^{k_2 t} C_B = \left(\frac{k_1}{k_2 - k_1}\right) C_{A0} \left[e^{(k_2 - k_1) t} - 1 \right] + C_{B0}$$

$$\Rightarrow C_B = \left(\frac{k_1}{k_2 - k_1}\right) C_{A0} e^{-k_2 t} \left(e^{k_2 t - k_1 t} - 1 \right) + e^{-k_2 t} C_{B0}$$

$$\Rightarrow C_B = \left(\frac{k_1}{k_2 - k_1}\right) C_{A0} \left(e^{-k_1 t} - e^{-k_2 t} \right) + C_{B0} e^{-k_2 t}$$

A complex reaction system

$$\frac{dC_C}{dt} = k_2 C_B \; ; \; C_B = \left(\frac{k_1}{k_2 - k_1}\right) C_{A0} \left(e^{-k_1 t} - e^{-k_2 t} \right) + C_{B0} e^{-k_2 t}$$

$$\frac{dC_C}{dt} = \left(\frac{k_2 k_1}{k_2 - k_1}\right) C_{A0} \left(e^{-k_1 t} - e^{-k_2 t} \right) + k_2 C_{B0} e^{-k_2 t}$$

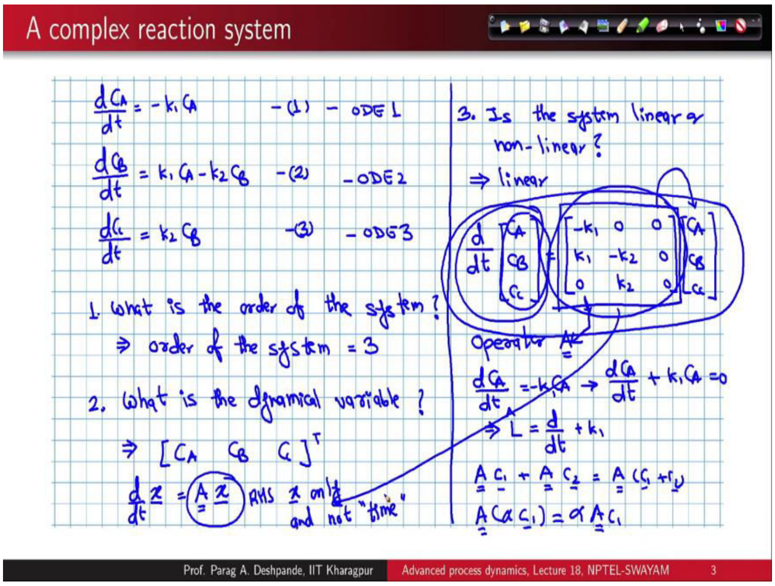
$$\Rightarrow C_C = \left(\frac{k_1 k_2}{k_2 - k_1}\right) C_{A0} \left(\frac{-1}{k_1}\right) e^{-k_1 t} - \left(\frac{k_1 k_2}{k_2 - k_1}\right) C_{A0} \left(-\frac{1}{k_2}\right) e^{-k_2 t} - C_{B0} e^{-k_2 t} + C_2$$

$$\Rightarrow C_C = \left(\frac{-k_2}{k_2 - k_1}\right) C_{A0} e^{-k_1 t} + \left(\frac{k_1}{k_2 - k_1}\right) C_{A0} e^{-k_2 t} - C_{B0} e^{-k_2 t} + C_2$$

At $t = 0$, $C_C = C_{C0}$

$$\Rightarrow C_{C0} = \frac{-k_2 C_{A0}}{k_2 - k_1} + \frac{k_1 C_{A0}}{k_2 - k_1} - C_{B0} + C_2 \Rightarrow C_2 = C_{A0} + C_{B0} + C_{C0}$$

$$\Rightarrow C_C = \left(\frac{-k_2}{k_2 - k_1}\right) C_{A0} e^{-k_1 t} + \left(\frac{k_1}{k_2 - k_1}\right) C_{A0} e^{-k_2 t} - C_{B0} e^{-k_2 t} + C_{A0} + C_{B0} + C_{C0}$$



Welcome back, we are studying Dynamical systems. As a matter mentioned in one of the previous lectures, that you would hardly find any system around us, which is inherently non dynamical in nature which means, which do not change with time. Under certain circumstances, you can find the systems which do not change with time can be made to change with time. And conversely, we can always have certain systems which change with time to behave statically or non-dynamically.

So, the transport processes which we study in chemical engineering, what we study in reaction engineering are all the systems which are inherently dynamical in nature. But, our traditional way of analysing such systems in transport processes or reaction engineering is a little different. But now that we know that when can looked upon any system which undergoes change with time as a dynamical system and we have a framework to understand and analyse the systems.

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Let us look into one problem from chemical reaction engineering, where we will take the example of a complex reaction system and I will compare and contrast how we analyse the systems traditionally in reaction engineering and how dynamical analysis can provide certain new perspectives to the analysis of such systems. So, we have today the analysis of complex reaction systems.

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So, the problem is in front of you, we consider a system of elementary reactions in series of the type A going to B going to C, so the speciality of this system is that it is a system of elementary reactions in series, there are three reactions A going to B going to C and since the reactions are elementary, we just follow the law of mass action or mass action kinetics and give

$$\frac{dC_A}{dt} = -k_1 C_A \quad \ldots(1)$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B \quad \ldots(2)$$

$$\frac{dC_C}{dt} = k_2 C_B \quad \ldots(3)$$

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So, it is not very difficult to see that our system in fact is a dynamical system because we have the change in concentration of species A with time change in concentration of species B with time and change in concentration of species C with time. The reactions are carried out in a batch reactor and the batch reactor is initially supplied with concentration C_{A0}, C_{B0} and C_{C0} of C of C_A, C_B and of A, B and C respectively. Now, what we need to do is we need to analyse this dynamical system and determine the effect of various parameters on the evolution of concentrations in the batch reactor.

So, let us first look into traditionally how would we address such a problem. So, I have the elementary reaction given as A going to B going to C. The three equations that I have $\frac{dC_A}{dt}$ is equal to, so for the first reaction, the rate constant is k_1 for the second reaction rate constant is k_2 the $\frac{dC_c}{dt}$ would be $-k_1 C_A$, $\frac{dC_B}{dt}$ would be $k_1C_A - k_2C_B$ and $\frac{dC_c}{dt}$ is equal to plus k_2C_B.

So, I can refer to these three equations as equation 1, equation 2 and equation 3. And to determine the time evolution of a C_A, C_B and C_C I need to solve these three dynamical equations. So, let us do this so what I see in equation one is that it involves only the concentration of A. So, what I can write here is $\frac{dC_A}{dt} = -k_1 C_A$, we have been looking into equations of this form all along this particular course, this is nothing but a autonomous first order system.

So, k_1 is a constant, then I can simply write this solution as $C_A = C_{A0}\, e^{-k_1 t}$, I hope you would appreciate that this is going to be the final solution procedure is not very difficult. Now, we would need to look into the solution of equation number 2.

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So, equation two is $\frac{dC_B}{dt} = k_1 C_A - k_2 C_B$ and we have already determined $C_A = C_{A0}\ e^{-k_1 t}$. So, if this is the case then I can write the equation 2 as the $\frac{dC_B}{dt} + k_2 C_B$ is equal to k_1 and in place of C_A I will write $C_{A0}\, e^{-k_1 t}$ so, this is an equation of the form $\frac{dx}{dt} + f(x) = g(t)$ and what I would do is I would use the integrating factor method to solve this problem.

So, my integrating factor in this case would be $e^{k_2 t}$ so, I will multiply $e^{k_2 t}$ on both sides. So, what I get is $e^{k_2 t}$ multiplied by $\frac{dC_B}{dt}$ + $e^{k_2 t}$ C_B. I also have k_2 here is equal to k_1 C_{A0}, $e^{-k_1 t}$ $e^{k_2 t}$.

So, this can be written as d by dt of $e^{k_2 t}$ multiplied by C_B which would be equal to k_1 C_{A0}, $e^{(k_2 - k_1)t}$. So, now I can integrate this as this $e^{k_2 t}$ C_B is equal to integration of the right hand side with respect to t it would be $\frac{k_1}{k_2 - k_1}$ C_{A0}, $e^{(k_2 - k_1)t}$ plus an integration constant and let us call this integration constant C_1.

Now, how do I determine the integration constant C_1. At t = 0 my initial concentration of B is C_{B0}. So, therefore, I can write C_{B0} is equal to $\frac{k_1}{k_2 - k_1}$ C_{A0} + C_1 which gives me C_1 as C_{B0} - $\frac{k_1}{k_2 - k_1}$ C_{A0}. So, I substitute this expression for C_1 where I would get $e^{k_2 t}$ C_B = $\frac{k_1}{k_2 - k_1}$ C_{A0} $e^{(k_2 - k_1)t}$ + C_{B0} - $\frac{k_1}{k_2 - k_1}$ C_{A0}.

So, this would be equal to C_B and in fact here I can continue using $e^{k_2 t}$. So, $e^{k_2 t}$ CB would be equal to what, I will take $\frac{k_1}{k_2 - k_1}$ C_{A0} a constant so, this will be $e^{(k_2 - k_1)t}$-1+ C_{B0} from where I get $C_B = \frac{k_1}{k_2 - k_1}$ C_{A0} $e^{-k_2 t - k_1 t}$ - 1 + $e^{-k_2 t}$ C_{B0} from where I can finally get this expression C_B is equal to $\frac{k_1}{k_2 - k_1}$ C_{A0}.

Now, can we simplify this expression this would be $e^{-k_1 t}$ - $e^{-k_2 t}$ + C_{B0}, $e^{-k_2 t}$. So, the time evolution of the concentration of B is given by the equation which is shown at the end C_B =

$\frac{k_1}{k_2-k_1}$ C_{A0} $(e^{-k_1t}$ - $e^{-k_2t})$ + C_{B0} e^{-k_2t}. So, we have solved for the evolution of concentration of A which was a simple exponential decay, C_A = C_{A0} e^{-k_1t}.

We also solve for the evolution of concentration of B which is given by these this little complex expression. But this basically tells you the dependence of evolution of B on the concentration of A which is the first part and on the concentration of B which is the second part. In a similar manner, we can solve for the evolution of C_C.

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So, C, we had the equation the $\frac{dC_C}{dt} = k_2C_B$ and we need to substitute for the expression for C_B. So, the expression for C_B that we got previously was, let me write down the expression C_B = $\frac{k_1}{k_2-k_1}$ C_{A0} $(e^{-k_1t}$ - $e^{-k_2t})$ + C_{B0} e^{-k_2t}.

Now, I will need to substitute this expression in my dynamical variable. So, I get $\frac{dC_C}{dt}$ = $k_2\frac{k_1}{k_2-k_1}$ $C_{A0}(e^{-k_1t}$ - $e^{-k_2t})$ + k_2C_{B0} e^{-k_2t}. So, before integration let Us quickly check if we have written this correctly yes. So, I can do this integration as C_C = k1 $\frac{k_2}{k_2-k_1}$ C_{A0} multiplied by $1/k_1$ minus of it $(e^{-k_1t}$ - $\frac{k_1k_2}{k_2-k_1}$ C_{A0} - 1 / k_2, e^{-k_2t} - C_{B0} e^{-k_2t} and this expression can be further simplified as C_C is equal to now, I can write this as minus of $\frac{k_2}{k_2-k_1}$ C_{A0} e^{-k_1t} + k_2 upon, in fact this this would be $\frac{k_1}{k_2-k_1}$ C_{A0} e^{-k_2t} $-$ C_{B0} e^{-k_2t} and we forgot one thing there would be one integration constant C_2 here would be an integration constant C_2.

So, this is the expression and what we can now do is use the initial condition. So, at t is equal to 0; C_C = C_{C0}, this is the initial condition which was given to us. So, therefore, I can write this as C_{C0} = - k_2 C_{A0} $\frac{1}{k_2-k_1}$ + C_{A0} $\frac{k_1}{k_2-k_1}$ - C_B + C_2 from where I can write C_2 as it should be C_{B0}, C_{A0} + C_{B0} + C_{C0}. So, now I have got the value of the expression for the integration constant from where I can write C_C as

$$C_C = \frac{k_2}{k_2-k_1} C_{A0}e^{-k_1t} + \frac{k_1}{k_2-k_1} C_{A0}e^{-k_2t} + C_{A0} + C_{B0} + C_{C0}$$

So, this was the expression the overall expression for the variation of concentration of C with time. Now, what we can see here is that we followed the conventional method that we started with individual expressions, we looked into the solution technique for the individual expressions sequentially, we solved the problem before solve for C_A, then we solve for C_B, then we solve for C_C. And we got the time evolution for the concentrations of C_A, C_B and C_C in the batch reactor.

Now, instead of following this approach, in which we consider the equations individually, we can do something like what we did in case of our dynamical analysis where we considered the matrix solution. Now, let us first ask ourselves this question that what is the order of the system?

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So, let us write the x of the dynamical equations, the dynamical equations will see the

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

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

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

These were the three equations which were known to me. So, the first question in front of me is that what is the order of the system? Remember, we are not asking about the order of the reaction, that is a different concept, if we consider this system of complex reaction kinetics as a dynamical system, then what is the order of the system?

So, we have three ordinary differential equations. So, therefore, the order of the system is 3. I have ODE1, I have ODE2, I have ODE 3. So, now the second question is what is the dynamical variable in the system? So, the dynamical variable is the variable whose time rate of change is provided by the model equation. So, therefore, for the current case our dynamical variable is a vector.

So, I have the dynamical variable as $[C_A, C_B, C_C]^T$. This is going to be my dynamical variable what else can I ask about this particular system is the system linear or nonlinear, is the system linear or nonlinear? It is not very difficult to answer this question because we have already solved this problem and this system is in fact a linear system. However, if you want to systematically prove this, then what you need to do is you need to identify the operator.

So, I can write this equation in terms of a matrix equation, which is

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

So, in the present case what is the operator? The operator is the matrix A. How do you know that the operator is a matrix A. Well, if you simply have $\frac{dC_A}{dt} = kC_A$ and in this case $-k_1C_A$ then you write the equation as $\frac{dC_A}{dt} + k_1C_A = 0$ from where you can easily identify the operator as $\frac{dC_A}{dt} + k_1$ in fact.

So, in the present case you will identify this as the matrix. So, matrix is operating upon the vector, the matrix is operating upon the vector to give you and to give you this left hand side $\frac{d}{dt}$. So, therefore, the operator in the present case is the matrix which you have multiplied here and it will not be very difficult to show that this particular matrix in fact follows a property like matrix $\underline{\underline{A}}$ operating on first solution vector C_1 plus matrix B matrix $\underline{\underline{A}}$ operating on second vector C_2 would be equal to matrix $\underline{\underline{A}}$ operating on C_1 plus C_2 and matrix $\underline{\underline{A}}$ operating on some constant α times 1 solution vector would be equal to α times A operating on C_1.

So, therefore, in this particular case you have the system which is linear. The final question is the system autonomous? It is not very difficult to see that in fact, the system is autonomous because you have this governing equation. And this governing equation can be written in the form $\frac{d}{dt}$ of the vector $\underline{x}$, x being $[C_A, C_B, C_C]$ is equal to $\underline{\underline{A}}$ matrix. $\underline{\underline{A}}$ matrix being in this matrix times the vector x again and you see on the right hand side you have $\underline{x}$ only and not time, you do not have explicit time on the right hand side.

So therefore, what we can say is that you have a system in which you have describe the variation of concentrations with time using individual equations. You could solve those individual equations using the usual method, in fact you may open the book by Fogler or by Levenspiel and you will find that you in fact have the same solution strategy described in those books which we adopted today. In the first analysis, not the dynamical analysis which we will take up now in the next lecture, but the first analysis and you will also find that you will get the same answer or the same expression for the solution expect that in all those books that initial concentrations for B and C which means C_{B0} and C_{C0} were assumed as 0.

So, if you substitute C_{B0} and C_{C0} in the expression we got today you would actually get the same expression which has been reported in Fogler or Levenspiel for that reason. So, and then if we convert this equation system of equation to a matrix equation the way we do the dynamical analysis then have a third order system which is linear and which is autonomous.

So let’s analyse in detail the solution methodology and as well as dynamical behaviour in the lectures to come. Thank you.