Advanced Process Dynamics
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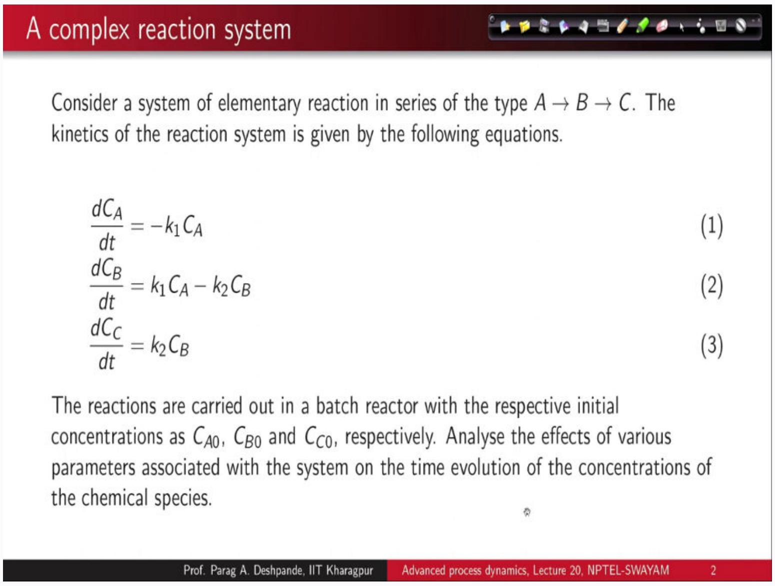
Lecture 20
Analysis of Complex Reactions Systems Continued



A complex reaction system

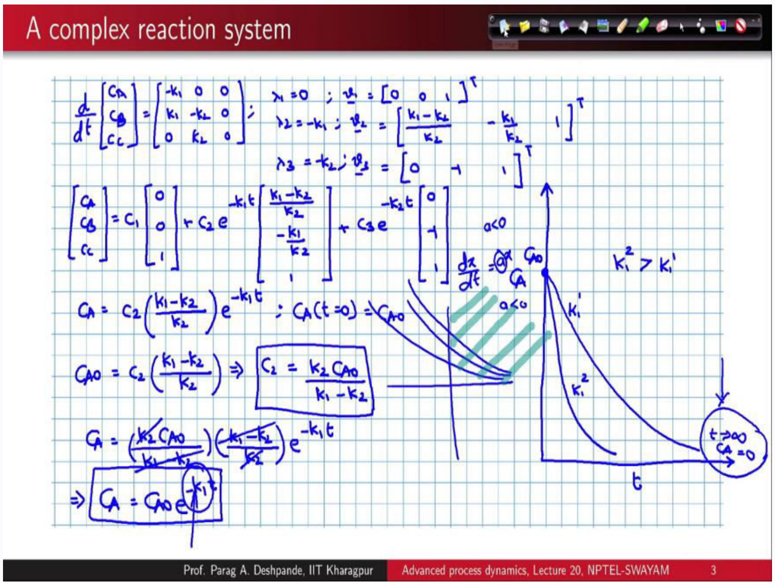
Consider a system of elementary reaction in series of the type $A \rightarrow B \rightarrow C$. The kinetics of the reaction system is given by the following equations.

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

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

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

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

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

$\lambda_1 = 0$; $\underline{v}_1 = [0 \quad 0 \quad 1]^T$

$\lambda_2 = -k_1$; $\underline{v}_2 = \left[\frac{k_1 - k_2}{k_2} \quad -\frac{k_1}{k_2} \quad 1\right]^T$

$\lambda_3 = -k_2$; $\underline{v}_3 = [0 \quad -1 \quad 1]^T$

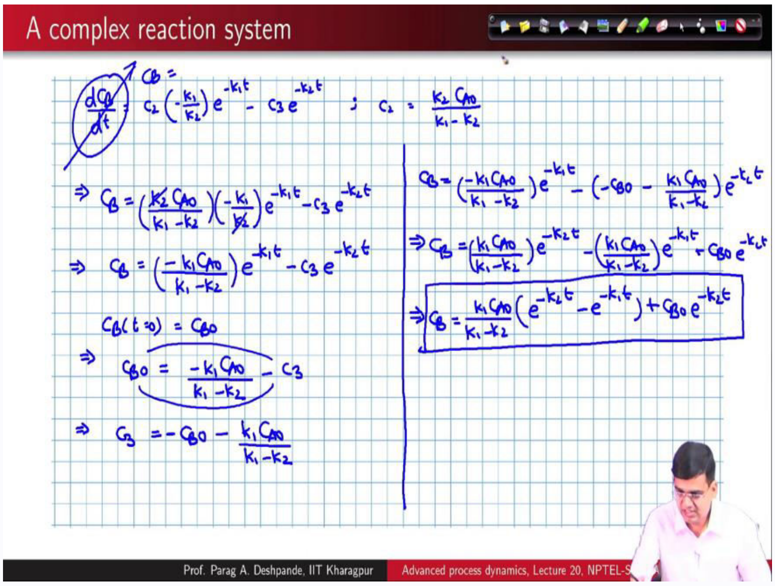
$$\begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix} = C_1 \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} + C_2 e^{-k_1 t} \begin{bmatrix} \frac{k_1 - k_2}{k_2} \\ -\frac{k_1}{k_2} \\ 1 \end{bmatrix} + C_3 e^{-k_2 t} \begin{bmatrix} 0 \\ -1 \\ 1 \end{bmatrix}$$

$C_A = C_2\left(\frac{k_1 - k_2}{k_2}\right) e^{-k_1 t}$; $C_A(t=0) = C_{A0}$

$C_{A0} = C_2\left(\frac{k_1 - k_2}{k_2}\right) \Rightarrow \boxed{C_2 = \frac{k_2 C_{A0}}{k_1 - k_2}}$

$C_A = \left(\frac{\cancel{k_2} C_{A0}}{\cancel{k_1 - k_2}}\right)\left(\frac{\cancel{k_1 - k_2}}{\cancel{k_2}}\right) e^{-k_1 t}$

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



A complex reaction system

$\cancel{\frac{dC_B}{dt}}\ C_B = c_2\left(-\frac{k_1}{k_2}\right)e^{-k_1 t} - c_3 e^{-k_2 t}$; $c_2 = \frac{k_2 C_{A0}}{k_1 - k_2}$

$\Rightarrow C_B = \left(\frac{\cancel{k_2} C_{A0}}{k_1 - k_2}\right)\left(-\frac{k_1}{\cancel{k_2}}\right)e^{-k_1 t} - c_3 e^{-k_2 t}$

$\Rightarrow C_B = \left(\frac{-k_1 C_{A0}}{k_1 - k_2}\right)e^{-k_1 t} - c_3 e^{-k_2 t}$

$C_B(t=0) = C_{B0}$

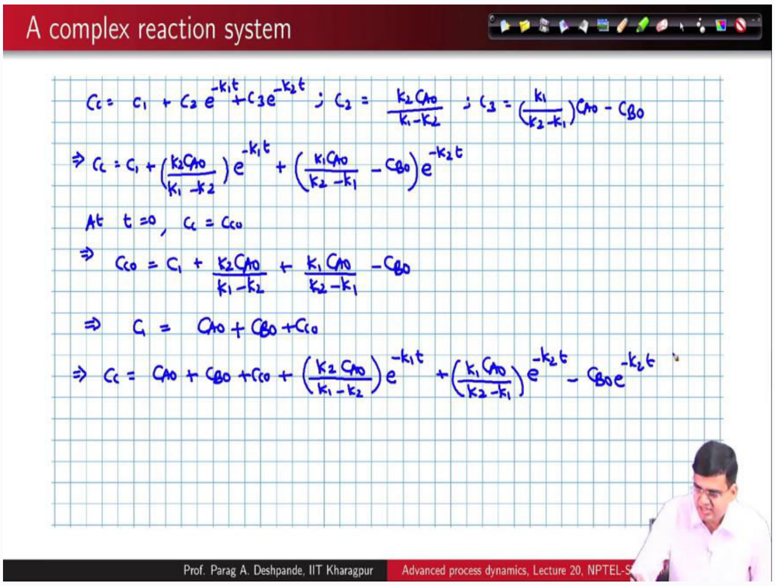
$\Rightarrow C_{B0} = \frac{-k_1 C_{A0}}{k_1 - k_2} - c_3$

$\Rightarrow c_3 = -C_{B0} - \frac{k_1 C_{A0}}{k_1 - k_2}$

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

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

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



A complex reaction system

$C_C = c_1 + c_2 e^{-k_1 t} + c_3 e^{-k_2 t}$; $c_2 = \frac{k_2 C_{A0}}{k_1 - k_2}$; $c_3 = \left(\frac{k_1}{k_2 - k_1}\right)C_{A0} - C_{B0}$

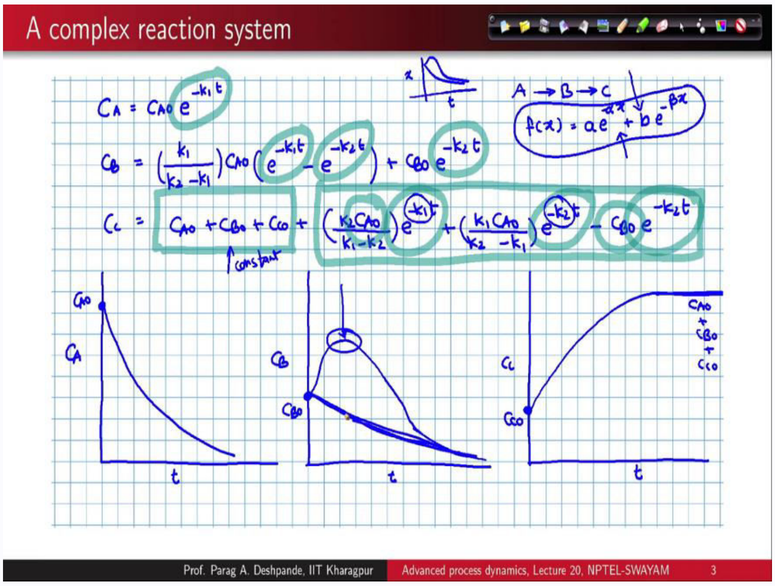
$\Rightarrow C_C = c_1 + \left(\frac{k_2 C_{A0}}{k_1 - k_2}\right)e^{-k_1 t} + \left(\frac{k_1 C_{A0}}{k_2 - k_1} - C_{B0}\right)e^{-k_2 t}$

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

$\Rightarrow C_{C0} = c_1 + \frac{k_2 C_{A0}}{k_1 - k_2} + \frac{k_1 C_{A0}}{k_2 - k_1} - C_{B0}$

$\Rightarrow c_1 = C_{A0} + C_{B0} + C_{C0}$

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



A complex reaction system

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

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

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

constant

$A \to B \to C$

$f(x) = ae^{\alpha x} + be^{-\beta x}$

So, let us continue our discussion on the complex reaction kinetics.

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We have reactive system of the type A going to B going to C.

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And we were solving this particular problem using the matrix method, let me write down the matrix equation as

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

The Eigen values and Eigen vectors for like this, $\lambda_1 = 0$, v1 was $[0\ 0\ 1]^T$. $\lambda_2 = -k_1$, $v_2 = [\frac{k_1-k_2}{k_2}\ \frac{-k_1}{k_2}\ 1]^T$. $\lambda_3 = -k_2$, the Eigen vector was $[0\ -1\ 1]^T$.

So, we saw that the solution to this system is like this,

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

Okay. So, I will now solve for each individual parts, so, let me solve for C_A, C_A would become C_1 x 0 is 0 so, I would have simply $C_2\,(\frac{k_1-k_2}{k_2})e^{-k_1 t}$.

So, now, I need to know the multiplicative constant C_2 and I know that C_A at time t is equal to 0 is C_{A0}. So, I can write this as C_{A0} is equal to $C_2\,(\frac{k_1-k_2}{k_2})$, from where I get $C_2 = k_2 C_{A0} / (k_1 - k_2)$. I can substitute this value of C_2, C_2 will be required over and again in the later sections as well.

So, let me highlight this so, I can then write $C_A = C_{A0}$, C_2 is k_2, $k_2 C_{A0} / (k_1 - k_2)$ multiplied by $(\frac{k_1-k_2}{k_2})e^{-k_1 t}$. From where k_2 gets cancelled out, $(k_1 - k_2)$ get cancelled out. So, I get $C_{A0}e^{-k_1 t}$. This is the solution for the evolution of concentration of A. Did we get the same expression using the previous analysis?

In fact, we did. I would encourage you to go back and check and ensure that we got the same expression but what is the meaning of this evolution that $C_A = C_{A0}e^{-k_1 t}$. We have come across this lot many times let me quickly draw C_A and time. So, if I start with an initial value C_{A0} then exponential decay simply means that as time t tends to infinity C_A would be 0 and in fact C_{Ae} was 0, we saw in the previous lecture.

What is the significance of the parameter k_1 so, let me draw 2 curves. This is k_1^1 and then this is k_1^2 two different rate constants. So, what is the inequality which I can write? I can write that $k_1^2 > k_1^1$. So, the faster the rate constant the faster would be the decay or the reduction in the concentration of A. But irrespective of the magnitude of k, I know that they are going to be always positive.

So, irrespective of their magnitude, I always know that as t tends to infinity, C_A would always go to 0 and this is very similar to the phase portraits that we drew for $\frac{dx}{dt}$; $a < 0$. I already have a negative sign here. See, I have a negative sign here. So, this is the case where $a < 0$, I know that these are all the phase lines which I can draw.

So, I am basically focusing on this portion of my phase portrait and I know that irrespective of the magnitude the fate of the system is that my concentration would tend to 0. So, then what can I write about C_B?

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So, let me do one thing, let me write down the expression for C_B from the previous matrix solution. C_B should be equal to $C_2 \frac{-k_1}{k_2}$ $e^{-k_1 t}$ - C_3 $e^{-k_2 t}$, where C_2 was already determined as k_2 C_{A0} / (k_1 - k_2). So, what I can do is, I can, also, there is one problem this is not C_{B0}, this is CB itself.

Please make this correction this is the expression for C_B. So, now I have this. So, I can write C_B as k_2 C_{A0} / (k_1 - k_2) - $\frac{k_1}{k_2}$ $e^{-k_1 t}$ - C_3 $e^{-k_2 t}$, from where I can write C_B = - k_1 C_{A0} / (k_1 - k_2), this these two would cancel out -k_1 C_A, (k_1 - k_2) $e^{-k_1 t}$ - C_3 $e^{-k_2 t}$. I need to determine C_3 and that can be determined by the initial conditions C_B at t = 0 is equal to C_{B0}. So, I can write C_{B0} = -k_1 C_{A0} / (k_1 - k_2) - C_3. So, C_3 is C_{B0} - k_1 C_{A0} / (k_1 - k_2), let us check whether this is correct C_3 goes on this side plus C_3, this will become plus C_3, C_B will come on this side. So, this will become minus this should be - C_3.

So, therefore, what I can write here is

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

So, this is the expression for C_B and you must in fact have gotten the exact same expression in the previous lectures as well for C_B. So, whether we solve this problem sequentially or using the matrix method you should get the same answer.

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Finally, for C_C from our matrix C_C was what? C_C was given as was given like this. So, I have this $C_1 + C_2\, e^{-k_1 t} + C_3\, e^{-k_2 t}$, where C_2 what was the expression for C_2? C_2 was $k_2\, C_{A0} / (k_1 - k_2)$ and the expression for C_3 which we got was this $\frac{k_1}{k_2-k_1} C_{A0} - C_{B0}$. So let me substitute all of these values to get the expression for C_C, $C_C = C_1 + C_2$ is $k_2\, C_{A0} / (k_1 - k_2)\, e^{-k_1 t} + C_3$ is $k_1\, C_{A0} / (k_2 - k_1) - C_{B0}\, e^{-k_2 t}$.

The only thing which is unknown here is the constant C_1. So, now at $t = 0$, $C_C = C_{C0}$. So, I can write $C_{C0} = C_1 + k_2\, C_{A0} / (k_1 - k_2) + k_1\, C_{A0} / (k_2 - k_1) - C_{B0}$ from where I can write C_1 as, this would be $C_{A0} - C_{B0}$ will become plus $C_{B0} + C_{C0}$, this is the expression for C_1.

So, therefore, finally, I get

$$C_C = C_{A0} + C_{B0} + C_{C0} + \frac{k_2}{k_1-k_2} C_{A0}\, e^{-k_1 t} + \frac{k_1}{k_2-k_1}\; e^{-k_2 t} - C_{B0}\, e^{-k_2 t}$$

and again this is the same expression that you would have gotten in the previous lectures. So, now, when we go ahead and analyse the effect of individual terms and analyse the dynamics.

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Let me first write down the final expressions for a quick summary. So, I have

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

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

$$C_C = C_{A0} + C_{B0} + C_{C0} + \frac{k_2}{k_1-k_2} C_{A0}\, e^{-k_1 t} + \frac{k_1}{k_2-k_1}\; e^{-k_2 t} - C_{B0}\, e^{-k_2 t}$$

So, the reason I wrote all of these final expressions in front of you is that now you can have a look into these expressions and try to understand the dynamics and try to establish the correspondence between the observations of Eigen values of the system and the deductions which you made just by looking at the eigenvalues and by explicit expressions in time which you have in front of you.

So, what about the behaviour of C_A. So, we have seen this, $C_A = C_{A0}e^{-k_1 t}$. We drew this and we know the explicit behaviour see C_A versus time, if this is the C_{A0} initial concentration, then your behaviour would look like this and we also saw the effect of the value of k_1. The behaviour of C_B is a little tricky would postpone it for a little while let us see what happens to C_C. C_C, let us see what happens to C_C.

In case of C_C, you have three terms, the last three terms which involve exponential of negative term again exponential of negative term and again exponential of negative term. This means that as t tends to infinity the effect of all of these terms would vanish, you would not expect any of these terms to be present, which means this entire section would have any meaning only during the initial stages and at later stages.

The only thing which would remain relevant would be this and C_{A0}, C_{B0} and C_{C0} are the initial concentrations which means that these are individually constants. So, this entire thing is a constant. So, if I start with an initial concentration C_{C0} then what I would expect is that as t tends to infinity, I reach this constant behaviour this would be $C_{A0} + C_{B0} + C_{C0}$ and that is precisely what we also guessed by looking at the Eigen value which was 0.

So, then I may intuitively join this like this. We can have the exact expression punched Desmos and we can look into this expression, but this is what I would expect the system to be anyway because I have the system going from minus A going to B going to see to C, since C is the ultimate product, you will always expect C to be present in the final reaction mixture because it is not reacting.

Now, what about B, B has these exponential terms 1, 2, 3. So, like this exponential term which was present in the first case of C_A. The exponential terms are present in the case of C_B as well. And in fact, in all the terms which are present as the solution for C_B exponential decays present so, therefore, the long-term behaviour of C_B would also be like this, but remember this is a long-term behaviour and I start with some C_B, I start with some C_{B0}.

Now, I have three exponentials involving 2 powers, k_1 and k_2. So now I have a system which looks like this, $f(x) = ae^{-\alpha x} + be^{-\beta x}$. I have the expression of this form in fact that is a third expression as well, but even if you consider these two then this is the expression which conforms to this particular form.

So, therefore, we saw in the previous lectures that while this confirms to, this is very similar to what you call as the over damped response of a second order system, this particular expression there is there was no guarantee that you do not have local extrema in your system which means that for that particular case you could have a solution which looked like this at x versus t is the exact same expression that you used previously for spring mass system.

But you could as well have an expression like this solution like this, which means that depending upon the initial condition, one thing which we often forget while doing this analysis and especially, this is one thing which is very often missed in the textbooks of reaction engineering is that we always do the analysis in terms of comparison of k_1 and k_2 what will happen when $k_1 > k_2$ what will happen when $k_2 > k_1$.

And depending upon that we draw either a situation like this or we draw situation like this and we say that for 1 case given greater than k_2, you will have one behaviour for the other case $k_2 > k_1$ you will have the other behaviour, but what we miss is that k_1 and k_2 are not the only parameters in the system. The other two parameters which we also have in the system are in fact C_{A0} and C_{B0} which means that whether you will get a local-extrema.

This is the local extrema and local maxima or you will not get will get a pure exponential decay would depend not only on the rate constants k_1 and k_2, but they would also depend upon the initial concentrations of C_{A0} and C_{B0}. Now, why very often we miss this during the conventional analysis. We missed this because the textbooks often assume that C_B is 0 and C_C is 0.

So, you have a constant parameter C_A and you C_{A0} on your system and therefore, you always compare k_1 versus k_2 but that is not the complete picture. The complete picture is that whether or not you get a local-extrema which means the concentration of C_B goes up and then starts coming down or it comes down directly right from the beginning depends upon C_{A0}, C_{B0}, k_1 and k_2.

And why does this happen? This happens because the rate of reaction is a function of not only the rate constants, which is generally impressed upon in the textbooks that the rate of reaction is a function of rate constant. So, you compare k_1 and k_2 it is also a function of concentration. So, when you have C_{A0} and C_{B0} in your picture, you need to consider C_{A0} and C_{B0} as well in your analysis of the parameters.

So, by looking at this particular example, you would have realised that we have so many dynamical systems around us in in practice and we can make use of the analysis of dynamical systems that we developed during the past four weeks for a better analysis of all of the systems. Till the last week until this lecture in fact, we have been considering linear systems. From the next week onwards, we will switch gears and start analysing nonlinear systems. Till then, goodbye.