Aspects of Biochemical Engineering
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Lecture – 15
Kinetics of Homogenous Chemical Reactions – V

The homogeneous chemical reaction both the theoretical part also some numerical problems I try to solve it and today the last part of this particular lecture that is on Kinetics of Homogeneous Chemical Reactions.

Now if you look at the in the previous lecture what we try to cover initially we discuss about the rate equations for the irreversible reaction then rate equation for reversible reaction then rate equations for the chain reactions. And then we try to find out how we can find out the time required for getting the maximum intermediate product concentration intermediate that product concentration in chain reaction or then we try to solve some kind of numerical problems try to calculate the activation energy of a chemical reaction.

Then try to analyze some the how the time of conversion related time of reaction how it is related with the percentage conversion of the substrate and today what I am going to do that I am going to discuss the typical type another special type of reactions what we call second order reaction because up till now mostly we covered the first order reaction.

So, we try to find out that how the second order reaction the problems of the second order reaction can be solved and also I have problems on the chain reaction and our 2 different approach how we can use for solving a chain reaction.

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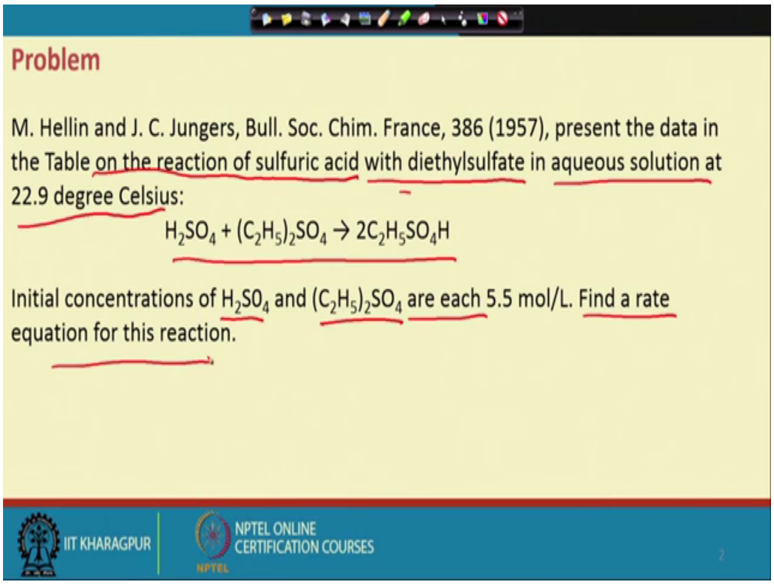

Problem

M. Hellin and J. C. Jungers, Bull. Soc. Chim. France, 386 (1957), present the data in the Table on the reaction of sulfuric acid with diethylsulfate in aqueous solution at 22.9 degree Celsius:

$$H_2SO_4 + (C_2H_5)_2SO_4 \rightarrow 2C_2H_5SO_4H$$

Initial concentrations of H_2SO_4 and $(C_2H_5)_2SO_4$ are each 5.5 mol/L. Find a rate equation for this reaction.

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So, first let me go through this problem that first problem is that this is we coated from that Hellin and Jungers that published in 1957, the presents the data the Table if you have table on the reaction of sulfuric acid and diethyl sulfate in aqueous solution at 22.9 degree Celsius and the reaction is this this is ice sulfuric acid in presence of diethyl sulphate it produces the ethyl by sulphate.

The initial concentration of H 2 so 4 and diethylsulfate are each 0.5.5 molds per volatile find the rate equation for this reaction, now previously we can remember that we try to solve the first order reaction we try to develop the rate equation for the first order reaction and this is the second order reaction we try to solve today.

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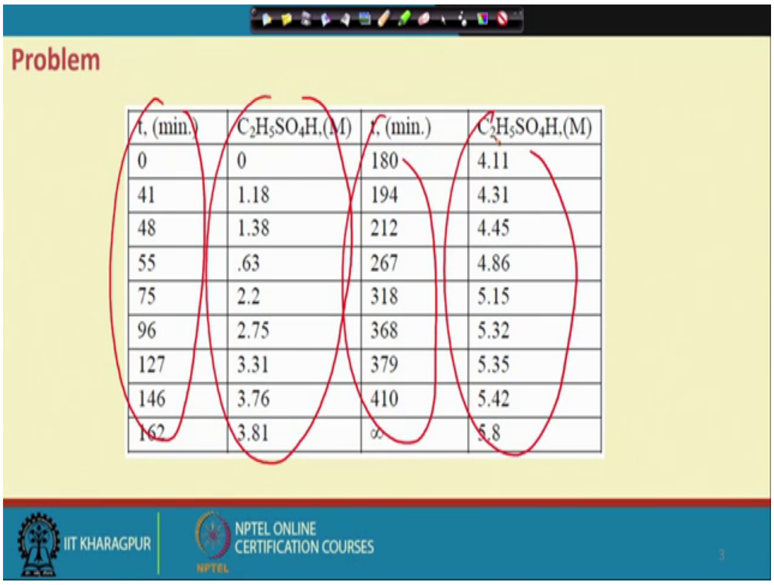

Problem

t, (min.)	$C_2H_5SO_4H$,(M)	t, (min.)	$C_2H_5SO_4H$,(M)
0	0	180	4.11
41	1.18	194	4.31
48	1.38	212	4.45
55	.63	267	4.86
75	2.2	318	5.15
96	2.75	368	5.32
127	3.31	379	5.35
146	3.76	410	5.42
162	3.81	∞	5.8

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Now this is the data that is given this is you can see that with respect to time how the product concentration that changes that has been given here this is all data is given here.

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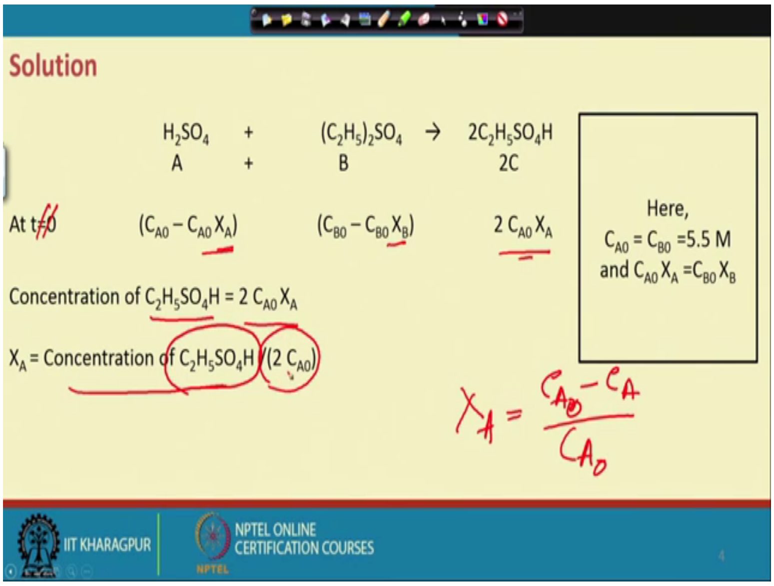

Solution

H_2SO_4 + $(C_2H_5)_2SO_4$ → $2C_2H_5SO_4H$

A + B 2C

At $t \neq 0$ $(C_{A0} - C_{A0}X_A)$ $(C_{B0} - C_{B0}X_B)$ $2\,C_{A0}X_A$

Here,
$C_{A0} = C_{B0} = 5.5$ M
and $C_{A0}X_A = C_{B0}X_B$

Concentration of $C_2H_5SO_4H = 2\,C_{A0}X_A$

X_A = Concentration of $C_2H_5SO_4H/(2\,C_{A0})$

$$X_A = \frac{C_{A0} - C_A}{C_{A0}}$$

Now, this is the reaction and at time t equal to 0 that that that C A C A will be C A 0, but at time t that what will happen that the X A will be converted, this is not t A 0 this is this should be at time t this is not t A 0 this is equal to C A 0 minus C A 0 into X A let us assume they X A, the conversion I told you previously also X A is the fraction that the substrate fraction that is converted this is C A minus C A 0 minus C C A 0 this is like this. So, we can this is the fraction of b that is converted and this is what that product formation take place.

The concentration of product can be expressed as this the 2 C A 0 into X A X A is the concentration of divided by 2 C A 0 because this is C A 0 this is also the equimolecular is there. So, he considered that you know that X A the fraction we can we can that is and C A that you know the bi-sulphate divided by 2 moles of initial substrate concentration.

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Solution

t, (min)	X_A	t, (min)	X_A
0	0	180	0.373
41	0.107	194	0.392
48	0.125	212	0.404
55	0.148	267	0.442
75	0.204	318	0.468
96	0.250	368	0.483
127	0.300	379	0.486
146	0.342	410	0.492
162	0.346	∞	0.527

Now, this is from this we can we can write this expression because if we have this value that is concentration of these divided by 2 C A 0 and C is 0 value is about A 5.; this is this is given here. So, we can calculate we can calculate we can find out the value of X A and just we can find out the value of X A here and with respect to time we can find out from the table.

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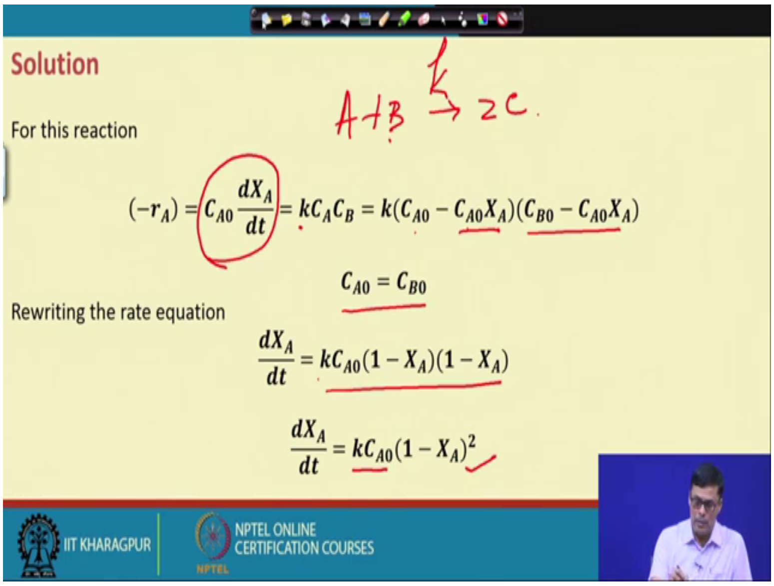

Solution

For this reaction

$A + B \xrightarrow{k} 2C.$

$$(-r_A) = \boxed{C_{A0}\frac{dX_A}{dt}} = kC_AC_B = k(C_{A0} - \underline{C_{A0}X_A})(\underline{C_{B0} - C_{A0}X_A})$$

$$\underline{C_{A0} = C_{B0}}$$

Rewriting the rate equation

$$\frac{dX_A}{dt} = \underline{kC_{A0}(1 - X_A)(1 - X_A)}$$

$$\frac{dX_A}{dt} = \underline{kC_{A0}}(1 - X_A)^2$$

Now, this is the correlation that we had because this is like this something like this A plus B gives 2 C like this; the reaction that we have there. So, this can be presented like this

this is k is the rate constant if you have. Now what we can write this is the rate of substrate degradation A or B whatever is there then this is equal to k into C A and C B and C A is equal to C A 0 into C A 0 into X A this is the fraction that is converted and that remains and here also that X A the same fraction equimolecular conversion is there.

So, we can assume this C A 0 minus C A that is there because C A 0 is equal to C B 0 that as per the problem is concerned then we can we can take the C A 0 common then and we can have the equation that like this. So, we can have this equation that is k into C A 0. So, here C A 0 and here also C A 0 if you if you if you take common then then the C A 0 squared is there. So, 1 C A 0 will cancel. So, another C A 0 will remain. So, 1 minus X A square that is that is there we can we can write this expression like this.

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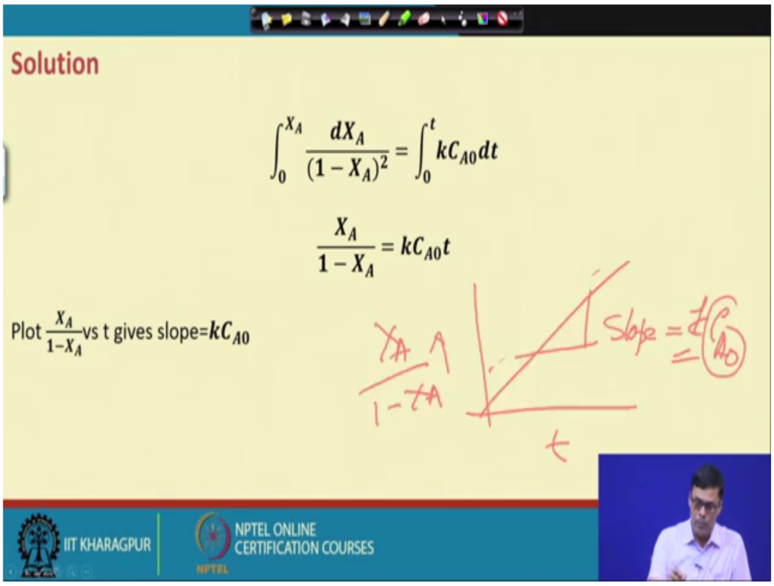

Solution

$$\int_0^{X_A} \frac{dX_A}{(1-X_A)^2} = \int_0^t kC_{A0}dt$$

$$\frac{X_A}{1-X_A} = kC_{A0}t$$

Plot $\frac{X_A}{1-X_A}$ vs t gives slope= kC_{A0}

Now, once you get this equation that this. So, I can I can take it in at this side 1 minus X A I can take it this side and t dt; I can take it this size. So, I can write this is that B X A divided by 1 minus X A square equal to k into C A is even then if you do the differentiation will get this equation, that X A by 1 minus X A k into C A. So, if we plot now if we plot X A verses 1 minus X A versus t, then this equation if you see that here if you plot X A by 1 minus X A, if you plot versus t if we plot this pass through the origin and slope will give you the value of n k into C A 0.

So, we know the C A 0 value so for we can find out the value of k.

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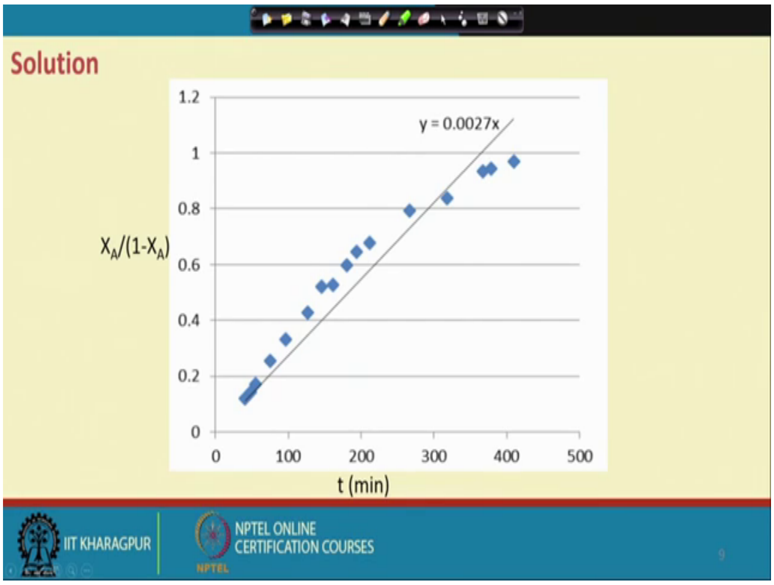

Solution

So, this is this is exactly that from the slope we can find out that value of k we can find out and this is how the k value is coming around this now.

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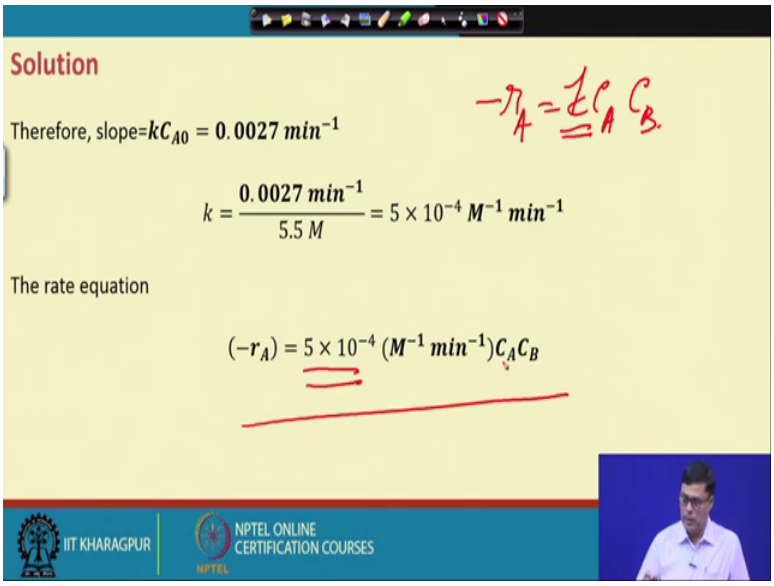

Solution

$-r_A = k C_A C_B$

Therefore, slope=$kC_{A0} = 0.0027\ min^{-1}$

$$k = \frac{0.0027\ min^{-1}}{5.5\ M} = 5 \times 10^{-4}\ M^{-1}\ min^{-1}$$

The rate equation

$$(-r_A) = 5 \times 10^{-4}\ (M^{-1}\ min^{-1}) C_A C_B$$

The once we get this k value then we know our rate equation what is our rate equation minus r A equal to k into C A by C B am I right. So, k now k value has been determined. So, we can put this k value here and this is how we can write the rate equation and again I am telling you if you want to do the validity of the equation, we can easily do by ourselves in that case we shall have to find a correlation between the time and the and the substrate concentration and you have perhaps the theoretical values theoretical plot and compare with the experimental plot from that you can do the validity of the experimental results.

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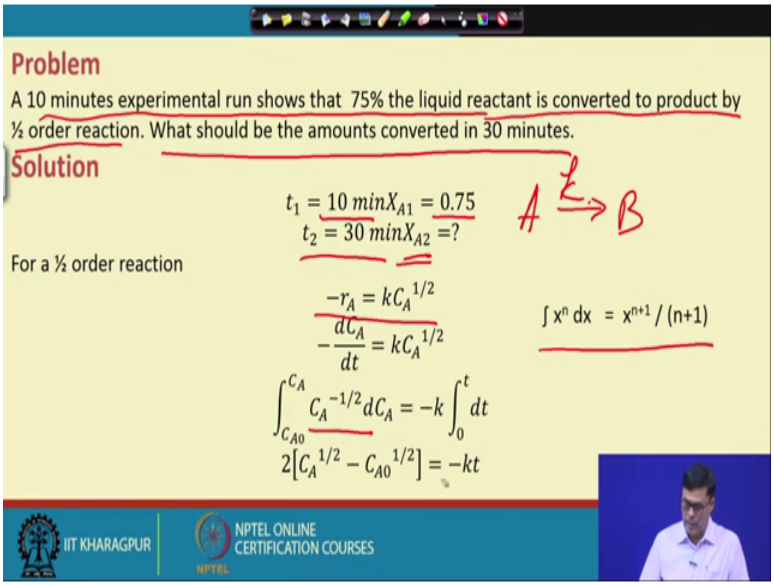

Problem

A 10 minutes experimental run shows that 75% the liquid reactant is converted to product by ½ order reaction. What should be the amounts converted in 30 minutes.

Solution

$t_1 = 10\ min X_{A1} = 0.75$

$t_2 = 30\ min X_{A2} = ?$

$A \xrightarrow{k} B$

For a ½ order reaction

$$-r_A = kC_A^{1/2}$$

$$-\frac{dC_A}{dt} = kC_A^{1/2}$$

$$\int_{C_{A0}}^{C_A} C_A^{-1/2} dC_A = -k \int_0^t dt$$

$$2[C_A^{1/2} - C_{A0}^{1/2}] = -kt$$

$\int x^n\,dx = x^{n+1}/(n+1)$

Next problem that is also very interesting that a 10 minutes experimental runs. So, that 75 percent liquid reactant is converted to product by half order reaction. So, up till now what we have discussed we have discussed mostly the single order reaction (Refer Time: 09:28) and also we double order reaction first order and second order reaction we consider, but this is the half order reaction and what will be the amount converted in thirty minutes so that we shall have to find out.

So, in this problem the 10 minutes and the fraction converted is 0.75 and Gaussian is the after 30 minutes what how much fraction of A will be converted. Now the equation half order reaction this if we assume A to B that if k is the rate constant I can write that minus r A equal to k into C A to the power half. So, I can write this as minus C A by dt came to C A to the power hub then we can take it here. Now this equation this is differential equation is they will the solving is like this X to the power n dx equal to X to the power n plus 1 divided by n plus 1.

Now, if you do the similar thing here we will get the solution here 2 into C A to the power half minus C A 0 to the power because integration is from C A 0 to C A equal to k into minus k into t.

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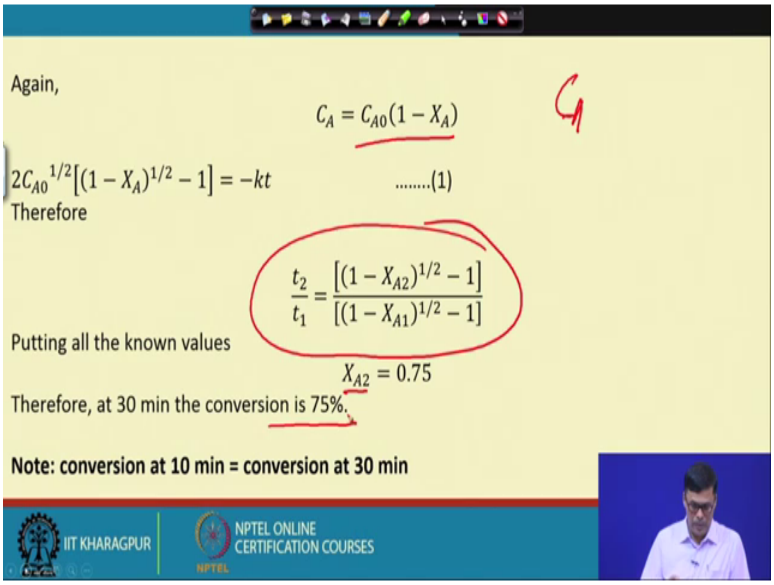

Again,

$$C_A = C_{A0}(1 - X_A)$$

C_A

$$2C_{A0}^{1/2}[(1 - X_A)^{1/2} - 1] = -kt \qquad ....(1)$$

Therefore

$$\frac{t_2}{t_1} = \frac{[(1 - X_{A2})^{1/2} - 1]}{[(1 - X_{A1})^{1/2} - 1]}$$

Putting all the known values

$$X_{A2} = 0.75$$

Therefore, at 30 min the conversion is 75%.

Note: conversion at 10 min = conversion at 30 min

Now, once that here we have this equation then we at the same time we know that C A equal to what C A equal to C A 0 into 1 minus X A at any point of time. So, in this equation you can put the value of C A then we have this equation and then for different temper to different time because the t 2 and t 1 if the fraction the 1 time X A 1 is converted and their time 2 X A 2 is converted that we can have the expression is like this.

Now, this if we put this value of X A 2 as 0.75 then after 35 30 minutes conversion is 75 percent. Now previously we have seen in the problem that that that also that initial conversion also that also 75 percent and again I can go back. If you look at now this here we what we have done that the problem was that 10 minutes there to go conversion 75 percent. Now when we calculate it here we calculated here then also we find that after 30 minutes the conversion is 75 percent.

So, both cases the conversion is same now we try to find out why this is happening and then what we have done we have we try to develop the correlation that we have here and with respect to with respect to this time that you see that, we can write this equation like this and we can solve it and we will get this equation and 10 is 0.75 then it is about 20, am I right then and then if we go for further then 20 equal to t by X A this 1 this is the correlation that we have; then we can write X A if we solve it X A equal to this equations. Now in this equation if we if we put the value of a different value of t, then you can find out the X A fraction.

So, then we can we can we can find a correlation.

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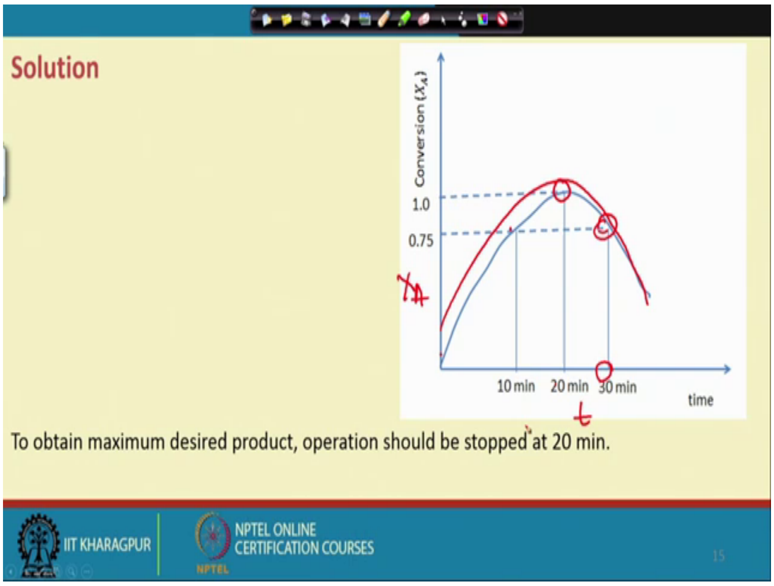

Solution

To obtain maximum desired product, operation should be stopped at 20 min.

We can find here you can find a correlation of physics am I right this is the X A and this is time. So, if we put this equation you will find this correlation like this; that means, that 10 minutes time that your 75 percent conversion 20 minutes time the 100 percent conversion for 30 minutes, again as per the calculation is concerned it is coming back to 75 percent as well our equation is concerned.

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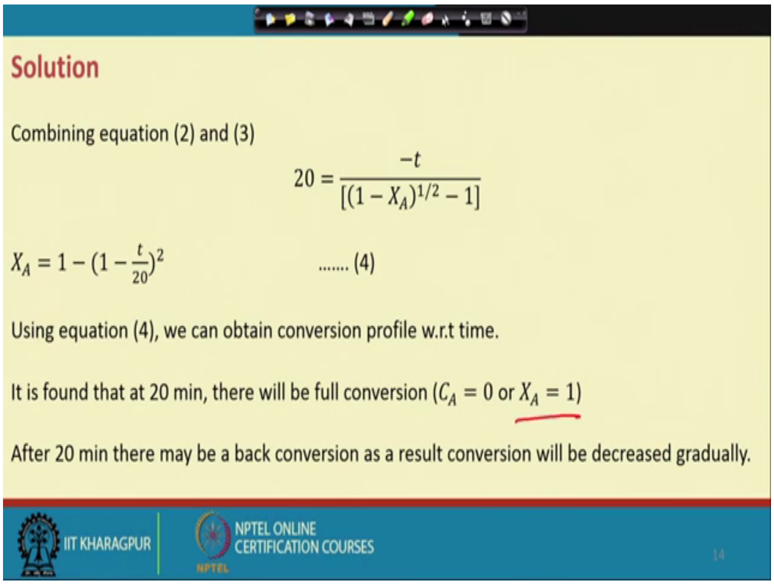

Solution

Combining equation (2) and (3)

$$20 = \frac{-t}{[(1-X_A)^{1/2}-1]}$$

$X_A = 1 - (1 - \frac{t}{20})^2$ .... (4)

Using equation (4), we can obtain conversion profile w.r.t time.

It is found that at 20 min, there will be full conversion ($C_A = 0$ or $\underline{X_A = 1}$)

After 20 min there may be a back conversion as a result conversion will be decreased gradually.

So, this is the this is the typical observation we have that at 20 minutes if you put the 20 minutes the corner X A will be X A will be X A will be 1 that in X A will be 1 mean 100 percent conversion of substrate take place, but there are 30 minutes we have 75 percent. So, that is that is why we try to find out that why this is happening how this is happening we try to develop the correlation and establish the fact like this.

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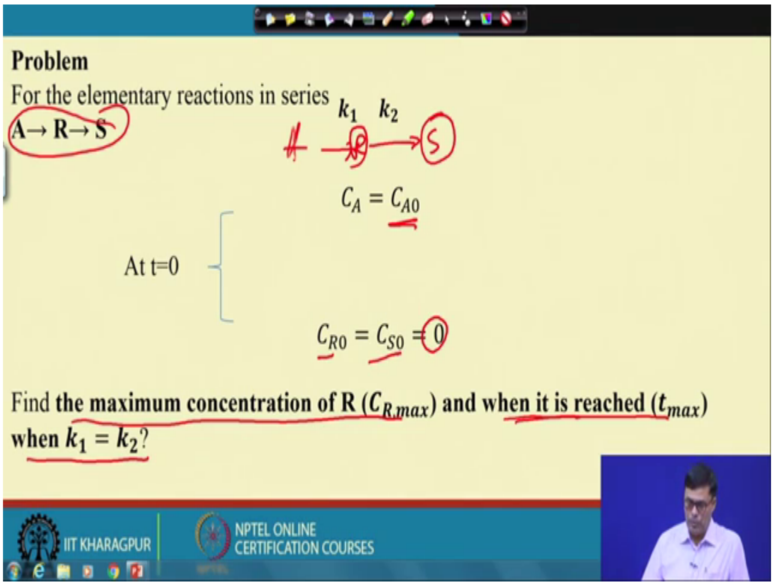

Problem

For the elementary reactions in series $A \rightarrow R \rightarrow S$

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

At t=0

$C_A = C_{A0}$

$C_{R0} = C_{S0} = 0$

Find **the maximum concentration of R ($C_{R,max}$) and when it is reached (t_{max}) when $k_1 = k_2$?**

Now, last problem that I want to discuss today that is chain reaction that we I have already discussed the theory part of it this unfortunately this is this has gone to this side. So, you look at A to R R to S. So, I can I can write here A to R R to S like this. So, this has shifted here.

So, it is like this now the for the elementary reaction is the reaction A 2 R R 2 S this is C f is A will see at t equal to 0 C A equal to C A 0 and mod that is the intermediate substrate concentration and final such A final product for and final for the concentration that will be equal to 0, this is the boundary condition is that the question is that maximum concentration of R what do you find the maximum concentration; when it is reached at t max when k 1 equal to k 2. Now previously we did not assume the k 1 equal to greater we assume that k 1 and k 2, they are different when you develop the correlation. Now this is a particular problem deals with that what will happen when k 1 is equal to k 2. So, we use 2 different approaches to solve this problem.

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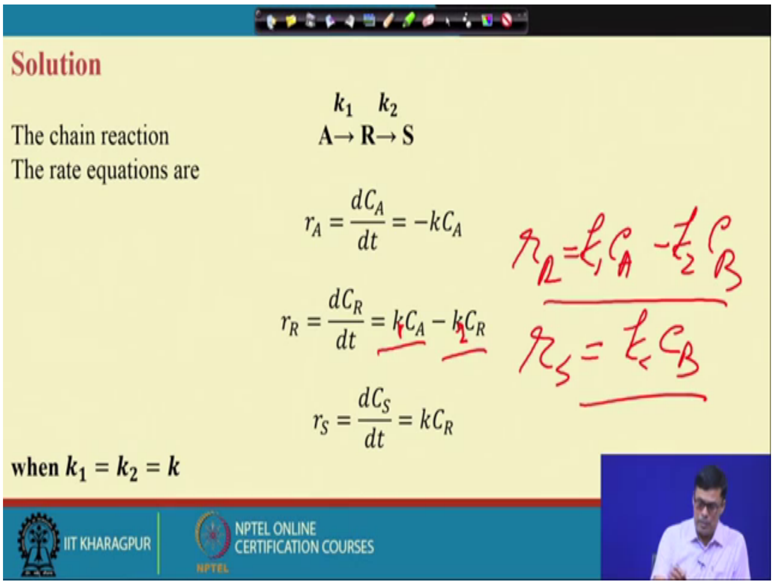

Solution

The chain reaction $\overset{k_1}{A \rightarrow} \overset{k_2}{R \rightarrow} S$

The rate equations are

$$r_A = \frac{dC_A}{dt} = -kC_A$$

$$r_R = \frac{dC_R}{dt} = \underline{k_1 C_A} - \underline{k_2 C_R}$$

$$r_S = \frac{dC_S}{dt} = kC_R$$

when $k_1 = k_2 = k$

$$\underline{r_R = k_1 C_A - k_2 C_B}$$

$$\underline{r_S = k_2 C_B}$$

Now, first we have this we know that this equation we can write for rate of degradation of r r A A it can be written k k 1 this will be k 1 and k 1 into C A and r R; r R equal to k 1 into C A this will be k 1 and this is k 2 not coming properly. So, I can write like this that r R equal to k 1 into C A minus k 2 into C R. This is unfortunate it is not come here. So, and rate of formation of r that r s will be what r s will be equal to k 2 into k 2 into C C V this is we have seen before also this is how it can be expressed.

Now, the reason it has been written that k 1 equal to k 2. So, we finally, it looks like this final equation, if you look at it looks like this because the reason is that k 1 equal to k 2 equal to k if we assume that then the equation will come like this then we can write the whole reaction like this.

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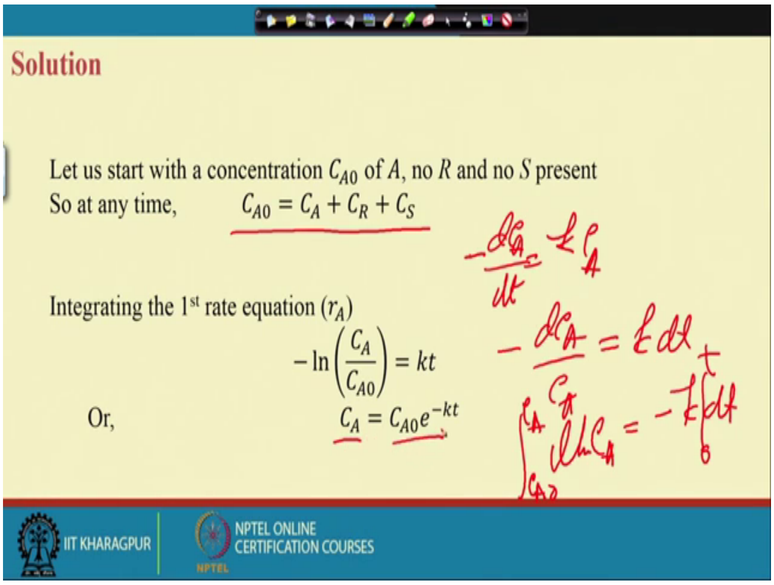

Solution

Let us start with a concentration C_{A0} of A, no R and no S present

So at any time, $C_{A0} = C_A + C_R + C_S$

Integrating the 1st rate equation (r_A)

$$-\ln\left(\frac{C_A}{C_{A0}}\right) = kt$$

Or, $C_A = C_{A0}e^{-kt}$

$$-\frac{dC_A}{dt} = kC_A$$

$$-\frac{dC_A}{C_A} = k\,dt$$

$$\int_{C_{A0}}^{C_A} d\ln C_A = -k\int_0^t dt$$

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Now, we have already seen that you know that total initial substrate concentration at any point of time is equal to C A plus C R plus C S because if we assume this is equally molecular conversion.

Now, if you look at the first that the substrate degradation that is equal to how you can write d C A by dt equal to k into C A am I right. So, we can put it here. So, minus d C A by C A equal to k into dt. So, this is equal to d l n C A. So, this I can put this is minus k into dt. So, if you put C A 0 into C A and this is 0 to t then we can write that ln ln C A by C A 0 if the minus this minus I can take it here and into minus kt. So, C A equal to C A 0 into e to the power minus kt.

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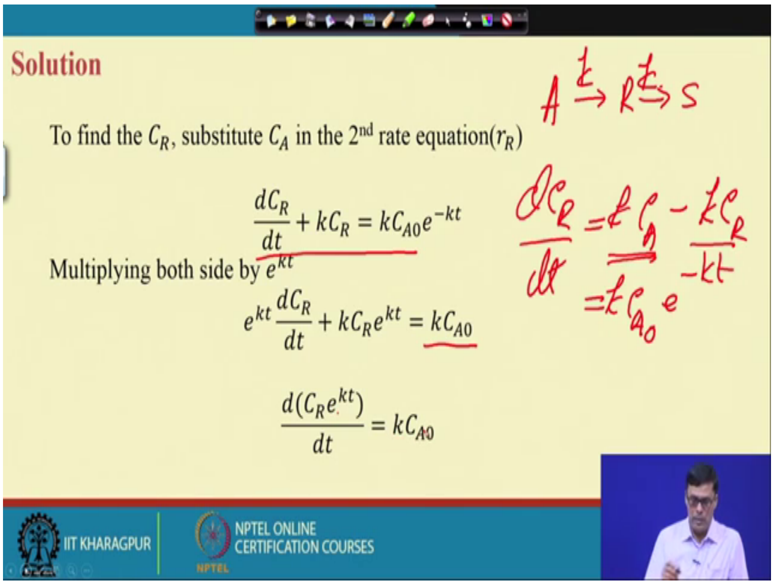

Solution

$A \xrightarrow{k} R \xrightarrow{k} S$

To find the C_R, substitute C_A in the 2nd rate equation(r_R)

$$\frac{dC_R}{dt} + kC_R = kC_{A0}e^{-kt}$$

$$\frac{dC_R}{dt} = kC_A - kC_R$$

$$= kC_{A_0}e^{-kt}$$

Multiplying both side by e^{kt}

$$e^{kt}\frac{dC_R}{dt} + kC_Re^{kt} = kC_{A0}$$

$$\frac{d(C_Re^{kt})}{dt} = kC_{A0}$$

Now, in the second part of the reaction because if you if you look at this is like this A to R R to S am I right. So, this is k and this is k. So, rate of rate of formation of R will be what k to into C A minus k into C R. So, now, I can take this k at this side. So, this is how it has come that this C R by dt plus k into C R equal to now this we have already find out C A equal to what C A equal to C A 0 e to the power minus kt. So, I can write this the expression like this.

So, if we multiplied both sides by e to the power k both side if I multiplied then e to the power minus k kt and minus and e to the plus kt that will cancel each other and we will be having k C 0. Now this this is equal to nothing, but d C R by e to the power kt by dt equal to k into C 0.

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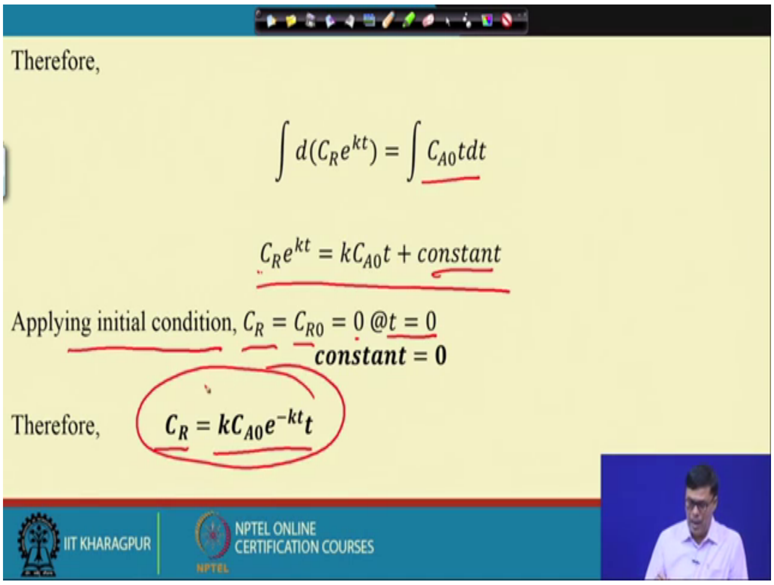

Therefore,

$$\int d(C_R e^{kt}) = \int C_{A0} t dt$$

$$C_R e^{kt} = kC_{A0}t + constant$$

Applying initial condition, $C_R = C_{R0} = 0 \ @ t = 0$

$$\mathbf{constant = 0}$$

Therefore, $\boxed{\mathbf{C_R = kC_{A0}e^{-kt}t}}$

Now then we can write that d C R by e to the power kt equal to what equal to C A 0 t into dt. Now this can be written in this form C r into e to the power kt equal to k k C A 0 into t plus constant. Now applying the initial conditions or boundary conditions at t equal to 0 R equal to R equal to R 0 equal to 0. So, constant will be 0 because if t equal to 0 then this also will be re C R equal to 0.

So, constant also will be equal to 0. So, this equation will be what C R into k into C 0 into t. So, C R if you write the expression for C R then e to the e to the power kt that will come this side. So, if you if you can write k into C A 0 e to the power minus kt into t this is this is the final expression that we have.

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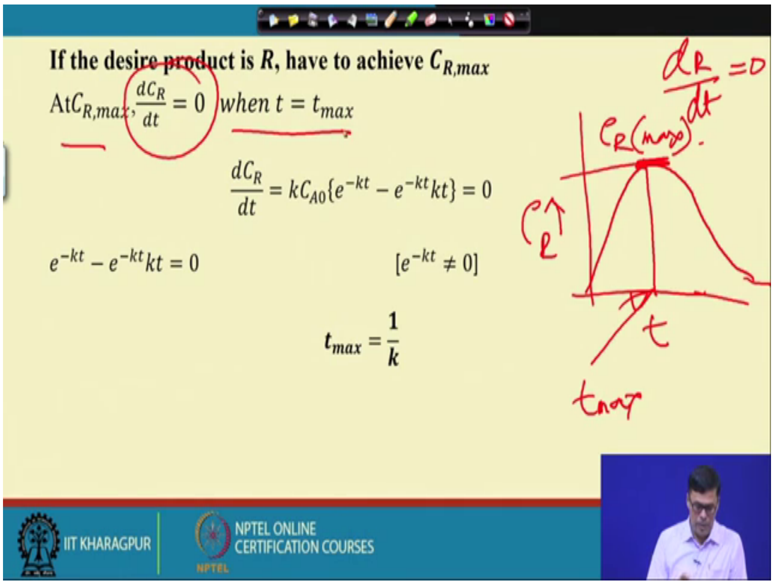

If the desire product is R, have to achieve $C_{R,max}$

At $C_{R,max}$, $\frac{dC_R}{dt} = 0$ when $t = t_{max}$

$$\frac{dC_R}{dt} = kC_{A0}\{e^{-kt} - e^{-kt}kt\} = 0$$

$e^{-kt} - e^{-kt}kt = 0$ $\quad [e^{-kt} \neq 0]$

$$t_{max} = \frac{1}{k}$$

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

Now we have already seen what we have seen that is C R when you plot C R versus t what kind of plot we have it is increases then decreases am I right this like the kind of plot we have.

Now, at t max this is equal to t max at t max this will be C R max. So, at this particular situation what will happen d C R by dt that should be equal to 0, what we have written here as C R max say d C R by d t equal to 0 when t equal to d max and if you put these conditions that you know in the previous equation.

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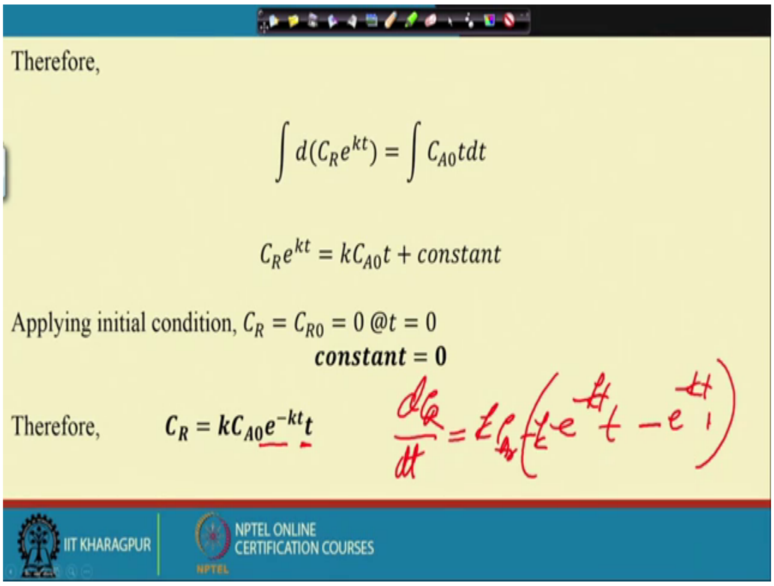

Therefore,

$$\int d(C_R e^{kt}) = \int C_{A0} t dt$$

$$C_R e^{kt} = kC_{A0}t + constant$$

Applying initial condition, $C_R = C_{R0} = 0\ @t = 0$

$constant = 0$

Therefore, $\quad \boldsymbol{C_R = kC_{A0}e^{-kt}t}$

$$\frac{dC_R}{dt} = kC_{A0}(-ke^{-kt}t - e^{-kt}1)$$

So, this equation in now if you if you if you differentiate this that then what will happen d C R, but here you see we have we have these 2 variables we have we have here e to the power minus kt and with our t. So, we can we can we can differentiate if you differentiate here what will be their C R by dt equal to k C A 0 you can take common actually then we can differentiate positive with respect to this will be minus k into e to the power kt into t, then minus we can write e to the power minus kt into 1 because t differentiation with respect to 1 is 1.

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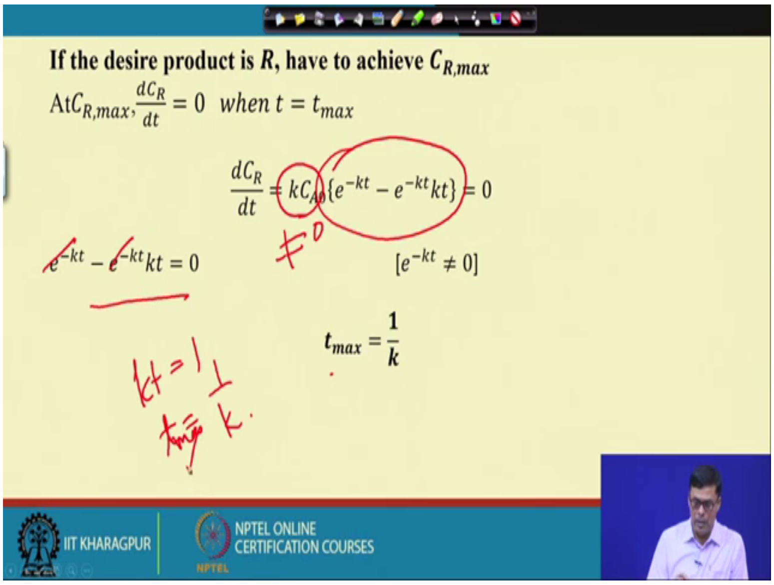

If the desire product is R, have to achieve $C_{R,max}$

At$C_{R,max}$, $\frac{dC_R}{dt} = 0$ when $t = t_{max}$

$$\frac{dC_R}{dt} = kC_{A0}\{e^{-kt} - e^{-kt}kt\} = 0$$

$\neq 0$

$$\cancel{e}^{-kt} - \cancel{e}^{-kt}kt = 0$$

$[e^{-kt} \neq 0]$

$kt = 1$

$t_{max} = \frac{1}{k}$

$$t_{max} = \frac{1}{k}$$

So, this is exactly this we can we can show it here if we differentiate that we will get this minus minus will be plus that you know we will get this equation like this e to the power k k 1 t equal to kt this is equal to this 1 that, then what we can do that we can we can we this cannot be equal to 0 am I right this cannot be equal to 0. So, if it is not be equal to 0 I can assume this is equal to 0 and if you put this equal to 0, then t max will be what t max equal to 1 by k. Because this this will cancel am I right this this will cancel. So, you your kt kt will be equal to 1 and if your kt equal to 1, then I can write t equal to 1 by k this we can write and these are t equal to t max.

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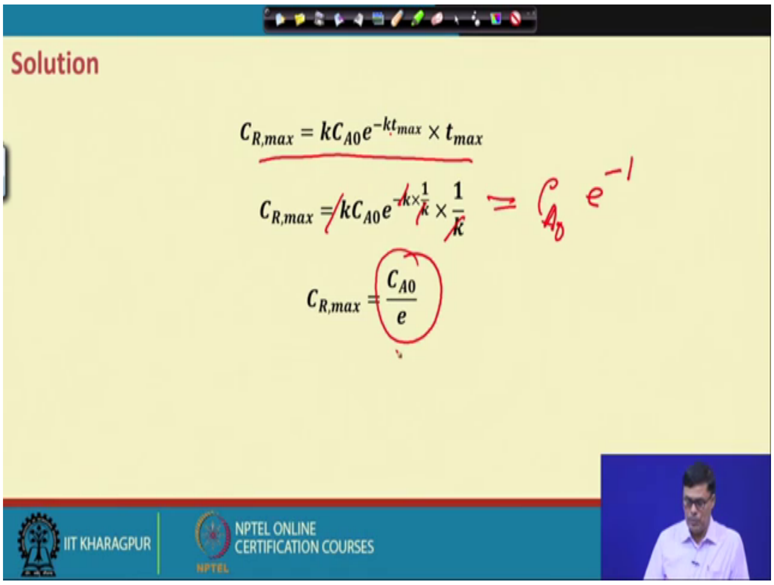

Solution

$$C_{R,max} = kC_{A0}e^{-kt_{max}} \times t_{max}$$

$$C_{R,max} = \cancel{k}C_{A0}e^{-\cancel{k}\times\frac{1}{\cancel{k}}} \times \frac{1}{\cancel{k}} = C_{A_0} e^{-1}$$

$$C_{R,max} = \boxed{\frac{C_{A0}}{e}}$$

Now, this t max value t max value you can you can put in the previous equation we had the previous equation is there. So, we can put the previous equation you put the t max equal to 1 by k and if we 1 by k this k; k will cancel with each other then, if we cancel then what will happen that will be having this will be C A 0 into e to e to the power minus 1, am I right it is cancelled it will be minus 1 and if it minus 1 we can right in this form the C R max equal to C A 0 into e the this is this is 1 approach the easy approach A simple approach logical approach through which we can solve this problem.

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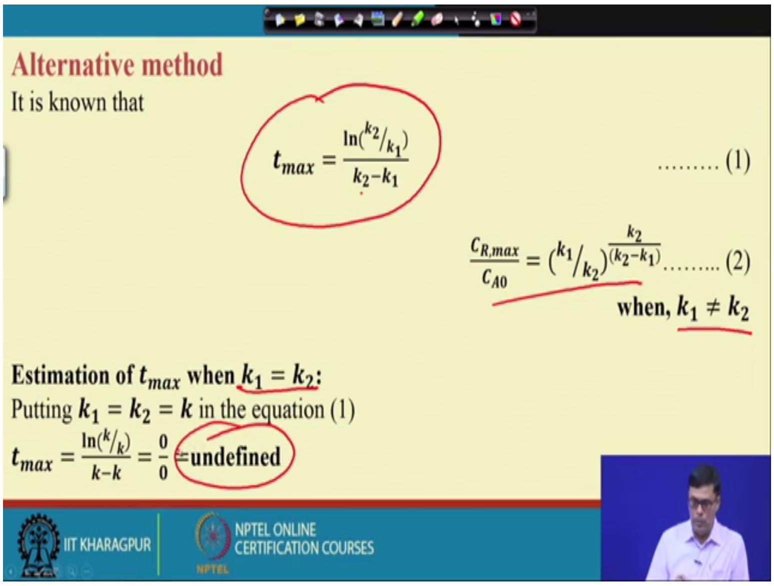

Alternative method

It is known that

$$t_{max} = \frac{\ln(k_2/k_1)}{k_2-k_1} \quad \text{......... (1)}$$

$$\frac{C_{R,max}}{C_{A0}} = (k_1/k_2)^{\frac{k_2}{(k_2-k_1)}} \quad \text{......... (2)}$$

when, $k_1 \neq k_2$

Estimation of t_{max} when $k_1 = k_2$:

Putting $k_1 = k_2 = k$ in the equation (1)

$$t_{max} = \frac{\ln(k/k)}{k-k} = \frac{0}{0} = \text{undefined}$$

The there is another approach that also we have now we can we shall have to go back to our early that derive equation, that why we have shown that t max equal to ln k 2 by k 1 k 2 minus k 1. Now here if we put k 1 this is this is valid when k 1 not equal to k 2 now when k 1 is equal to k 2, then what is happening that this will be 0 and this also the log 1 equal to 0 and k minus k equal to 0. So, it is undefined 0 by 0 is undefined.

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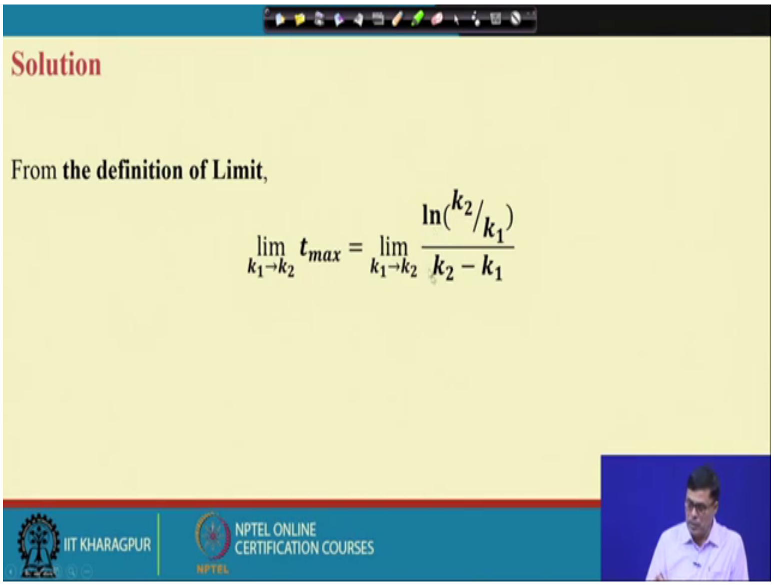

Solution

From **the definition of Limit**,

$$\lim_{k_1 \to k_2} t_{max} = \lim_{k_1 \to k_2} \frac{\ln\left(k_2/k_1\right)}{k_2 - k_1}$$

Now, here if we put the limit that limit k tends to k 2 k ones tends to k 2 t max they were limit will be this limit ln k 1 tends to k 2 ln k 2 by k 1 k 2 minus k 1 then this is not equal to exactly 0.

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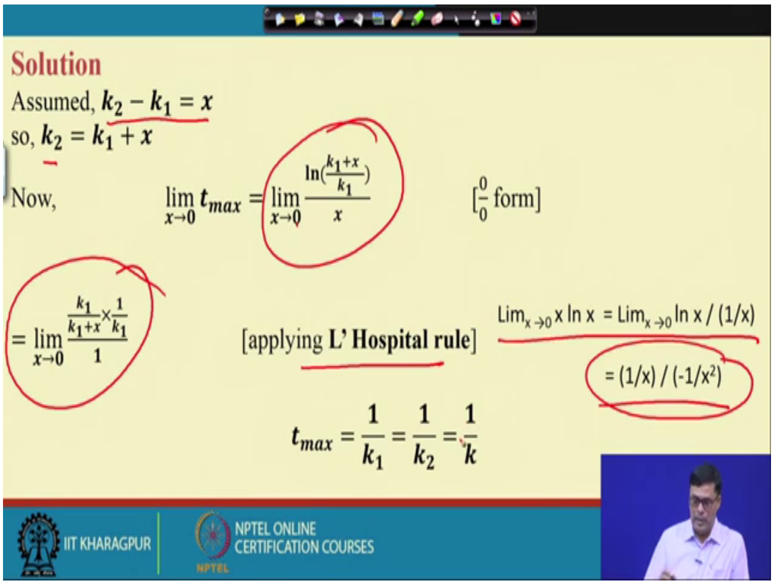

Solution

Assumed, $k_2 - k_1 = x$

so, $k_2 = k_1 + x$

Now, $\lim_{x \to 0} t_{max} = \lim_{x \to 0} \frac{\ln\left(\frac{k_1 + x}{k_1}\right)}{x}$ $[\frac{0}{0}$ form$]$

$= \lim_{x \to 0} \frac{\frac{k_1}{k_1 + x} \times \frac{1}{k_1}}{1}$ [applying **L' Hospital rule**]

$\mathrm{Lim}_{x \to 0}\, x \ln x = \mathrm{Lim}_{x \to 0} \ln x / (1/x)$

$= (1/x) / (-1/x^2)$

$$t_{max} = \frac{1}{k_1} = \frac{1}{k_2} = \frac{1}{k}$$

If so if we then we can write k 2 minus k 1 equal to X this we can write k 2 minus k 1 equal to x. So, k 2 will be equal to X k 1 1 plus k 1 plus X then I can I can I can modify the equation like this, then then if we if we put you put the law the hospital rule the hospital rule equation is like this if you limit X tends to 0 X ln X limit this will be like this. So, we can write in this form the sames form; we can applied here; we can come in this form and if we apply if you this form then we will find that this is will cancel then k 1 k 1 will cancel this will be 1 by k 1 and same X tends to 0, I can ignore X then it will be 1 minus k 1 and then then since k 1 equal to k 2 I can write 1 by k 2 equal to 1 by k.

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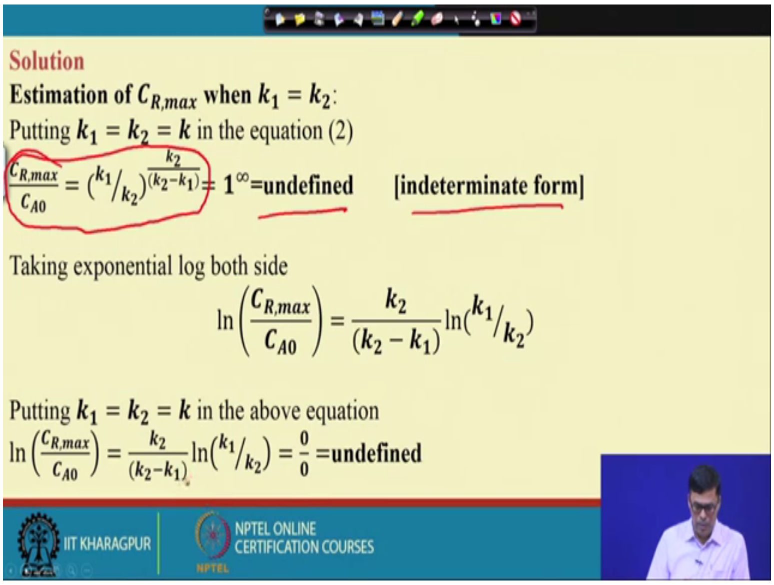

Solution

Estimation of $C_{R,max}$ when $k_1 = k_2$:

Putting $k_1 = k_2 = k$ in the equation (2)

$\frac{C_{R,max}}{C_{A0}} = \left({}^{k_1}/_{k_2}\right)^{\frac{k_2}{(k_2 - k_1)}} = 1^{\infty}$**=undefined** **[indeterminate form]**

Taking exponential log both side

$$\ln\left(\frac{C_{R,max}}{C_{A0}}\right) = \frac{k_2}{(k_2 - k_1)} \ln\left({}^{k_1}/_{k_2}\right)$$

Putting $k_1 = k_2 = k$ in the above equation

$\ln\left(\frac{C_{R,max}}{C_{A0}}\right) = \frac{k_2}{(k_2 - k_1)} \ln\left({}^{k_1}/_{k_2}\right) = \frac{0}{0}$ **=undefined**

Now, second approach that we have again we shall have to go back toward early that what we have derived, then in this we have shown you that C R 0 by C A 0 equal to this now here also if we put k 1 equal to k 2 then this will be 1 and this is 1 minus 0 1 minus 0 equal to infinity this is undefined; whatever what do you call is the indeterminate form. Now this equation also we can we can we can we can we have seen; this is undefined this way also we can find this undefined.

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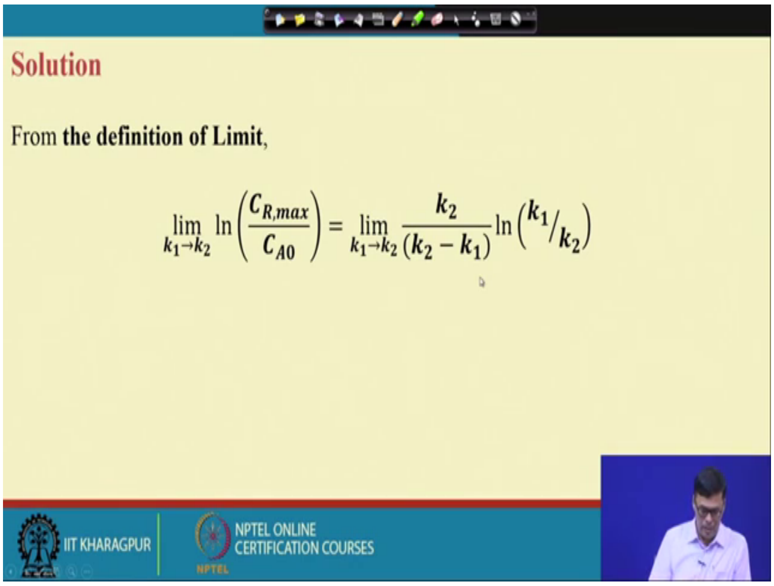

Solution

From **the definition of Limit,**

$$\lim_{k_1 \to k_2} \ln\left(\frac{C_{R,max}}{C_{A0}}\right) = \lim_{k_1 \to k_2} \frac{k_2}{(k_2 - k_1)} \ln\left({k_1}/{k_2}\right)$$

Now if you come if you put the limit that this is k 1 strange to k 2 we can we have this equation like this then this is the this is this let us see how we can solve it.

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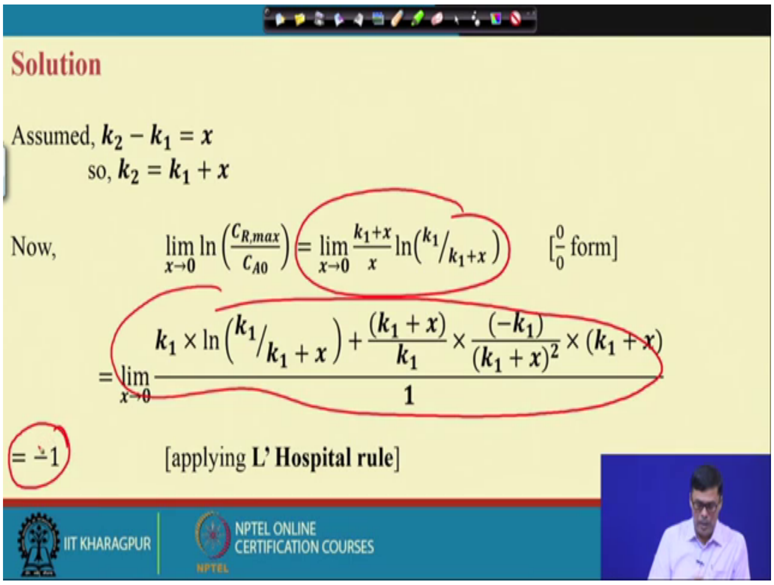

Solution

Assumed, $k_2 - k_1 = x$

so, $k_2 = k_1 + x$

Now, $\lim_{x\to 0} \ln\left(\frac{C_{R,max}}{C_{A0}}\right) = \lim_{x\to 0} \frac{k_1+x}{x} \ln\left({}^{k_1}/_{k_1+x}\right)$ $\left[\frac{0}{0}\text{ form}\right]$

$$= \lim_{x\to 0} \frac{k_1 \times \ln\left({}^{k_1}/_{k_1+x}\right) + \frac{(k_1+x)}{k_1} \times \frac{(-k_1)}{(k_1+x)^2} \times (k_1+x)}{1}$$

$= -1$ [applying **L' Hospital rule**]

Then again we can we can have we can assume k 2 minus k 1 equal to X k 2 equal to k 1 plus X then we can write this equation in this form and then if we solve applying this law hospital rule then we will get this is equal to minus 1.

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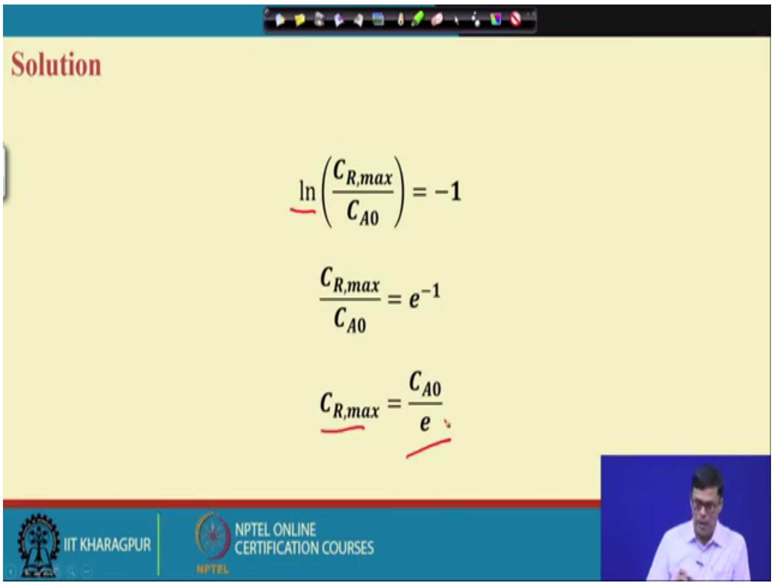

Solution

$$\ln\left(\frac{C_{R,max}}{C_{A0}}\right) = -1$$

$$\frac{C_{R,max}}{C_{A0}} = e^{-1}$$

$$C_{R,max} = \frac{C_{A0}}{e}$$

Then if this is equal to minus 1 then this is like this then then C R by C max equal to C A 0 equal to C A 0 equal to this ln is there. So, ln I can I can I can ln if we take it ln out that C R max by C A 0 equal to e to the power minus e 1 and C R max equal to C 0 by e. So, this is how we can we can solve this equation in other approach, but I feel that the first approach might be computable easier as compared to the second approach. So, what I want to conclude this homogeneous reaction kinetics because here we try to find out the different equations of for different type of reactions both the reversible irreversible reaction also of different types that we have simple A to b reactions, we have parallel reaction, we have auto catalytic reaction and we have also the chain reaction and another reaction we have the reversible reactions.

So, we try to derive the rate constant as well as the order of reaction; of this reaction; of this equation; of these particular reactions and to establish the rate equation. We try to justify when you write any kind of rate equations we shall have to do the validation of the experimental results and to validate the experimental results, we shall have to find A correlation between time versus substrate concentration and then we can compare with the experimental results and if the deviation is less than 5 percent then it is acceptable if more than 5 percent which are have to modify this equation. The way we try we try to solve different equations I hope the conception on the reaction kinetics will be will be little bit clear to you.

Thank you very much.