Aspects of Biochemical Engineering
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Lecture – 14
Kinetics of Homogenous Chemical Reactions – IV

Welcome back to my course Aspects of Biochemical Engineering; that in the last lecture I try to discuss some numerical problems. And numerical problem mostly built with the irreversible reactions. And in this irreversible reactions that we considered that you know pasteurization process we consider the relations between the substrate conversion with respect to time and also we try to find out the activation energy of A particular chemical reaction that how we can find out also how to calculate the metabolic rate of the human system.

Now, this particularly presentation dictate we also we will discuss some numerical problems and these numerical problems will mostly deal with the reversible process, also 1 or 2 problem with the real problem that we have with the irreversible process that also we will discuss.

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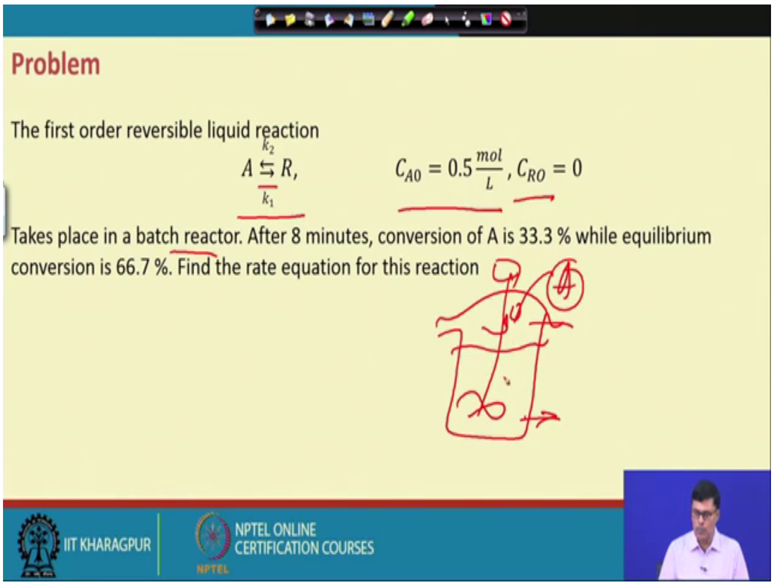

Problem

The first order reversible liquid reaction

$A \underset{k_1}{\overset{k_2}{\leftrightarrows}} R$, $C_{A0} = 0.5\frac{mol}{L}$, $C_{R0} = 0$

Takes place in a batch reactor. After 8 minutes, conversion of A is 33.3 % while equilibrium conversion is 66.7 %. Find the rate equation for this reaction

Now, first let us discuss with the with the reversible process, now we have taken a very simple situation that, we have the if you look at here you know the first order reversible reaction is the given like this A to R and k 1 is the rate constant for the forward reaction and k 2 is the rate constant for the backward reaction.

Now, C A 0 C A 0, we will consider as the initial substrate concentration that is 0 and initial product concentration C R 0 equal to 0. I take place in a batch process and I want to tell you that you might be aware that what is called batch process, in the batch process we take the material suppose this is a reactor and in the reactor we take the substrate suppose A is the substrate, we take at a time and allow the reaction to take place and after the reaction is over you take it out. In between you are not putting anything to the reactor that this is we consider as a batch process.

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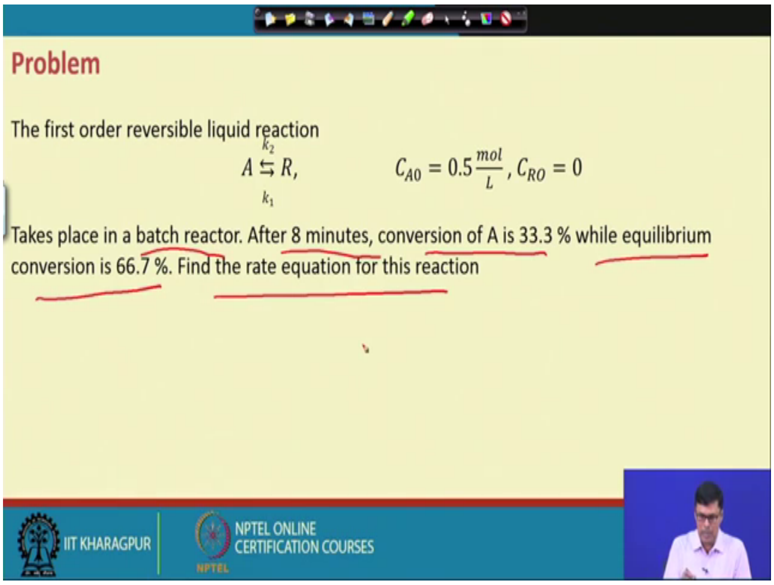

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Takes place in a batch reactor. After 8 minutes, conversion of A is 33.3 % while equilibrium conversion is 66.7 %. Find the rate equation for this reaction

So, in the batch process that that after 8 minutes this conversion of A is 33.3 percent while the equilibrium conversion is 66.7 percent find out the rate equation for this particular eq. Now what is the rate equation for this with the as for example, if you look at that rate of forward reaction and that we can find out in the next slide.

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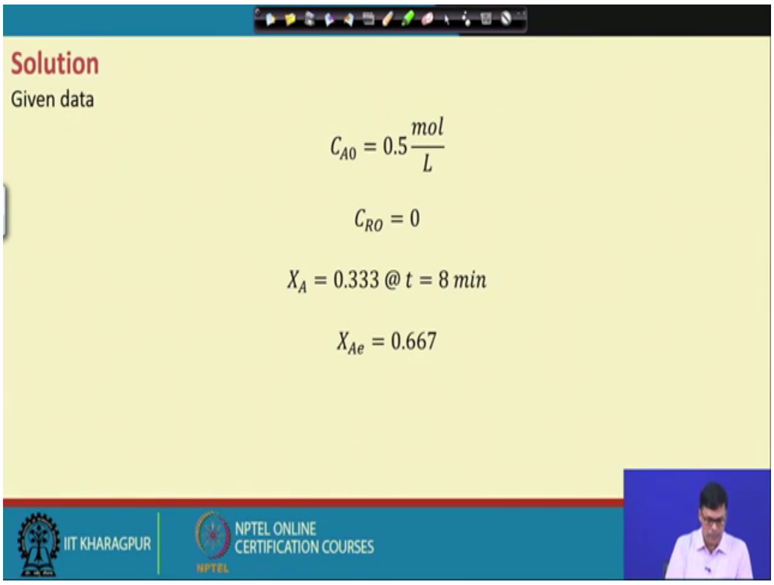

Solution

Given data

$$C_{A0} = 0.5\frac{mol}{L}$$

$$C_{RO} = 0$$

$$X_A = 0.333 \; @ \; t = 8\,min$$

$$X_{Ae} = 0.667$$

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This rate of we can write in terms of rate of substrate degradation or rate of product formation.

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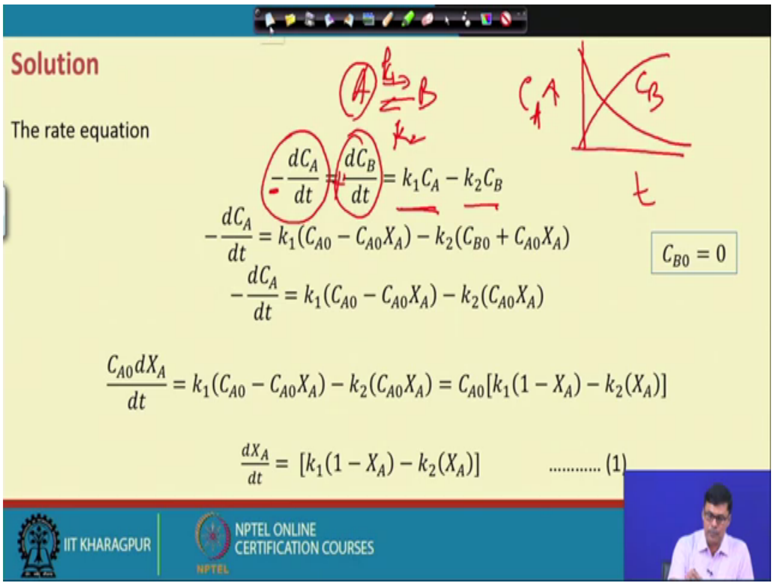

Solution

The rate equation

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

$$-\frac{dC_A}{dt} = \frac{dC_B}{dt} = k_1C_A - k_2C_B$$

$$-\frac{dC_A}{dt} = k_1(C_{A0} - C_{A0}X_A) - k_2(C_{B0} + C_{A0}X_A)$$

$$\boxed{C_{B0} = 0}$$

$$-\frac{dC_A}{dt} = k_1(C_{A0} - C_{A0}X_A) - k_2(C_{A0}X_A)$$

$$\frac{C_{A0}dX_A}{dt} = k_1(C_{A0} - C_{A0}X_A) - k_2(C_{A0}X_A) = C_{A0}[k_1(1 - X_A) - k_2(X_A)]$$

$$\frac{dX_A}{dt} = [k_1(1 - X_A) - k_2(X_A)] \qquad \text{............ (1)}$$

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Substrate degradation is this is A 2 A is converted to this is B; am I right, this is k 1 and this is k 2. So, it is like this minus when you when you when you talk about substrate it is like this this is C A and this is time.

The C A always will decrease with respect to time. So, it is negative slope. So, that is in the negative slope; they are negative. Now if you B we consider it is always this is C B.

So, it is positive slope. So, it is positive. So, here is positive here is negative now this is this is the k 1 into C A the k 1; k 1 into C A is the rate of forward reaction and k 2 into C B is the backward reaction. Now if you if you want to write in terms of that conversion that suppose we assume that we assume X A is the conversion.

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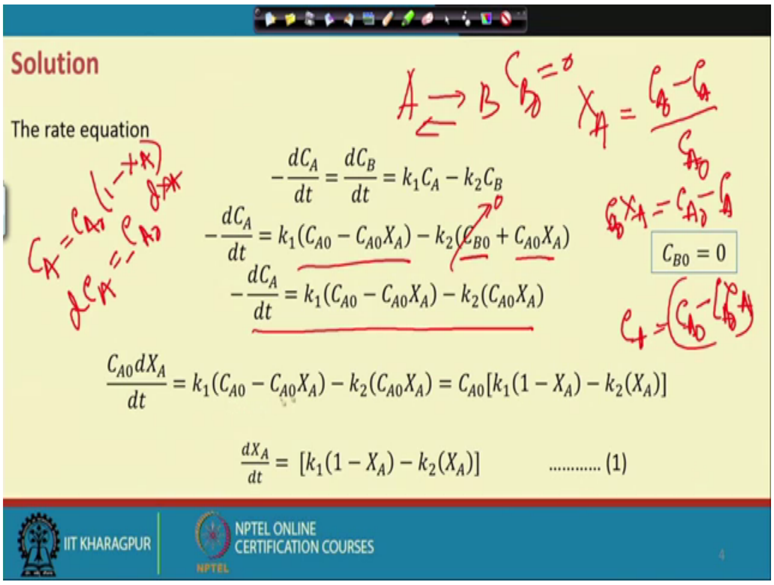

Solution

The rate equation

$$-\frac{dC_A}{dt} = \frac{dC_B}{dt} = k_1C_A - k_2C_B$$

$$-\frac{dC_A}{dt} = \underline{k_1(C_{A0} - C_{A0}X_A)} - k_2(\overset{0}{\cancel{C_{B0}}} + \underline{C_{A0}X_A})$$

$$\underline{-\frac{dC_A}{dt} = k_1(C_{A0} - C_{A0}X_A) - k_2(C_{A0}X_A)}$$

$$\frac{C_{A0}dX_A}{dt} = k_1(C_{A0} - C_{A0}X_A) - k_2(C_{A0}X_A) = C_{A0}[k_1(1 - X_A) - k_2(X_A)]$$

$$\frac{dX_A}{dt} = [k_1(1 - X_A) - k_2(X_A)] \qquad \text{............ (1)}$$

$$\boxed{C_{B0} = 0}$$

$A \rightleftarrows B$ $C_{B0} = 0$ $X_A = \frac{C_{A0} - C_A}{C_{A0}}$

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

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

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

$dC_A = -C_{A0}\, dX_A$

What is the X A; X A, I told you C A 0 minus C A by C A 0 this is the fraction that is converted.

So, this is C A 0 now so fraction that is converted. So, I can write that that you know this C A how you can write C A equal to here I can I can do this this is C A 0 into X A this is C A 0 we are equal to C A 0 minus C A. So, C A if you write C A equal to what C A 0 minus C A 0 into X A. So, this is exactly what we have written here. Now in case of B the situation is little bit different we have B it is the; whatever A is converted to B the way X A is converted. So, that that is that is C A 0 into x A is the that is the converted to B.

So, this will be C B 0 plus C A 0 into X A now here this equation we can we can if we assume that we have in this problem we have seen that C B 0 equal to 0 we have mentioned that C B 0 equal to 0 at time 0. So, if this is equal to 0 if it is 0 then this equation can be written in this form. Now once you write in this form then this equation this is C A what is C A C A equal to C A 0 into 1 minus X A and then we can write d C A is equal to what d C A equal to C A 0 is constant. So, I can write minus d X A, I can write like this. So, it is what we have written here that d and d C A equal to minus C A 0 into d X A this is equal to and this is the equation that we have and then we can take the c A 0 common whole figure I can take that 0 and this C A is 0 and this C A 0 we can cancel and if we cancel we will get d X A by t dt equal to k 1 into 1 minus X A minus k 2 into X A.

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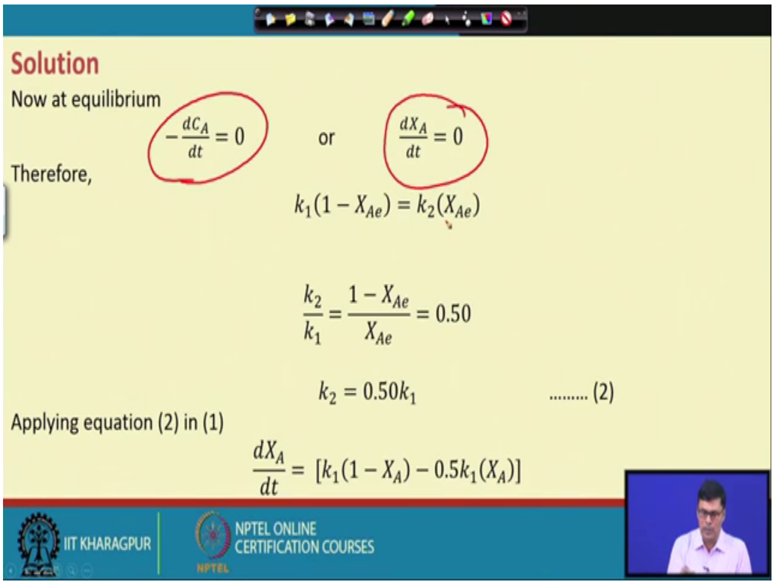

Solution

Now at equilibrium $-\frac{dC_A}{dt} = 0$ or $\frac{dX_A}{dt} = 0$

Therefore,

$$k_1(1 - X_{Ae}) = k_2(X_{Ae})$$

$$\frac{k_2}{k_1} = \frac{1 - X_{Ae}}{X_{Ae}} = 0.50$$

$$k_2 = 0.50k_1 \qquad \text{......... (2)}$$

Applying equation (2) in (1)

$$\frac{dX_A}{dt} = [k_1(1 - X_A) - 0.5k_1(X_A)]$$

Now, I had equilibrium condition I told you rate of forward reaction should be equal to rate of backward reaction. So, if it is like this then what will happen minus d C A by dt or db by d d cb by dt that should be equal to 0. Then this is equal to this we can we can also write in this form d X A by dt that also we should be equal to 0. That equilibrium condition k 1 into k 1 into 1 minus X A that should be equal to k 2 into X A. Now we can we can see it here that this is equal to 0.

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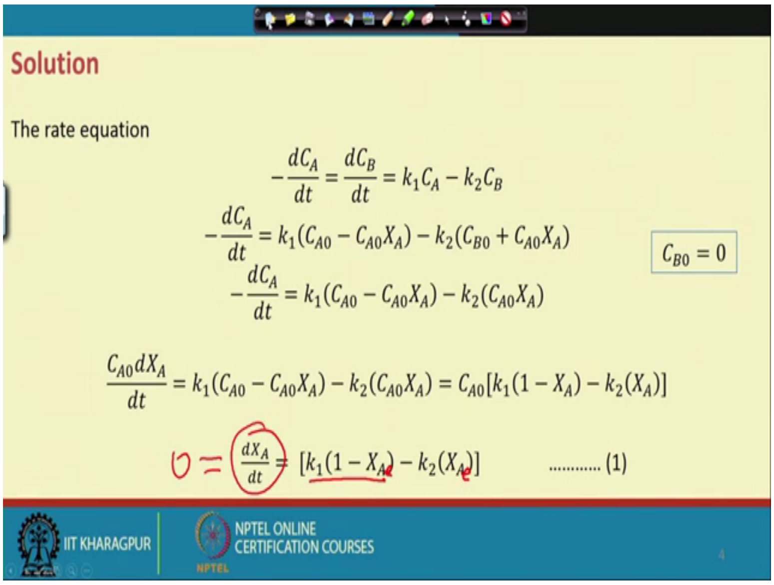

Solution

The rate equation

$$-\frac{dC_A}{dt} = \frac{dC_B}{dt} = k_1C_A - k_2C_B$$

$$-\frac{dC_A}{dt} = k_1(C_{A0} - C_{A0}X_A) - k_2(C_{B0} + C_{A0}X_A) \qquad \boxed{C_{B0} = 0}$$

$$-\frac{dC_A}{dt} = k_1(C_{A0} - C_{A0}X_A) - k_2(C_{A0}X_A)$$

$$\frac{C_{A0}dX_A}{dt} = k_1(C_{A0} - C_{A0}X_A) - k_2(C_{A0}X_A) = C_{A0}[k_1(1 - X_A) - k_2(X_A)]$$

$$0 = \boxed{\frac{dX_A}{dt}} = [\underline{k_1(1 - X_{Ae})} - k_2(X_{Ae})] \quad \text{..........} (1)$$

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If this is equal to 0 then we can write this say k 1 into 1 minus the X A and this X A we can mark it X A e e means equilibrium condition.

So, I can write here this is equilibrium condition and this is the equilibrium condition. So, what we have written here this is like this.

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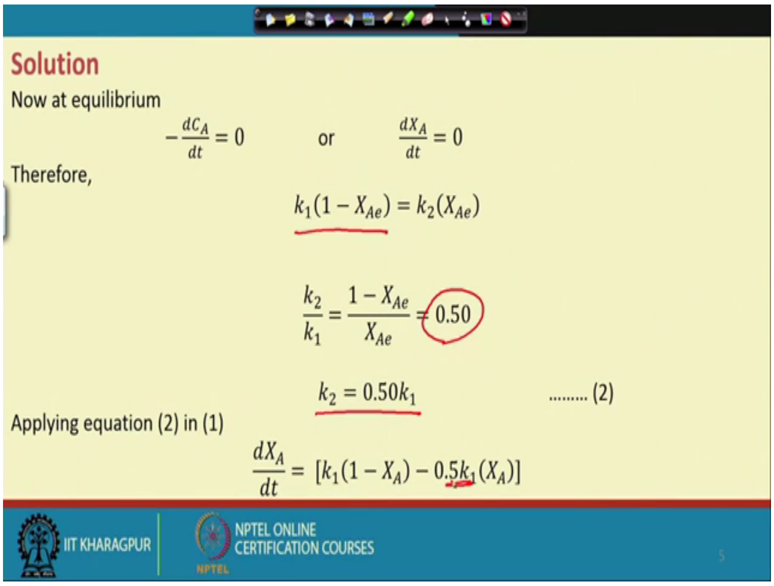

Solution

Now at equilibrium

$$-\frac{dC_A}{dt} = 0 \qquad \text{or} \qquad \frac{dX_A}{dt} = 0$$

Therefore,

$$\underline{k_1}(1 - X_{Ae}) = k_2(X_{Ae})$$

$$\frac{k_2}{k_1} = \frac{1 - X_{Ae}}{X_{Ae}} = \boxed{0.50}$$

$$\underline{k_2 = 0.50k_1} \quad \text{.........} (2)$$

Applying equation (2) in (1)

$$\frac{dX_A}{dt} = [k_1(1 - X_A) - 0.5k_1(X_A)]$$

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This is k 1 into 1 minus X A e equal to k 2 into X A e. So, k 2 by k 1 equal to this equal to 0.5 then we can write k 2 equal to k 2 equal to what 0.5 into k 1. Now this value we can prove the previous equation that I show you; this A this the k 2 value we can put it here.

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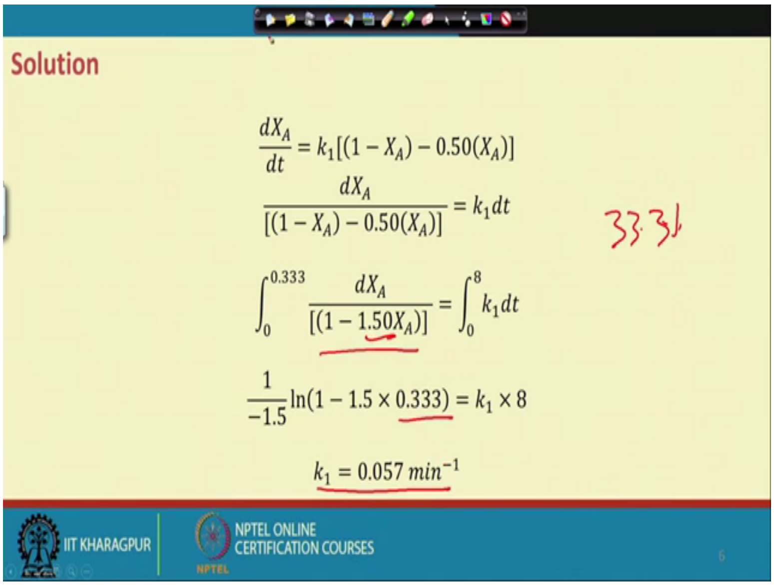

Solution

$$\frac{dX_A}{dt} = k_1[(1 - X_A) - 0.50(X_A)]$$

$$\frac{dX_A}{[(1 - X_A) - 0.50(X_A)]} = k_1 dt$$

33.3/

$$\int_0^{0.333} \frac{dX_A}{\underline{[(1 - 1.50X_A)]}} = \int_0^8 k_1 dt$$

$$\frac{1}{-1.5}\ln(1 - 1.5 \times \underline{0.333}) = k_1 \times 8$$

$$\underline{k_1 = 0.057\ min^{-1}}$$

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Then we can write this equation like this then finally, we can write this and it will come like this, then if you like in the log form it is 1 minus this. So, in 1.33 because the conversion 8 minute conversion is 33.3 percent so we can write 0.333 and this is the this is minus 1.5 and k 1 value we can easily calculate we can find out this is equal to 0.057 minutes inverse.

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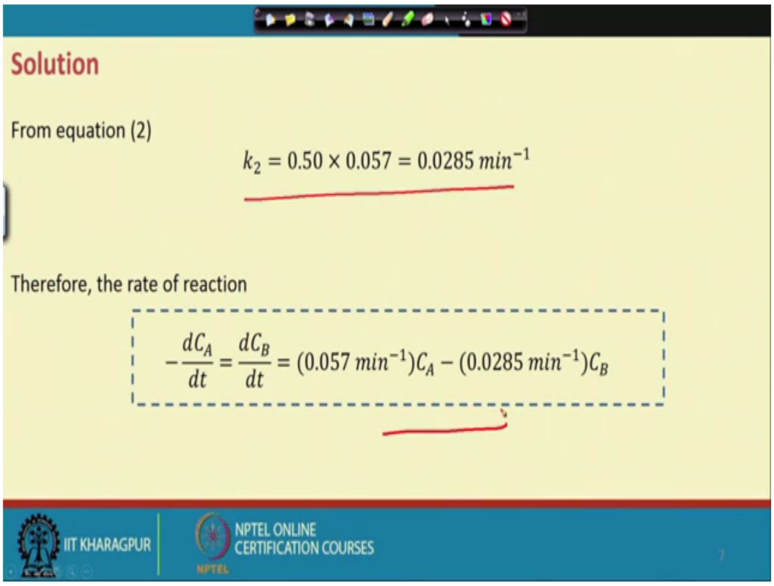

Solution

From equation (2)

$$\underline{k_2 = 0.50 \times 0.057 = 0.0285\ min^{-1}}$$

Therefore, the rate of reaction

$$\boxed{-\frac{dC_A}{dt} = \frac{dC_B}{dt} = (0.057\ min^{-1})C_A - (0.0285\ min^{-1})C_B}$$

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Then if you know the k 1 value then we can find out the k 2 value also, k 2 value we can calculate this we know the correlation we can form that we can find out this is 0.5 into this. So, what was the final rate expression that we have in the reversible process minus d C A by dt equal to minus d C B d C B by dt equal to 0.057 minute inverse into C A and 0.0285 minute inverse into the C B. So, this is the final equation that we have.

So, in a reversible reaction we can find out the rate expression very easily.

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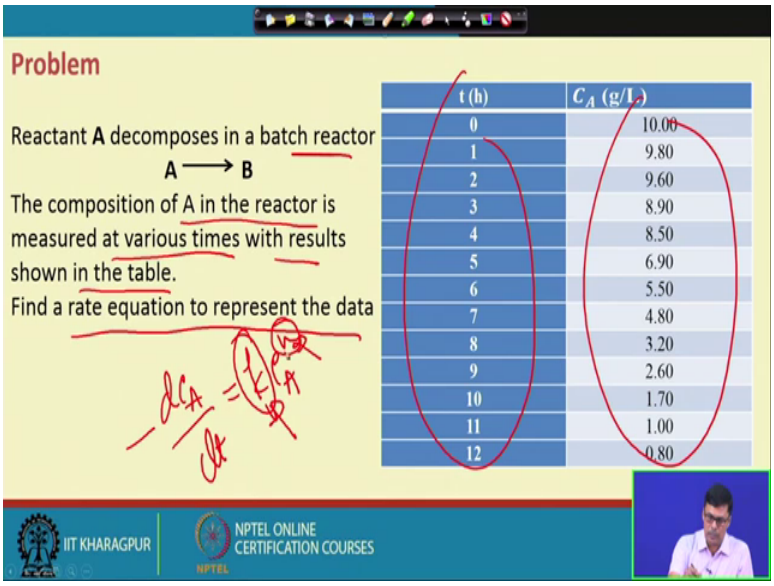

Problem

Reactant **A** decomposes in a batch reactor

$$A \longrightarrow B$$

The composition of A in the reactor is measured at various times with results shown in the table.

Find a rate equation to represent the data

$$-\frac{dC_A}{dt} = k C_A^{n}$$

t (h)	C_A (g/L)
0	10.00
1	9.80
2	9.60
3	8.90
4	8.50
5	6.90
6	5.50
7	4.80
8	3.20
9	2.60
10	1.70
11	1.00
12	0.80

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Now, let me go to the second problem second problem also very important and this is a little bit this is also with respect to the batch process and with that we have taken a different data you know that that numerical data and real process we want to analyze, them and try to let us see how we can analyze this process. The what is the problem is that reactant A decomposes in a batch reactor A to B the composition of A in the reactor is measured at the various time with the result shown in the table find out the rate equation to represent the. So, we shall have to what is the rate equation that we have here minus d C A by dt this is equal to k into C A to the power n.

So, what we shall have to do is we shall have to find out the value of kn n what is the k k is the rate constant n is the order of reaction; both the value from these experimental results we can we shall have to find out the both the value of k and n now question how we can find out.

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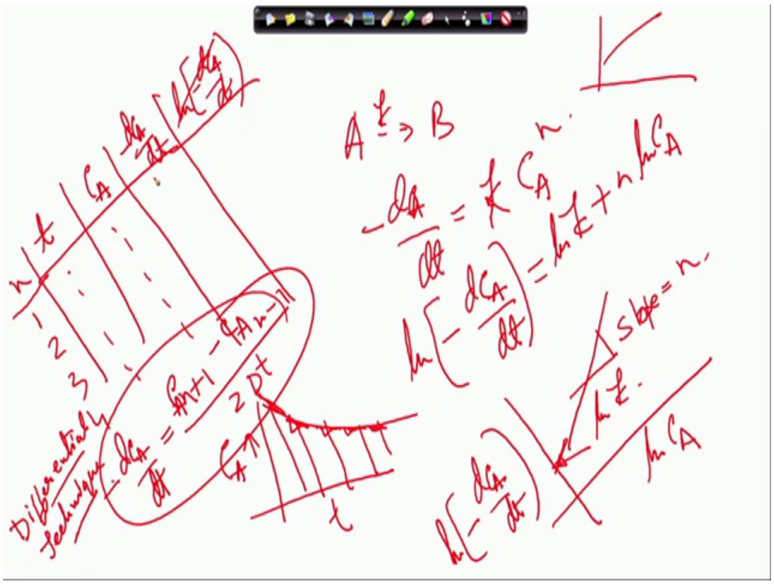

I showed you brief you before also that you know that how we can I can do it again this is like this that is minor d C A by dt this is equal to k 1 into C A to the power n. If we or we can take the 1 because this is single reaction we can simply write the k simple right the k that is good enough.

Now, this I can write that. So, we have in this in this problem, we have at different time, we have the t value we have at different t values, we have given that. Now what we can do here we can take log this is the natural log minus d C A by dt equal to ln k plus n ln C A. Now if we write this then if we plot minus ln d C A by dt versus ln C A will get a straight line and this slope will give you the value of n and the intercept will give you the value of ln k.

So, here you have different values this is this is given. So, you can easily find out what is the minus d C by dt and I told you that we use the differential technique what is the differential technique differential technique is that minus d C A by dt equal to C A n plus 1 minus C A n minus 1 divided by 2 del t and n is the sampling point this is n is the sampling 1 2 3 4 5. So, you know we can we can throw differential technique we can find out and where I try to mention why we use the differential technique because actually we if we look at the C A profile with respect to time if you plot it you will get this kind of plot.

Now, at different time if we want to make a slope. Now what you we shall have to do is we shall make a tangent here at the point of interest this point we shall have to make a tangent and the this tangent we can make a slope and this slope we shall have to calculate. Now question comes when we make A tangent there will be should be some kind of human error my tangent and you tangent will be little bit differ from each other.

So, that is called human error to avoid this kind of situation we go for differential technique this is called differential technique this is called differential technique that we use just to find out this that the minus da by d t. Now they so once you have this then you can have minus d C A ln d C A by dt or if you want to use directly you use the log graph paper we have different you log graph paper is available, you can pull directly the data here and you can have your slope here there you do not have to find the log here you directly you can and C A also you can log if your scale is log directly you can put the data and you can you can find this you can find the slope n.

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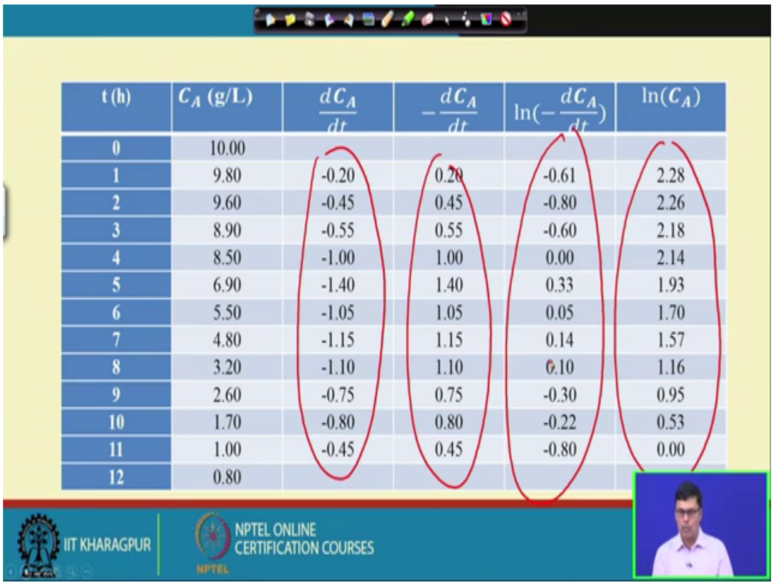

t (h)	C_A (g/L)	$\frac{dC_A}{dt}$	$-\frac{dC_A}{dt}$	$\ln(-\frac{dC_A}{dt})$	$\ln(C_A)$
0	10.00				
1	9.80	-0.20	0.20	-0.61	2.28
2	9.60	-0.45	0.45	-0.80	2.26
3	8.90	-0.55	0.55	-0.60	2.18
4	8.50	-1.00	1.00	0.00	2.14
5	6.90	-1.40	1.40	0.33	1.93
6	5.50	-1.05	1.05	0.05	1.70
7	4.80	-1.15	1.15	0.14	1.57
8	3.20	-1.10	1.10	0.10	1.16
9	2.60	-0.75	0.75	-0.30	0.95
10	1.70	-0.80	0.80	-0.22	0.53
11	1.00	-0.45	0.45	-0.80	0.00
12	0.80				

Now, this is how you can calculate. So, this is your time and C A that is given and through differential technique we can find out the value of d C A by dt this is all and then we can find out the this is d C A by dt minus you can have positive and this is like this and then we can we can take the log value log value we can easily find out and ln C A. In that case, if we have this log value, then you do not have to use the log graph paper normal graph paper will work if you have normal graph paper you could just put the value what do you call centimeter graph paper that will give you the slope.

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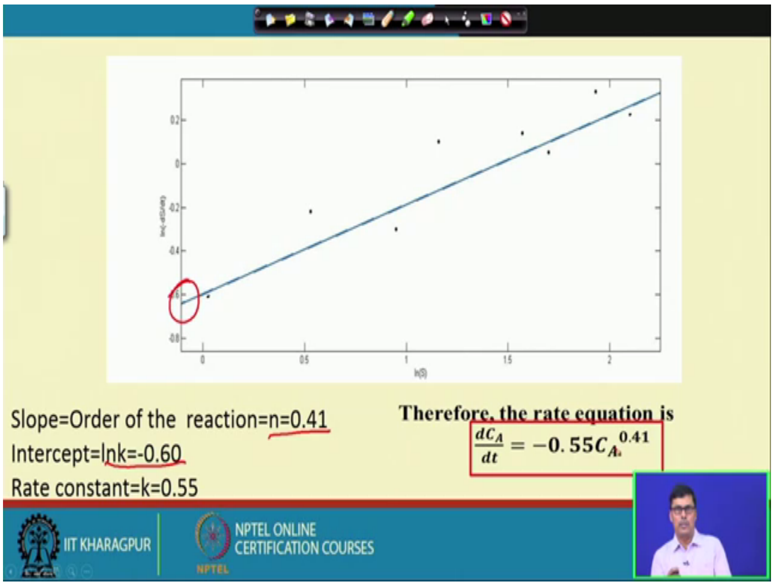

Slope=Order of the reaction=n=0.41

Intercept=lnk=-0.60

Rate constant=k=0.55

Therefore, the rate equation is

$$\boxed{\frac{dC_A}{dt} = -0.55C_A^{0.41}}$$

Now, this is exactly what we have done this is the normal graph paper you can see this is 0.8 point this is normal graph paper and if we plot we can have A straight line plot and from the slope we will get the n value is 0.41 and for the intercept we get the value of ln k that is 0.6 where k equal to 0.55. So, and our equation you can remember d C A by dt equal to minus this is minus was here do we be moving it here well minus 0.0.55 C A to the power 0.41. So, from the experimental results we can easily find out the rate equations and you know that I was talking about that you know once A; you find out this kind of equation though you can do the validation of the equation.

Let me show you how you can do the validation of the equation that is suppose in this in this equation what you have done you have find out d C A, by dt equal to 0.55 C A to the power some value you have taken make it 4.44 let us assume that.

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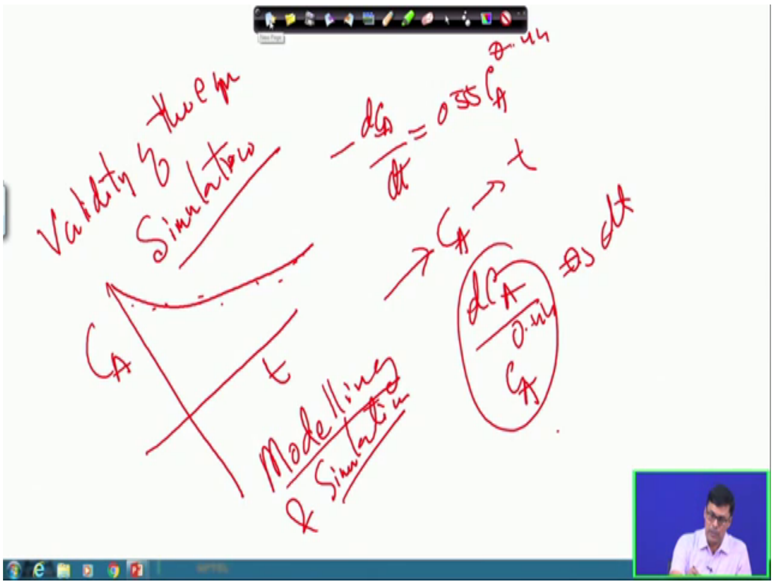

So, what I want to know then want to tell you. So, you from this if you solve this equation, you can find a correlation between C A and t, because you can you can bring in here d C A by C A to the power maybe 0.44 equal to dt 0.55 dt. So, you can solve it you can find the correlation between. So, you can have correlation between C A and t.

So, what you can do there you can put the different value of t in this equation you can find out the C A value. So, you have C A and t. So, theoretically you have you can draw this line like this theoretical at because n number of points you can take n number of t points. So, you can have the very nice plot here. Now then you put your experimental data, but in the table we have find that you put the data will be might be looking and looking like this and then you can find out the deviation percentage deviation of the experimental results from the theory result and find out what is the percentage of deviation. If we find the percentage of deviation is more than 5 percent then this is not acceptable you have to modify the equation, but if it is less than 5 percent then it is acceptable.

So, this is how we can what you call the validity of the equation validity of the equation or we call it the simulation. So, basically we have what you call when you write any equation mathematical equation we call it modeling, we call it modeling and modeling and simulation the modeling deals with the mathematical representation of the process and simulation deals with the validity of the mathematical equation about how much the validity we have as for your mathematical equation is concerned.

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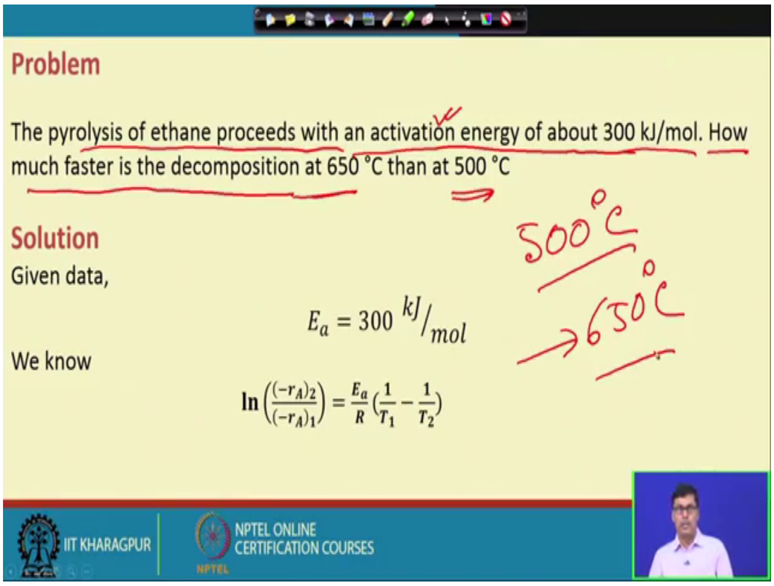

Problem

The pyrolysis of ethane proceeds with an activation energy of about 300 kJ/mol. How much faster is the decomposition at 650 °C than at 500 °C

Solution

Given data,

$$E_a = 300\ {}^{kJ}/_{mol}$$

We know

$$\ln\left(\frac{(-r_A)_2}{(-r_A)_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

500 °C

→ 650 °C

Now, let us let me go to the second next problem; the next problem this deals with the pyrolysis process that pyrolysis of ethane proceeds with A activation energy of about 300 kilo joules per mole. So, here I want to point out that in the last lecture we calculated the activation energy of a particularly process where in the particular process what we call pasteurization process. Now here the problem is little bit different, they here the activation energy is given and what we shall have to find out that how much faster is the decomposition, if we increase the temperature to 65; 650 degree centigrade form and that 500 degree centigrade.

So, this problem deals with that if we increase the temperature from 500 degree centigrade to 650 degree centigrade what is the how the rate of decomposition is increases. I hope that you know that what is called pasteurization process pasteurization process is kind of process where we burn the material in limited amount of oxygen not we incineration process means we give the give the of this efficiently oxygen to the for the for the for the burning of the material, but in the pyrolysis process we give the restricted amount of oxygen air to the process.

So, our product here mostly we have carbonaceous material with carbon and some kind of liquids formation that oil bio oil formations take place. Now here our this problem deals with that how we can find out that what is the if we increase the temperature what for how many fold up that rate of reaction increases.

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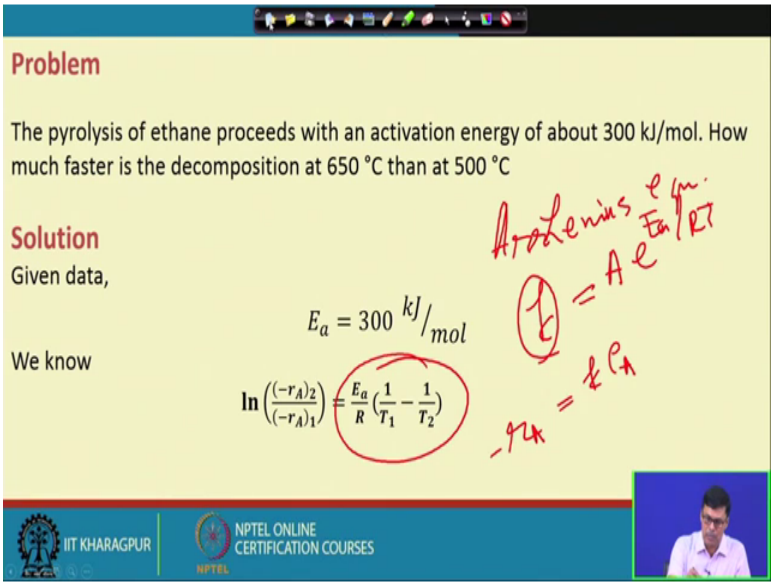

Problem

The pyrolysis of ethane proceeds with an activation energy of about 300 kJ/mol. How much faster is the decomposition at 650 °C than at 500 °C

Solution

Given data,

$$E_a = 300\ {}^{kJ}/_{mol}$$

We know

$$\ln\left(\frac{(-r_A)_2}{(-r_A)_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Arrhenius eqn.

$$k = A e^{E_a/RT}$$

$$-r_A = k C_A$$

So, if you look at this again I shall have to go to the Arrhenius equation Arrhenius equation is that k 1 or you know that let me take it out k equal to A e to the power E a by R T this is the equation that we have.

Now, in the rate equation we know that what is the rate r A equal to r rate equal to minus r A equal to k into C A. So, this k is proportional to re. So, I can write this; we can replace this with the r A value. So, at different temperatures so we can we have already shown you that how this the equation has been derived. So, let us see how this equation has been derived suppose we have k 1 into what you call at t 1 At T 1 t 1 equal to A e to power E A by R T 1 and we right the A t 2 we have k 2 equal to A e to the power minus E a by R T T 2.

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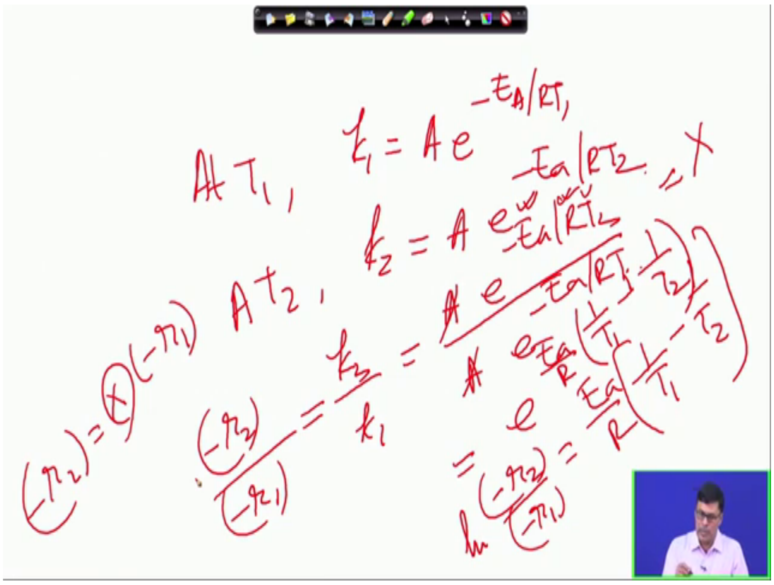

$$\text{At } T_1,\quad k_1 = A e^{-E_A/RT_1}$$

$$\text{At } T_2,\quad k_2 = A e^{-E_a/RT_2} = X$$

$$\frac{(-r_2)}{(-r_1)} = \frac{k_2}{k_1} = \frac{\cancel{A} e^{-E_a/RT_2}}{\cancel{A} e^{-E_a/RT_1}} = e^{\frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}$$

$$\ln \frac{(-r_2)}{(-r_1)} = \frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

$$(-r_2) = \boxed{X}(-r_1)$$

So, we can write the k 2 by k 1 is equal to A e to the power minus E a by R T 2 divided by A into e to the power minus E a by R T 2 divided by A into e t o the power e e A by r t 1. So, this this will cancel. So, I can write here I can write this is equal to minus r 2 and this is equal to or here you can write r 1 minus r 1 this is equal to like this. So, if you if you take it, but then what will you get e equal to then E a this is r 1. So, you can write E a by R I can take common 1 by T 1 minus 1 by T 2 this we can write.

So, if you take log this will be what minus r 2 by minus r A r 1 this is equal to E a by r 1 by T 1 minus 1 by T 2 T 2 is there. So, the in this problem what we have we have we shall have to find out or you know that here I can put this value because we shall have what fold up for the rate of reaction increases. So, simple we put this A value R value T value in the both the equation and we find out how many what is the result suppose we get X. So, X fold increase. So, I can write minus r 2 is equal to X into minus r 1.

So, X fold increase of reaction that will take place.

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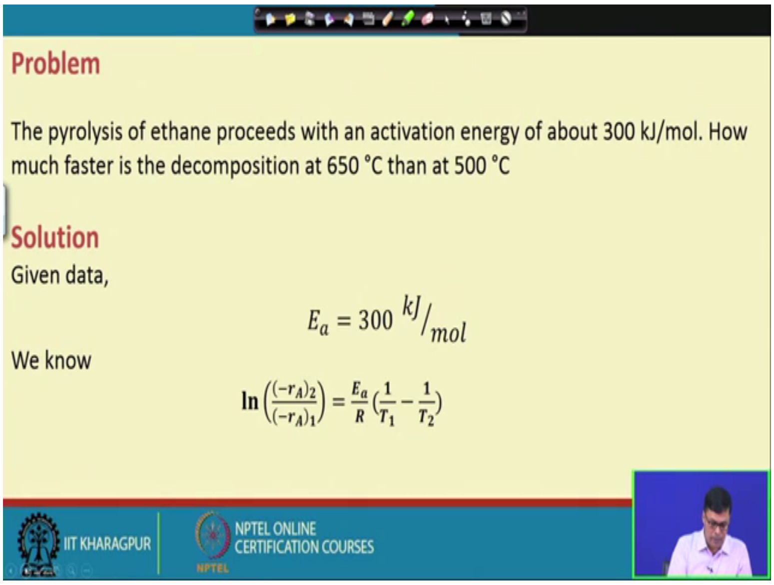

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So, this is this is this equation I showed you how it has come and then this is the this ln by this that the equation is that if you put the values and you will get this equation final equation you will get like this and this is coming like this.

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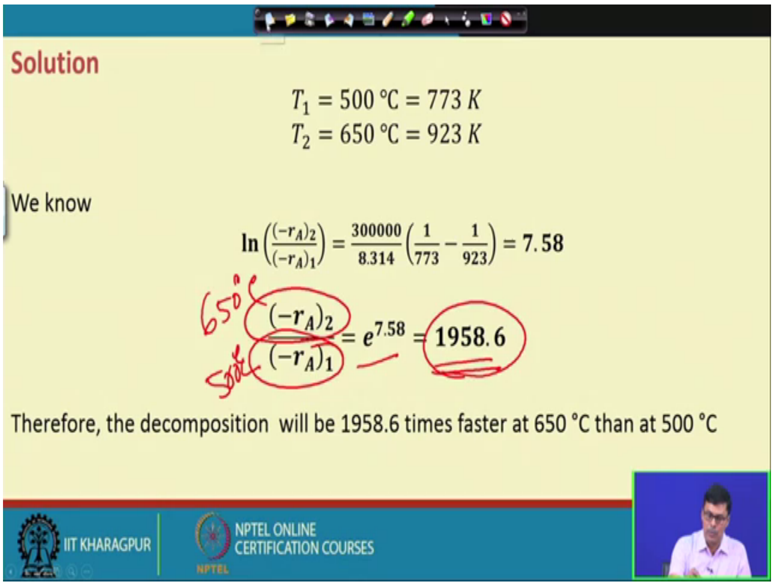

Solution

$$T_1 = 500\ °C = 773\ K$$
$$T_2 = 650\ °C = 923\ K$$

We know

$$\ln\left(\frac{(-r_A)_2}{(-r_A)_1}\right) = \frac{300000}{8.314}\left(\frac{1}{773} - \frac{1}{923}\right) = 7.58$$

$$\frac{(-r_A)_2}{(-r_A)_1} = e^{7.58} = 1958.6$$

650°C

500°C

Therefore, the decomposition will be 1958.6 times faster at 650 °C than at 500 °C

So, it indicates that you know that as I mentioned; that means, rate of that reaction as 650 degree centigrade this is 650 degrees centigrade and this is this is 500 degree centigrade. So, if you look at the difference that the as compared to say 500 degree centigrade 650 degree centigrade the rate of reaction will be 1958.6 volt.

So, this is A very interesting thing that you know that we can find out that by increasing temperature what is the percentage enhancement of the rate of reaction that take place in this particular lecture we try to discuss some kind of reversible reaction and the reversible reaction initially, we find out under equilibrium conditions the rate of forward reaction equal to rate of backward reaction and in that particular condition we can find out the ratio of we know the concentration because 66.7 percent of substrate converted. So, we can easily find out that A kc value kc value is A nothing, but concentration of product divided by concentration of substrate and which is equal to k 2 by k 1.

So, we can find out the relationship between the k k 2 and k 1 and then we can put the value in the our reversible reaction then we can solve this equation and find out the value of k 1 and once you know the k 1 we can calculate the value of k 2, then we can write the rate expression and I showed you how we can do the simulation of this particular equation because modeling in sim ,whenever we write any kind of mathematical model we shall have to validate mathematical model we always we shall have to compare with the experimental results and just to find out, what is the percentage deviation there if the deviation is less than 5 percent is acceptable is more than 5 percentage that have to modify this equation.

Then we discuss with another problem of this pyrolysis that is the first another problem of the reversible reaction where we try to find out experimentally how we can determine the value operate constants and the order of reaction that we estimated. And then finally, we discuss with discuss 1 pyrolysis process and in the pyrolysis process that are usually I told you pyrolysis process usually take place in the restricted amount of oxygen and this equation this particular problem deals with as you in enhance the temperature from 500 to 650 degree centigrade what is the how much fold of reaction that will take place.

So, this is the problem we discussed in that lecture I hope this will be useful to you to understand the process in a better way.

Thank you very much.