Course on Industrial Biotechnology Professor Debabrata Das Department of Biotechnology Indian Institute of Technology Kharagpur Lecture No 05 Chemical Reaction Kinetics

My next presentation is that chemical reaction kinetics, now in the chemical in the last class I discuss the how the different chemical reactions we can write the rate equations for the different type of reactions and we can remember that I told you that that if you look at the biochemical process the mostly the reactions that takes place either they are reversible in nature and also they are the chain reaction.

In the microorganism we have metabolic pathways in the metabolic pathways that that you have a series of reactions and you have you have different steps and the different steps and the individual steps are we have the reversible in nature. So we try to in the last lecture we come across this the reversible and in the reversible reaction we have forward reaction, we have backward reaction and we have come across the equilibrium constant kC which is nothing but equal to concentration of product divided by concentration of substrate.

Then also in the chain reaction we try to establish that how the concentration of different component in the reaction mixture can be expressed, that in the in the chain reaction we have different components A, B, C, D so how the different these components will keep on changing with respect to time and how we can develop the equation for that.

Fine 2:14) **Irreversible parallel reaction** $A \xrightarrow{k_1} R \\ A \xrightarrow{k_2} S$ **The rates of change of the three component** $-r_A = -\frac{dC_A}{dt} = k_1C_A + k_2C_A = (k_1 + k_2)C_A \\ r_R = \frac{dC_R}{dt} = k_1C_A \\ r_S = \frac{dC_S}{dt} = k_2C_A$

(Refer Slide Time 2:14)

Now today I want to go little bit more on this and you will find that other type of reaction that we have we have parallel reaction parallel reaction means that this is the substrate same substrate may be it is producing two different products this is R and S. So if you have this kind of two different products so we call it parallel reaction or site reaction, then the rate expression rate of substrate that degradation can be expressed as k1 into CA plus k2 into CA and here you can you can CA take the common k1 plus k2.

Then rate of formation R you can always express as k1 into CA and rate of formation of S you can the this is parallel reaction also we can write like this.

(Refer Slide Time 3:36)



Another very interesting thing is that autocatalytic reaction what is the autocatalytic reaction where A plus R and produce R and R is the product and R itself again as a catalyst to carry out the reaction. So that is that is why we call it autocatalytic reaction and if you take into the account in the microbial system particular it is largely applicable in the microbial system what is happening particularly in the (()) (3:31) fermentation process we use sugar for the formation of cell mass.

Now sugar is converted to cell mass and again again cell mass again it will like the substrate and produce cell mass. So this is a kind of autocatalytic reaction we can we can take into account.

Now if you have that kind of reaction how you can express this is rA equal to minus dCA by dt equal to k into CA by CR, when C0 is the initial concentration it can be expressed as CA

plus CR, CA0 plus CR0 is constant and rate expression can be written like this. So this is how we can express the autocatalytic reaction.

(Refer Slide Time 4:20)

Problems			
Problem 1:	t (h)	C_A (g/L)	
Reactant A decomposes in a batch reactor	0	10.00	
$A \longrightarrow B$	1	9.80	
The composition of A in the reactor is	2	9.60	
measured at various times with results	3	8.90	
shown in the table.	4	8.50	
Find a rate equation to represent the data	5	6.90	
	6	5.50	
	7	4.80	
	8	3.20	
	9	2.60	
	10	1.70	
	11	1.00	
	12	0.80	
Solution: Suppose order of the reaction is n. and kin Then, the rate equation is $\frac{dC_A}{dC_A} = \frac{1}{2}$	etic rate constant $-kC_A^n$	t is k.	
dt dt	A		
Taking exponential log both side of the equation			
$\begin{pmatrix} dC_A \end{pmatrix}$			
$\ln\left(-\frac{1}{\omega dt}\right) =$	$= n \ln(C_A) + \ln k$		
By plotting $\ln(-\frac{ds}{dt})$ vs $\ln(C_A)$			
Slope=n, intercept=lnk			

Now I am going to discuss some problems, now first problem that I want to discuss that is let us assume the reactant A decomposes in a batch reactor A to B and the composition in the A in the reactor is measured at various time with results showing in the table. Find the rate equation to represent the data, this is very simple simplest this problem that we have, what basically what I told suppose this is a reactor, we have reactor and what is the reaction we have A to B am I right.

So you take the A in the in the system A you take and let the batch process you take the material at a time, let the reaction takes place. Now at different time you draw the sample and and find out at different time what is the concentration of CA, that has been given in this problem. So you have to find out the rate equation, what is the rate equation, actually we have we have shown you this rate equation for this will be minus dCA by dt equal to k into CA to the power n, am I right. Where k is the rate constant and n is the order of reaction.

So we shall have to find out both these things, so if we want to do what we shall have to do that that we can take a log here you can see you can take a log here minus dCA by dt equal to n log minus sign I can take it here lnCA and (ln) plus lnk there I can write like this and if you plot log log graph paper. Now what we can plot this is (()) (6:25) I can I can plot ln minus dCA by dt and this is ln CA, if you do this you will get a straight line and slope this is slope will give you the value of n and and this intercept will give you the value of lnk. So you can find out the A and k value.

(Refer Slide Time: 7:00)

t (h)	$C_A (g/L)$	$\frac{dC_A}{dt}$	$-\frac{dC_A}{dt}$	$\ln(-\frac{dC_A}{dt})$	$\ln(\mathcal{C}_A)$
0	10.00			<i>a.</i>	
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				
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So in this problem how you will solve I can show you, so here you you see that we have different C and we find out dCA by dt. Now how you calculate the dCA by dt let me show you, minus dCA by dt, I can calculate like this (()) (7:16) CAn plus 1 minus CAn minus 1 divided by 2 del T, this is called differential technique this is called differential technique, very simple what is the n is the is the sampling number sampling number so you have suppose here here you put n and n 1, 2, 3, 4 like this you can have different numbers and this us site n n you see that here CAn plus 1.

Now if you consider here n plus 1 means at this point if you want to calculate minus dCA by dt, how you can calculate how you can calculate that CAn plus 1 that means you have to take the value here CA2, then CAn minus 1, that means 1 minus 1 equal to 0, so initially at the 0

(()) (8:33) whatever the concentration is there you you find out and that difference and 2T del T, what is the time difference, del T is the time difference you multiply that very simple you can do that.

So you can write this value, though this is how this table has been prepared, this is the we have this values, then we take the log value and then log CA value is given there.

(Refer Slide Time: 8:58)



Then we can have log log graph paper, we plot this and we within we find out the value of the k value is 0.55, n value is 0.41 and so your equation is coming like this.

Now I want to add little bit here because suppose this equation is coming like this dCA by dt equal to minus 0.55 CA to the power 0.41, ok. So we we get the value of k, we get the value

of n. Now here this is the correlation between CA and T, so I can write this how I can write this equation dCA by CA to the power 0.41 this is equal to minus 0.55 into dt. So you can easily find out we can find out the correlation between CA.

Now we can put the value at different time we can find out the value of CA, so what you can do that this CA value we have already determined that in the (()) (10:17) system that experimental value we have this is experimental value. Now we can calculate theoretical also and we can assume the t, we can we can we can assume the value of t and we can find out the corresponding value of CA.

So these point I can I can write it here and we can find out what is the what you call theoretical value and then compare with the experimental value and try to find out the deviation and if your deviation is more than 5 percent then this equation is not valid but if it is less than 5 percent then we can (()) (11:03) this is called what you call modeling and simulation, that also I want to point out this is I can elaborate this like this.

(Refer Slide Time: 11:12)





Now second problem is very interesting that milk is pasteurized if it is heated to 63 degree centigrade for 30 minutes, we know pasteurization what is pasteurization pasteurization is process through which we can remove the pathogenic organisms, ok and but if it is heated to 74 degree centigrade it only needs 15 seconds for the same results. You know that there is a technique called HTST technique what is the HTST technique high temperature short time, this is usually applicable with the industry, why because if you use the HTST technique then the quality of the product we can maintain to a great extent and what in this problem what you have to find out the activation energy of this sterilization process, very interesting that problem that we have.

So what is the data given that 30 minutes at temperature T this is the 63 degree centigrade so equivalent kelvin temperature will be 336 degree kelvin, the 15 then 15 seconds this is

mistake this is 15 seconds and this is this is will be 347 so please make the correction here and and this equation is like this k equal to k0e to the power E by RT, what is k0 it (()) (12:41) constant E is the activation energy, R is the gas constant, this is the absolute temperature.

Now I can write this equation like this and and reaction time we have already seen what is the reaction time rate of reaction minus dCA by dt, reaction time always inversely proportional to time. If the time the time time is less than the rate of reaction should be high the inversely proportional, if the time is more that means the rate of reaction will be less. So this is the this is the so we can write ln k2 by k1 equal to ln t1 by t2, Ea R and 1 by Ta minus 1 by then we can find out the Ea equal to 422000 Jules per mole. So this is the activation energy of this reaction.

So this is simply how we can calculate the activation energy (()) (13:43) chemical reaction. So we we if we anybody interested to find out the activation energy of a chemical process that you taken it will be find out if they have the data with the with the at different temperatures.

(Refer Slide Time: 14:00)

Problem:			
Liquid A decomposes by first-order kinetics, and in a batch reactor 50% of A is			
converted in a 5-minute run. How much longer would it take to reach 75%			
conversion?			
Solution:			
Given data, $K_{i} = 0.50 \ t_{i} = 5 \ min$			
$X_{A13} = 0.50, t_1 = 5 min$ $X_{12} = 0.75, t_2 = 7$			
For 1 st order reaction			
$-r_A = -\frac{dC_A}{dt} = kC_A$			
Where, $k \rightarrow$ reaction rate constant			
Integrating, $-\int_{C_{A0}}^{C_A} \frac{dC_A}{c_A} = \int_0^t k dt$			
$-\ln\left(\frac{C_A}{C_{A0}}\right) = kt$			

A - B. 50% A . Converted in

The next problem that I have the liquid A decomposes by first-order kinetics (()) (14:10) this is A liquid A decomposes first-order kinetics in a batch reaction 50 percent A is converted in 5 minutes run. How much how longer would it take to reach 75 percent conversion?

So the simple the reaction is the situation is something like this, so you have A to B reaction that we have so what is saying the 50 percent of A will be converted in 5 minutes, am I right. Now what the question comes that for the conversion of 75 percent of A how much time is required, ok how much time is required, ok.

So what we have done here is see that minus rA as rightly we know that that will be minus dCA by dt in a k into CA we assume this is the first-order this is already mention first-order kinetics. Now this is the this is range between CA0 to CA and k into dt, this we can write ln CA by C kt.

(Refer Slide Time: 15:35)

Integrating,	$-\int_{C_{c}}^{C_{A}}\frac{dC_{A}}{c}=\int_{0}^{t}kdt$	
	$-\ln\left(\frac{\overrightarrow{C_A}}{\overrightarrow{C_A}}\right) = kt$	
It is known that	$C_A = C_{A0}(1 - X_A)$	
Now,	$-\ln\left(\frac{C_{A0}(1-X_A)}{C_{A0}}\right) = kt$	
	$-\ln\left(\frac{(1-X_A)}{1}\right) = kt$	
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Then then we can we have come across this equation CA equal to CA0 1 minus XA XA is the fraction of A that is converted so we can come across this equation.

(Refer Slide Time: 15:47)

It can be written $\frac{\ln(1 - X_{A2})}{\ln(1 - X_{A1})} = \frac{t_2}{t_1}$ $t_2 = t_1 \times \frac{\ln(1 - X_{A2})}{\ln(1 - X_{A1})}$	
Putting all the known values $t_2 = 5 \times \frac{\ln(1 - 0.75)}{\ln(1 - 0.50)}$ $t_2 = 5 \times 2$	
$t_2 = 10 min$	
Therefore, 75% conversion will be achieved in 10 minutes	
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And finally we we can write that the conversion of A this is this is the t2 and t1, the two time conversion and if you take the ratio and finally we can find out the t2 that is coming about 10 minutes. So 75 percent initially that we the question was that for (()) (16:10) conversion take place 5 mean 5 minutes 75 percent conversion take place how much time is required, answer is 10 minutes, so very simple that we have.

So we can easily calculate this that if we if we know if you can do the analysis of the system and this is very much required for our biochemical processes because there our substrate is converted into product and we are interested that to find out that how much time is required to get the desired conversion of the product that you know that is that we time to time we can find out and I have several problem that there we can find out which one is economic if we go for 99 percent conversion whether it is economic or 90 percent conversion we have some problem we have some problem we can discuss in due course and we can we can do the analysis of the process.

(Refer Slide Time: 17:11)



Now the last problem that I going to discuss that is the again the I told you the biological process is a chain reaction A to R and R to S, so we have two rate constant one is k1 and k2.

Now what what you have to find out that at t0 CA equal to CA0, CR0 equal to CS0 that is the the equal to 0, to find out the maximum concentration of R and when it tmax when k1 equal to k2.

What is here what we are basically looking for that that that that we have seen in the chain reaction when you have the profile with respect to time, this is the concentration then this CA will keep on decreasing with respect to this is A to R R to S, so this CA will decrease with respect to time like this, then R will decrease like this, this is CR and if you look at CS this will be like this, this is the CS, the concentration of C will be like this.

Now what we are in this problem what they are looking for that here this is the intermediate concentration of the product. Now question come at what time we can attain the maximum value this is called this is what is this is this is called CR max and we here we call tmax, the tmax is the time at which the R the intermediate that concentration of the product that will be maximum.

So this this problem deals with that let us and and at the same time they mention that what will happen when k1 equal to k2.

Assignment:	
The chain reaction $A \xrightarrow{k_1} R \xrightarrow{k_2}$	s
The rate equations are	
$r_A = \frac{dC_A}{dt} =$	$-k_1C_A$
$r_R = \frac{dC_R}{dt}$	$=k_1C_A-k_2C_R$
$r_S = \frac{dC_S}{dt}$	$= k_2 C_R$
Integrating the 1 st rate equation (r_A)	,
$-\ln\left(\frac{c}{c_{\lambda}}\right)$	$\left(\frac{4}{0}\right) = kt$
Or, $C_A = C_A$	$_{40}e^{-kt}$
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(Refer Slide Time: 19:12)

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Then let us see this how we have solved this problem. Now we we know the rate equation this is rA this is the rA equal to that dCA by dt minus there is k1 into CA, rR equal to this and this is rate of forward reaction, this is rate (forward) backward reaction and rS equal to k2 into CR, that we have seen in the last class. Now here that you know that when you take the first reaction that we have already seen that minus dCA by dt equal to k1 into CA, am I right.

So we can write minus dCA by CA equal to k1 into dt. Now here this is equal to dln CA minus this is equal to k into dt, this will be what CA0 to CA and this is 0 to t, k is constant. So what we can write ln minus CA by CA0 k into t, so the CA by CA0 will be what will be e to the power minus kt, what will be CA CA equal to CA0 into e to the power minus k into t, so we can easily find out this is how it has it has it has it has find out here we can easily see that.

(Refer Slide Time: 20:54)



And now if you if you come to the next step that we have the rate of formation of that you know that R that how this how it is so we have this equation already we have this equation how we can write that dCR by dt plus k2 into CR, am I right this is equal to k1 into CA, this is what we have done in the last second case this is like this. Now the CA this is k1 CA we already we determined CA equal to CA0 e to the power minus k1t, ok.

Now if you multiply it both sides now here what is happening k1 equal to k2 k21 equal to k2 and multiplying both sides by by e to the power (mi) k1t, if we multiply it by this what we will what we will get we will get this equation, we will get this equation, this is e to the dCR by dt k1 into CR e to the power this and this is and, now here e to the power k1t into e to the power k1t minus k1t this will cancel each other this will be 1, am I right and and so this will

be what this will be nothing but this equation if you if you look at that e to the power k1t dCR by dt k1 CR e to the power k1t this is plus equal to k1 CA0 am I right, that is cancel.

Now here this is nothing but d e to the power k1t into R CR by dt this is equal to k1 into CA0, ok. Now this equation this so the what we can write now e to the power k1t into CR here CR equal to k1 CA0 0 to t this is dt plus constant, so this we can write like this.

Now now here we can put the boundary condition what is the boundary condition boundary condition is that that at t equal to 0, because we have seen that you know profile that this is like this, this is CA and this is you have CR. So here this is the 0, this is time, this is concentration. So at time t 0 I can assume CR equal to 0, this is equal to 0, and if CR equal to 0 then this will be 0, this constant will be this they will be equal to this is the k1 constant will be will be 0, because this is also 0, this is also 0, so constant will be 0.

So here whole equation will be what equation will be CR will be equal to I what I can write CR equal to k1 CA0t e to the power minus k1t, because I I took this the k k k1t this side so it is minus k1t.

(Refer Slide Time: 25:18)

If the desire	e product is R, have to achieve $C_{R,max}$	
For $C_{R,max}$,	$\frac{dt}{dt} = 0$ ($\omega t = t_{max}$	
	$\frac{dC_R}{dt} = k_1 C_{A0} \{ e^{-k_1 t} - e^{-k_1 t} \times k_1 t \} = 0$	
	$e^{-k_1t} - e^{-k_1t} \times k_1t = 0$	$[e^{-k_1t} \neq 0]$
	$t_{max} = \frac{1}{k_1}$	
	$C_{R,max} = k_1 C_{A0} e^{-k_1 t_{max}} \times t_{max}$	
	$C_{R,max} = k_1 C_{A0} e^{-k_1 \times \frac{1}{k_1}} \times \frac{1}{k_1}$	
	$C_{R,max} = \frac{C_{A0}}{e} = 0.3678C_{A0}$	
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 $C_R = E G_0 t e^{-4T}$ E=E=E. dia = & Go (e- Et + e E, te C1

Now if you come this side, then if you if you do the differentiation dCR by dt how we can do this what is the two variables we have this, this and this.

So we can write k1 k into CA0 I can take this and this is differentiation with respect to t this will be minus k1t kt not k1t because k1 equal to I can write k1 equal to k2 equal to k, I can write like this, so it is k kt then we have minus then what I can write that t will be there and this will be k1t into e to the power k1t, this we can write this and this is equal to 0 because because I I if you if you look at here that CR by respect to time at this at this particular when when tmax the CR by dt this will be rate of formation of CR that should be equal to 0, that will be under steady state (cond) this will be 0, under steady state condition this will be 0.

So this is the conditions so at tmax it will be 0, now this cannot be 0, so if this cannot be 0 I can assume this this is equal to 0, so I can write e to the power minus kt equal to k1 into t e to the power minus kt, am I right, this, this will get cancel. So I can write the t equal to 1 minus k, this we can write. So this is the this is the tmax value now this tmax value now we have the expression for already we have the expression for CR the in the thus I can write CR max how we can write CR max equal to k into CA0 t is what 1 by k e to the power this is minus k multiplied by 1 by k, so this is this will cancel, this will be minus and this is this will cancel.

So I can write this is CA0 to the power e, so and e value this is equal to 0.3678 into CA0. So I can easily calculate the value of CR what is the maximum value of CR I can easily calculate in this particular problem. So so in conclusion I want to tell that is it it is possible to write the rate equations it is any any kind of rate equation we can we can easily write we can also find out rate constant we can find out the order of reaction and then we can we can because this

this is very much required to find out the correlation between the substrate concentration and the time because the because the because the any when we carry out any kind of reaction we are interested to find out at what time we have what percentage of substrate conversion takes place.

I was talking about that in the industry when we carry out any kind of reaction that naturally most of the industry we are looking for efficient process and efficient process we wanted to have higher substrate conversion efficiency. Now when you go for the higher substrate conversion efficiencies we require more time. Now question comes whether it is economic or not.

So that we shall have to find out and for that the preliminary thing that we should know that how to determine the time required for that conversion I hope this will be very useful for you for for finding out the time of (conver) time required for getting a desired conversion of any kind of chemical or biochemical process, thank you.