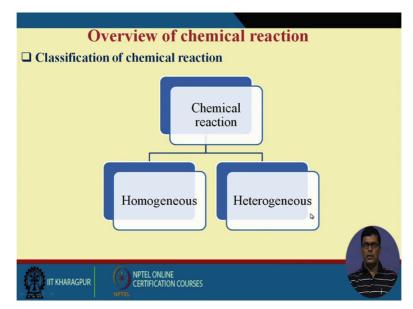
Course on Industrial Biotechnology Professor Debabrata Das Department of Biotechnology Indian Institute of Technology Kharagpur Lecture No 04 Chemical Reaction Kinetics

Now I am going to discuss about the Chemical reaction kinetics as we know that our fermentation industry is the or you know biochemical industry is one of the major unit that we have that is the bioprocess and in the bioprocess that the biochemical reaction that takes place. Now question comes that how the reaction takes place to understand this mode of reactions and how to study the kinetics of those reaction first we should we should we should know how the chemical reaction takes place, how study the chemical kinetics then we can come to the biochemical reaction kinetics.

So today I want to discuss the chemical reaction kinetics and here I want to tell that this reaction usually takes place in a reactor and reactor basically is a vessel where the chemical reaction takes place and and bioreactor basically vessel in which reaction takes place in presence of the biomolecules.

(Refer Slide Time: 1:31)



So so first I want to give the overall this know what is the classification of the chemical reactions we have this this all the chemical reaction can be classified in two different class one is called homogeneous reaction and another is the heterogeneous reaction.

(Refer Slide Time: 1:53)

Classification of chemical reaction
 Homogeneous reaction The reaction takes place in one phase alone e.g. formation of ammonia from hydrogen and nitrogen; conversion of glucose to fructose by glucose isomerase etc.
 Heterogeneous reaction
At least two phases are required to proceed the reaction e.g. burning of wood; microbial reaction etc.
Simultaneous mass transfer and reaction occur
If diffusion rate> reaction rate, then reaction is controlling factor
> If diffusion rate< reaction rate. Diffusion is controlling factor
IIT KHARAGPUR OPTEL ONLINE CERTIFICATION COURSES

Now what question comes what is homogenous reaction and what is heterogeneous reaction. Now homogeneous reaction means if the reaction takes place we know there are three different phases one is gas, another is liquid, and another is solid. If the reaction takes place in only one phase we call it homogeneous reaction and mostly that in the solid actually there is no reaction takes place. So mostly the reaction takes place either in the gaseous phase and in liquid phase.

If the reaction takes place only in the liquid phase we call it homogeneous reaction, if it takes place only in gaseous phase we call it the homogeneous. Now examples suppose the ammonia formation with the help of nitrogen and hydrogen, this is all are gas because the nitrogen is gas, hydrogen is gas (())(2:41) ammonia is also gas. So this is a pure what you call homogeneous reaction.

Now we have different examples of the enzymatic reactions, as for example I told you the glucose when we go and we convert into fructose because fructose we know it is 10 times sweeter than glucose and this is largely used for the diabetics patients and we use the enzyme called glucose isomerase enzyme. So naturally the all are remain in the one phase liquid phase that is why we call it homogeneous reaction.

Now next is the heterogeneous reaction heterogeneous reaction means it it it should contains more than one phase because either minimum two phase should be present in the reaction mixture, I can I can give a very simple example of the burning of wood because when wood we burn in presence of oxygen it produce carbon dioxide and water. So you know that your product is gas, your wood is solid material burnt then react with the oxygen that is in the gaseous form. So this is the example of the heterogeneous reaction.

Now we talk about the microbial reaction microbial fermentation process in the microbial fermentation process what we have basically do we we use the microorganism in the microorganism they are insoluble mass that then they use any take the the soluble material from the fermentation block and and they use for their growth and metabolism purpose and we get our desired product. So so this is the example because the one is your burning of wood another is the microbial fermentation process that is the example of heterogeneous reaction kinetics.

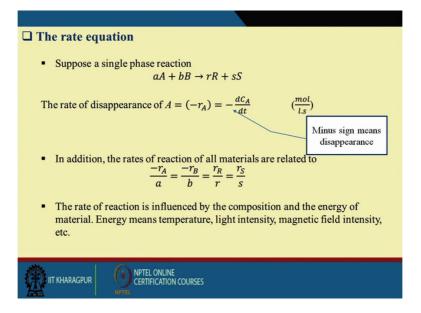
Now question comes how it is differ from the homogeneous reaction. Now in case of heterogeneous reaction what is happening since there is a presence of two phases, one phase should come in contact with the other phase then and only then the reaction will take place otherwise no reaction will take place.

So you know that when the one phase come in contact with the other phase we call it diffusion this is they diffuse to the surface and then when they react and forms the product then again it should diffuse back to the bulk. So you know that diffusion phenomena plays very important role in the in the in the heterogeneous reaction process, so here two things simultaneously takes place the diffusion as well as the reaction.

Now now very interesting thing that if the diffusion rate is more as compare to rate of reaction then reaction is the controlling factor. So because what what do you mean by that because if you because if we want to improve the rate of product formation process than what we will have to do we shall have to improve the reaction rate then only we can get the more product when rate of diffusion is more in case of rate of reaction.

Now in case of reverse if rate of diffusion is less as compared to rate of reaction than you have to increase the diffusion. So that your product formation can be increased. So these are the things how we can we can we can we can handle so to get the more product formation in the process. So now the reactions that I am going to discuss here that how the simple reaction and how we can analyze this reaction.

(Refer Slide Time: 6:28)

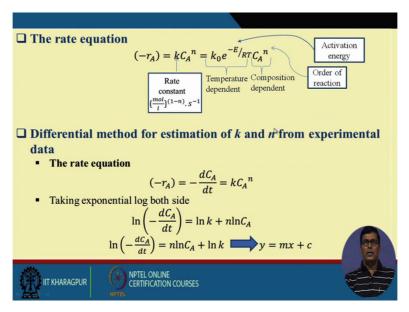


This is I want to give you very typical examples one or two examples that I shall give you, this is the aA plus bB with the rR and sS, this is if you write the rate of disappearance of A it is minus rA equal to minus dCA by dt why why minus because the A is the substrate as the reaction take place then with respect to time if you look at the profile that they keep on decreasing with respect to time.

So rate of degradation of the substrate is considered the negative profile and rate of formation of the product this is positive it will keep on increasing with respect to time. Now if you look at if you look at rate of formation of R obviously it will plus dCR by dt rate of formation of that is also the rate of formation of product that we can write. Now if you if you if we want to want to relate correlate all this rate of reaction I can write like this rA by a equal to minus rB by b equal to rR by r and rS by r this is how you can (())(7:44) this reaction.

Rate of reaction influence by the composition and the and the energy of material. Energy means temperature, light intensity, magnetic field intensity, etc. So these are the different now here again I want to again point out the the unit of this is very important, if this is this is CA is the concentration of A and CA is concentration of A usually express moles per unit volume moles per liter, moles per it can be it can be expressed in other way also it can be expressed mass per unit volume grounds per liter it can be used any any kg per cubic meter whatever it is. And time can be expressed in the in seconds, minutes, hours whatever we can this is how we can express the rate.

(Refer Slide Time: 8:38)

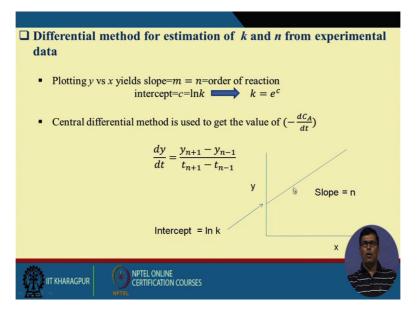


Now here the rate rate of suppose simple rate of reaction how we can write A convert it to B how we can write this rate expression minus rA equal to k into CA to the power n, what is k k is the rate constant and what is the n n is the order of reaction.

Now both are the experimental parameter and how this this experimental as shown you how the experimental parameter we can determine and k again depends on temperature as for (()) (9:11) equation this k equal to k0e to the power E by RA and I was talking about in the last class I was talking about the E is the activation energy so that if we study this reaction at different temperature then we can determine the activation energy of the particular reaction that we can determine.

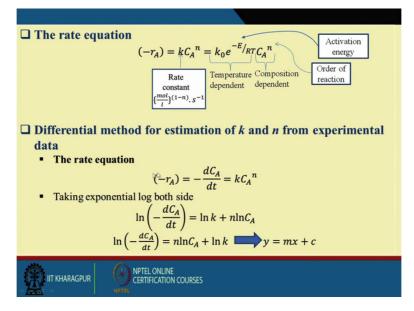
Now now let me come back here that when there is a nth order reaction the expression is ythis minus rA equal to minus dCA by dt k into CA to the power n. If you take the log it will be it will be what minus log minus dCA by dt equal to log k this is k plus n this is n will come here n log CA, am I right. So this is this is equal to this is nothing but similar to the your straight line equation this is y equal to mx plus c, because but only the problem is that this here you have to plot the log log in the log log graph paper, because this is log log minus dCA by dt and this is log because this is constant the k is constant k is not the variable. So CA is the variable. So you have to plot log minus dCA by dt versus log CA.

(Refer Slide Time: 10:41)



And and then if you if you if you plot it then you will you will get a slope and slope we can we can we can find the slope here and this slope will give you the value of n and intercept will give you the value of ln k, this is the then you can find out the value of k.

(Refer Slide Time: 11:02)



Now here I want to point out again that if you if you unit of k also very important. Now here you have mentioned here what should be the unit of k the unit of k depends on the order of reaction as the order of reaction changes unit also changes and for example if the order of reaction is 0 0 order reaction then this will that moles per liter, per second. If order of reaction is first order reaction then this will be 0, then it will be second inverse, if order of reaction is

2 then it would be inverse, the mole per liter inverse into second inverse. So you know that so unit of k depends on the order of reaction this is very important.

Fist order reversible reaction
$A \stackrel{\underline{k_2}}{\underset{k_1}{\longrightarrow}} R$
At equilibrium, forward reaction rate (k_1C_A) =backward reaction rate (k_2C_R) $\frac{C_R}{C_A} = \frac{k_1}{k_2}$
The equilibrium constant is defined as:
Equilibrium constant= $K_c = \frac{concentration of product}{concentration of reactant} = \frac{C_R}{C_A} = \frac{k_1}{k_2}$
D _a
IT KHARAGPUR CERTIFICATION COURSES

(Refer Slide Time: 11:50)

Now in the biological system we have we have previously I was discussing about the irreversible reaction but in the biological reaction if you look at most of the biological reaction they usually takes place reversible they are reversible reversible means they have a forward reaction and they have a backward reaction you see there is a forward reaction, there is a backward reaction.

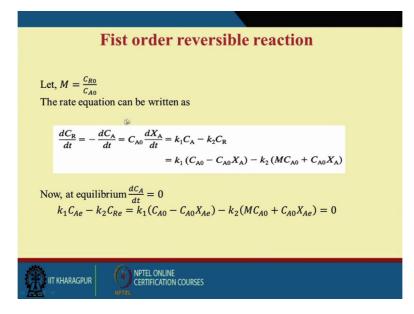
Now and since there is a forward reaction, and there is a backward reaction that equilibrium conditions what will happen the rate of forward reaction should be equal to rate of backward reaction and under this equilibrium condition what will happen that is this is a ripple then I can write this is equal to CR by CA, CR what is CR concentration of product, what is CA concentration of substrate. This is equal to k1 k1 is the rate constant for the forward reaction, k2 is the rate constant for the backward reaction.

So this this ratio is considered as the equilibrium constant this KC KC is the concentration of product by concentration of reaction. Now here I want to point out suppose in in in since biochemical reaction the mostly this reversible in nature now question comes how we can increase the production, we can increase the production in two ways as soon as the if if we increase the amount of substrate that in this system, then we can get more product because this ratio KC is constant KC is equal to concentration of product versus concentration of substrate more will be product, less substrate less will be product.

The another way we can increase the substrate concentration the product concentration as soon as the product formed if we can take it out some other means as for example ethanol where it forms ethanol can be (())(13:50) vacuum I can I at a low temperature we can take it out. So more more glucose can be converted into the ethanol.

So you know that so in the reversible reaction through approach through which we can increase the product concentration either you increase the substrate concentration or as soon as the product formed if you take it out from the system then we can increase the productivity of the process.

(Refer Slide Time: 14:22)

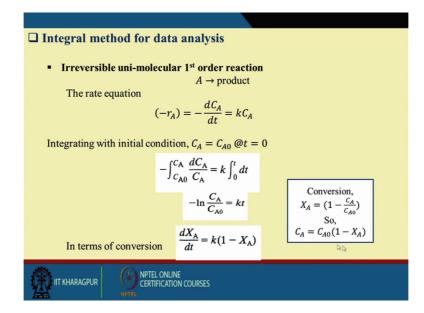


Now now that a reaction the same is now I can I can I can consider this is CR0 by CA0, CR0 means initial product concentration, CA0 is the initial substrate concentration. Now if you analyze the if you if you write the previous equation that dCR by dt what is dCR by dt is the rate of product formation equal to minus dCA by dt what is minus dCA by dt rate of substrate degradation, this is equal to I can write CA0 because what is CA CA is the concentration of substrate at any time t at any time t latest they have if the conversion factor is the ratio is the XA then CA this will be nothing but CA0 into XA, but XA CA0 is constant so that will come out here and so your equation will be dXA by dt this is equal to R and the concentration of R and SA and S

Now k1 into CA can be written as CA0 because CA0 is the initial substrate concentration and CA0 this is initial substrate concentration and the how much is it converted. So so this multiplied if CA0 initial concentration and how much is converted if that difference will give you how much that substrate that remain that is that is that is here and here what is M into M

into CA0 is what is the CR0, am I right. The the this is the initial product concentration and plus this whatever conversion take place that is CA0 in XA, so this is the product formation takes place so k2 into this. Now at equilibrium this will be equal to 0, so I can write this is equal to this equation can be written like this.

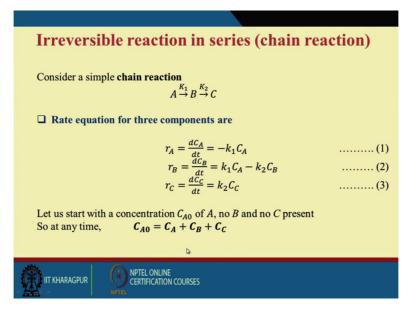
(Refer Slide Time: 16:21)



Now now let us do some analysis of the irreversible reaction also this is the simple (())(16:26) first order reaction this is we consider A into B, A is the substrate and we are getting the product we can write like this.

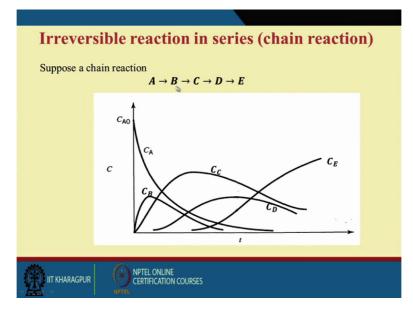
Now how we can analyze this this is simply we analyze that this CA by dt I can I can I can take this CA I can take the CA here, I can take CA here and k into that into 0 to t dt here, this is equal to ln say minus ln CA by CA0 integration CA0 to CA, this is equal to k into t, the conversion factor I told you XA equal to CA0 minus CA by CA0 that is why how much product is fraction of the substrate that is converted into product and this is equal to dXA by this we can convert this is nothing but CA0 that you know this this we can we can write in the form of dXA by dt equal to k into 1 minus XA, we can write it we can put this here we can write in this form.

(Refer Slide Time: 17:43)



Now another thing that I want to point out that that in the in the biochemical industry the biochemical metabolic processes mostly they are the chain reaction and chain reaction and reversible reaction.

(Refer Slide Time: 18:08)



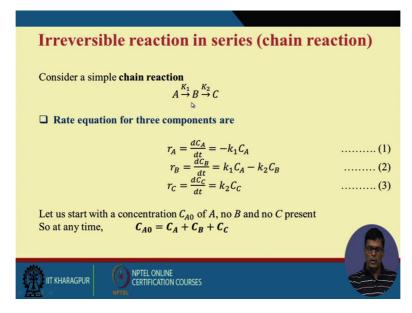
Now question comes how we analyze the chain reaction that first of all let me show you this is the chain reaction this the A to B B to C C to D like this this is the chain reaction that we have and if you look at the A this is CA that that is first component will keep on decreasing with respect to time, am I right.

And and if you look at the B C D the then B formation takes place then again decreases and as soon as the B formation takes place this C formation takes place C formation and decreases then again D formation takes place and then E formation and finally that product that we have E this will keep on increasing this will not decrease, this will keep on rising with respect to time.

So this is kind of profile that we have with respect to different substrate that is that different that a composition of the reaction mixture that how the different metabolic formation takes place. Now over what why I am showing you this that our intension is to find out suppose we are interested for this (compo) B now we r interested to find out that at what time the CB will be maximum.

Suppose I am interested with the metabolic C then I am interested when when the C condition will be maximum. If I am interested in D then question comes that when the D will be maximum. So this intermediate chain reaction if we do the analysis we can if we find out that at what time we can get the maximum this intermediate product formation will take place and this is the final product forming.

(Refer Slide Time: 19:58)



Now let us show you the analysis how you can analyze the this chain reaction suppose I have taken into consideration a simple reaction A to B B to C, the A to B that it was assume that this is the rate constant and this is small k this is not capital k and this is small k2, this is the rate constant for the B to C and let us assume they are all irreversible reaction we assume that

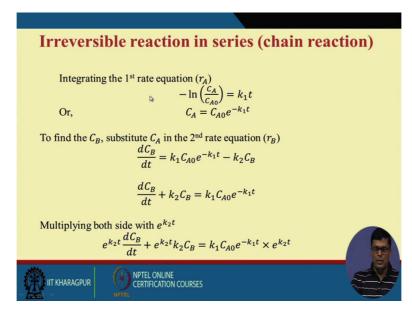
then rate of formation rate of degradation of substrate A it will be equal to k1 into CA, am I right.

Now rate of formation of these will be something different, rate of formation how how you can calculate the rate of formation of B because rate of formation of B is that rate of formation of B minus rate of degradation of B because two things simultaneously occur in the intermediate compound rate of formation of B and rate of degradation of B. So if you look at rate of formation of B the k into CA and rate of degradation of B the k2 into CB.

So this is this is how it can be written and rate of formation of C always we can write like this this dCA by d k2 into CC. So this is how the rate expression we can write for all these different steps rate of formation of A, rate of formation of B, rate of formation of C how we can write like this.

Now one thing I I can assume the CA0 what is CA0 CA0 is the initial substrate concentration, this is equal to since it is a equimolecular conversion I can write CA0 equal to CA plus CB plus CC this is like this I write so at the zero point there is no nothing no B and C is there but that is the time of reaction takes place then C will be converted to B B will be converted to C. So but CA0 will remain constant CA0 will be CA plus CB plus CC.

(Refer Slide Time: 22:08)



Now now if you look at the first reaction that rate reaction we have this is I can write what In CA by CA0 k1 into t, now this this equation if you like this equation I can I can take the CA here dCA by CA minus k1 into dt, am I right and this is equal to DCA by CA dln CA now dln

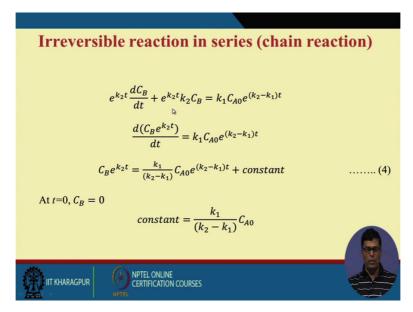
CA we can integrate CA0 to CA then this is 0 to t. So we can write what we can write this is we can write this is ln CA0 to CA0 and into k1 into t.

Now if you if you so what will be the value of C CA equal to CA0 because this will be e to the power minus k1 t and this is so this equation will this equation will give you the concentration of A at any time t. So suppose if I know the value of CA0 and if I know the value of k k1 the rate constant of the first step so if we simple put the time the 5 minutes, 6 minutes, 7 minutes, 8 minutes so you can find at different time what is the concentration of CA that we can easily determine on the basis of this equation.

Now let us come to the second part now we can we have seen second part is that rate of formation of B is equal to k1 into CA minus k2 by CB, am I right. Now now this I can write because here CA I can I can already we have determined CA equal to CA0 e to the power minus k1 t, so I can write like this.

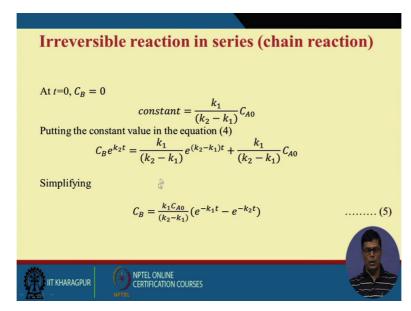
Now here if you look at this I can again change over this this side and then we multiply it both sides by e to the power k2t and if we multiply by k2t it will come like this.

(Refer Slide Time: 24:28)



And finally we get this now if this is equal to that d CB e k to the power k2 t by dt equal to k1 into CA e to the power k2 minus k1 t, so this is equal to then CB will be equal to k1 by k1 minus k2 into this I can I can Write like this and this is the constant plus constant.

Now what is the boundary condition boundary condition is that when t equal to 0, CB equal to 0, t equal to 0, CB equal to 0 same this will be 0 then constant will be equal to this one only that sign might be changed little bit that.

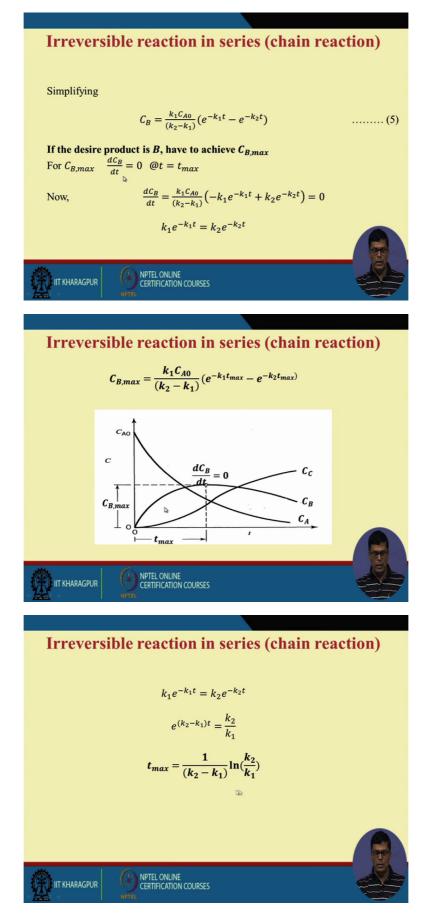


(Refer Slide Time: 25:16)

So I can write this constant is like this and rooting this value then this equation will come like this and simplified form CB is like this, so from this equation I can easily find out the correlation between the concentration of B at time t, because you see all are constant the k1 is constant, k2 is constant, CA0 is constant.

So if you want to find out the value of B at any time t, just put the value the time here you will get the value of CB. Now initially we can you can remember that I have written that CA0 CA0 equal to I have written CA0 equal to CA plus CB plus CC. Now you have the expression for CA, you have the expression for CB. So CC you can easily find out because this is constant. So CC will be equal to CA0 minus CA minus CB, so I can easily find out that, ok.

(Refer Slide Time: 26:22)



Now question comes that how you can find out the t max at what time the the CB will be max the if you if you if you look at this figure that here this is the profile of CB that here when CB is maximum then this dCB by dt equal to 0, am I right.

So I can what I can do I can differentiate this with respect to time and we can get this equation and this will be equal to 0 and if it is equal to 0 then this cannot be equal to 0, so I can write this equals to this, this equals to this we can write and if we write this equal to then t max will be equal to this.

Now initially we have this equation that already we derived I have already derived this equation in this equation if we put the value of t max here then we can easily find out the CB max, so this is how we can find out the t max and CB max of the chain reaction, this is largely applicable in the biochemical processes, thank you.