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Lecture – 12 Kinetics of Homogeneous Chemical Reactions – II

Welcome come back to my course aspects of biochemical engineering. In the last lecture I started the kinetics of homogeneous chemical reactions, and as I mentioned that before we understand the biochemical reaction engineering, we should we should have some kind of thorough idea on the chemical reaction engineering. And in the last lecture I try to concentrate on that what are the different classifications of the chemical reaction, I told you that whatever chemical reactions we have broadly it can be divided into two different class, one is called homogeneous reaction another is heterogeneous reaction.

Now in case of homogeneous reaction, the reaction take place in one particular phase. As we know we have three different phases, one is gas liquid and solid. Now when the homogenous reaction take place mostly this take place either gas or liquid phase, in the solid pure solid phase reaction is really available. Now in case of heterogeneous reaction that more than one phase present there either gas liquid or liquid solid the more than one phase should be present in the reaction mixture. So, bottlenecks of this particular heterogeneous reaction is that one phase has to diffuse to the surface of the other phase, and then and only then the reaction take plane after the reaction is over the whatever product is formed, the products supposed to diffuse from the surface of the other phase to the and diffuse to the next phase now.

So, diffusion as well as reaction both we shall have to consider in case of heterogeneous reaction, now if your rate of diffusion is less then as compared to rate of reaction, then diffusion will be the controlling factors and in case of rate of reaction is less as compared to rate of diffusion than rate of reaction is a controlling factor. Then I try to or we talk about some kind of mathematical modeling, mathematical modeling is the mathematical modeling is the mathematical representation of the process. Now we started with some kind of chemical reaction in the chemical reaction we try to write the reaction kinetics equation.

And this equation rate equations is kind of modeling and today I last class I tried to discuss about the irreversible reaction, the how we can analyze in in addition to that we also discussed the parallel reaction, also auto catalytic reaction with largely applicable in the biological system. Now today that we had, I am going to concentrate on two different reactions one is called tips before the glucose is converted to pyruvic acid.

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Now that and if you look at the individual steps more all the steps more less they are reversible in nature. So, from this metabolic pathway, we understand the biochemical reactions are they are mostly the chain reaction that is, 1, 2, 3, 4 the 10.

Different steps are involved before you get the pyruvic acid one mole of pyruvic acid produces two moles of a one mole of glucose produces two moles of pyruvic acid. Now if you look at the individual steps we will find that reversible in nature. So, the biological system we have both chain reaction as well as the reversible reaction, the today I want to discuss both the chain reaction and the reversible reactions.

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Now, if you look at irreversible that chain reaction, what we have seen in the glucose metabolic pathways, they tell steps are involved because before the glucose is converted to pyruvic acid. Now here we have taken one instance that A to B, B to C, C to D, D to E the different products that we have and intermediate product that is B C D we have.

Now if you look at the; that concentration profile of the different component present in the chain reaction is it like this. If you look the first component A that is keep on decreasing with respect to time and last component E, if you see that is keep on increasing with respect to time. But all intermediate compound like B C D they are rising then decreasing rising and dictating.

The one thing I want to emphasize here then (Refer Time: 05:25) B formed C cannot be formed (Refer Time: 05:28) C formed D cannot be formed that is very important. So, in case of this intermediate that chain reaction, that the strategy is that that no first component that is substrate will keep on decreasing with respect to time and last component to keep on rising with respect to time all intermediate compounds they will increase then decrease. So, this is the how this reaction looks.

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Now, let us consider a very simple chain reaction that we have what that let me let me consider a very simple that reaction that is A to B, B to C.

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This is kind of irreversible that simplest chain reaction that we have let us assume this is the rate cause rate of rate constants k 1 and in this step the rate constant is k 2. Now if you want to write the rate of substrate degradation d C A by d t this will come around k 1 into CA. If you consider the first order kinetics, now if you if you want to write c v by rate of formation of the intermediate compounds then this will be what rate of formation k 1 into rate of formation of A and p also degree degraded to C. So, this will be k 2 into c.

B now if you want to this we can consider number one equation, this we consider number two equation and another is d C c by d t this will be equal to k 2 into CB. So, this is three equation. Now here if you want to draw a profile of the three component present in the reaction mixture. So, I have showed you in the chain reaction the past component C A will keep on decreasing with respect to time and b this will be increase and then will decrease this is the C B and last component will keep on increasing with respect to time that is C c. Now here what we are interested? We are interested to develop the equation for C A then C B then C c. So, individual equation how we can correlate with respect to time.

So, that if we put the time that in that equation we can get the respective value, then I forgot to mention in the last class there is another term called the simulation, that because when you write any kind of model suppose we can we have written this model we determine the value of k 1, after I showed you how k 1 and n value can be determined; then when you put these values there then we can simulate the we can put the weekend we can just solve this equation and we can develop the theoretical correlation, between the concentration of substrate with respect to time and then we compared with the experimental results. And when you compare with the experimental results we try to calculate; what is the percentage deviation of this results. And if the percentage deviation is less than 5 percent then it is acceptable is the more than 5 percent then we do certain model motivation of this equation.



Now, here now next step and that if you look at this equation what I have written before then I (Refer Time: 09:07) of availability t C A by d t equal to equal to k 1 into C A, now I can write this is d C A by C A this is equal to k 1 into dt this we can write. Now this is equal to d ln C A and this is minus k 1 into dt. Now if you do the integration this is C A 0 to C A and this is 0 to t then what we will get? This is ln minus ln C A by C A 0 this is equal to k 1 into t am I right? Now this equation I can write in this form a equal to C A 0 into e to the power minus k 1 t.

So, because you know C A 0 is constant and k 1 is a constant now in this equation if you put the of t because one minute, two minute, three minutes whatever value respects. So, what we have what I wanted to mean. So, we have experimentally we have developed the equation with respect to time this suppose this was the experimental value, then in the theoretical of this value theoretical value also we can find out here what is respective value we can find out, and then we can easily calculate what is the percentage deviation we have as with respect to the experimental phone, from that we can write the validity of the particular equation. So, this is number four equation that we have we should remember that.

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now next that next you can remember I told you C B by d t ct is equal to k 1 into C A minus k 2 into C B am I right we have written k 1 into C A minus k 2 into C B. So, this I can rearrange like d C B by d t plus k 2 into C B this is equal to k 1 into C A. Now both side if you multiplied by e to the power k 2 t e to the power k 2 t and this is the to the power k 2 t, then what equation you will get here we can write this as d C B into e to the power k 2 t by d t.

I can write like this and here we this is also here we have we have done some mistake, here it would be already k 1 k 1 is there, this we can write k 1 and multiplied by k minus 1 was there and into multiplied by e to the power k 2 t because we multiply both sides by e to the power k 2 t. So, this I can write k 1 C A e to the power k 2 minus k 1 into t this we can write. Now this equation from this equation we can write C B into e to the power k 2 t this should be equal to what this should be equal to k 1 into this is C A 0 c 0 is a constant and this is k 2.

Minus k 1 and this is e to the power k 2 minus k 1 into t this we can we can write this plus constant. Now we have the boundary condition what is the boundary condition at t equal to 0 C B should be equal to 0, because (Refer Time:13:22) degraded that that we cannot be form if it is that I can assume this. Now if we assume the C B equal to 0 this first portion will be 0 then then here if you put t equal to 0 then this will be 0. So, what

we can write the constant equal to minus k 1 C A 0 into k 2 minus k 1 this we can write; now this this equation I can put it here this is constant.

Now, I can erase this, I can; I will take it out and I can again put this value here that this this also I can remove and here we can put minus this minus this is k 1, C A 0, k 2 minus k 1 this I can I can write now once. So, your equation what is the equation you have C B into e to the power k 2 t equal to this, now if you divide this side with e to t e to the power k 2 t then what will get you will get C B equal to C A 0 divided by k 1 k 2 minus k 2.

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K 2 minus k 1 then here you can find out e to the power k 1 t minus e to the power k 2 t you can find out now the another thing is that and here and then we can calculate that. Now we have seen that the C B versus t what is the profile that we have it is like this. Now we are interested to calculate the value of this point; what is this point where this point C B will be maximum? So, this we call t max at this point d c v by d t because this hat is the plateau. So, this will be equal to 0. So, now, if you if you differentiate this C B by d t then what will get C A 0.

Minus k 2 minus k 1 now here I can write most probably here we have k 1 and here minus k 1, e to the power k 1 t plus k 2, e to the power k 2 t. Now what we can write this is again it is k 1. So, what we can write this will be equal to 0 now this cannot be equal to

0. So, I can assume this is equal to 0 now if you put this equal to 0 what you can write? The k 1 by k 2, k 1 by k 2 equal to what?

Equal to I can write e to the power k 2 t by e to the power k minus one t am I right. So, if you take it up the; what will get e to the power k 1 minus k 2 t, this we can write this is k 2 then this is if you take log, log then k 1 by k 2 equal to k 1 minus k 2 into t. Now here the t you can write t equal to what? T equal to one by k 1 minus k 2 ln k 1 by k 2. So, we can this is equal to t max because this is the time you can easily now in this equation if this value t max value you put here we get the c v max value. Now we can easily calculate the z max value this is how you can find out.

The time at which we can get the maximum intermediate product formation now here we have shown in this particular slide you can see this is A to B, B to C now that is the rate of degradation of a this is minus this minus I can take it here, this is k 1 into C A then rate a rate of formation of B, I can write this and rate of formation of C I can write this.

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Now, here we know that the total concentration initial concentration of a would be equal to concentration of at any point of time this since this is the equal molecular conversion. The equimolecular conversion means one mole of converted to him one mole of B, one mole of B converted one mole of C.

So, I can write C A 0 equal to C A plus C B plus C c; this we can write. Now from the first equation we have seen that this is a d c ln C A by C A 0 equal to (Refer Time: 19:11) this is equal to this I have already shown you how we got this.

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Now in case of intermediate product formation this is again this is equal to this d C B by d t equal to this this I have already shown, and then we bring it here then we finally, write the equation like this.

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Now, when you do the differentiation of this then finally, we come across this equation d C B into e to the power k 2 t equal to k 1 by k 2 minus k 1 is C A 0, e to the power k 2 minus k 1 t plus constant. Now we put the boundary condition at t equal to 0, C B equal to 0 then the constant value will be this much.

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Then finally we have come across this equation, I showed you the C B equal to k 1 C A 0 k 2 minus k 1 e to the power minus k 1 t minus e to the power k 2 t this way we can we can get and this is. So, in this equation if we look at that everything is constant k 1 is constant C B k 2 is constant. So, C A 0 is constant. So, if you put the time t, then you can easily find out we can we can easily find out the correlation between C B versus t, you can you can have the this is called theoretical correlation that you can easily find it out that if you put the different at different time, just you put the time value you will get the value of C B here.

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Irreversible chain reaction Simplifying	
$C_B = \frac{k_1 C_{A0}}{(k_2 - k_1)} (e^{-k_1 t} - e^{-k_2 t})$	(5)
At $C_{B,max}$, $\frac{dc_B}{dt} = 0$ when $t = t_{max}$	
Now, $\frac{dt}{dt} = \frac{1}{(k_2 - k_1)} \left(-k_1 e^{-k_1 t} + k_2 e^{-k_2 t} \right) = 0$ $k_1^{(k_1)} e^{-k_1 t} = k_2 e^{-k_2 t}$	
	(Å)

Now, this is I showed you that once you get this equation if you want to find out C B max, you can easily do that and at that this ad C B max the d C B by d t equal to 0; if we differentiate will get this.

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Now here you see that this this is the equation I have already derived and that ultimate if you take it at the bottom, this is we can write t max equal to k into k log min this is this equation we can we can write like this.

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Now, our final equation is coming like this when we put the C B max value in this equation, we get this C B max equal to we put the value we can easily find out what is the C B max value we can easily calculate. So, with this cell equation we can now I told you regarding the Cc, we can also do it very easily because I told you C A 0 is equal to what C A plus C B plus C c; am I right? Now what will be C c value; this will be C A 0 minus C A.

Minus C B. So, we have already determined the expression for C A already we have determined the expression of B. So, if we put this equation here we can easily find out the C c value. So, we can what we have done C c with respect to time this is how it is increasing, this we can easily this that we can easily find out that if you put this equation.

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Now, this is a t max value already we have calculated, now C R max that equation, we have we have shown you that t max value we put that now this t max value; we can substitute there and we can get this equation.

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Then finally, we get this if we if you simplify this it will come this equation, this final equation is that they here you see that C B max and. So, everything is constant you put everything in the form of constant. So, you can find out we can put the value we can find

out the c l max value of C B max value we can easily calculate. This is though we have written C B max this should be C B max.

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So, you can make the correction now, this is how.

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We can write and this is a final equation rearranging we can get this equation.

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Fist order reversible reaction	
$A \stackrel{k_2}{=} R \qquad A \stackrel{k_2}{=} R \qquad K_2$	
At equilibrium forward reaction rate (k_1C_A) =backward reaction rate (k_2C_R)	
$\frac{C_R}{C_A} = \frac{k_1}{k_2} = \frac{1}{100} = $	
The equilibrium constant is defined as:	
Equilibrium constant $K_c = \frac{concentration of product}{concentration of reactant} = \frac{C_R}{C_A} = \frac{k_1}{k_2}$	
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Now as I pointed out that that most of the biochemical reaction they are reversible in nature, reversible means you can see there is a forward reaction there is a backward reaction. So, it is like this if I write like this is a; this is k 1 this is k 2 and this is odd. So, the at the equilibrium condition rate of forward reaction should be equal to rate of backward reaction what is the rate of forward reaction k 1 into C A, k 1 into C A equal to k 2 into C R. So, now C R by C A equal to equal to k 1 by k 2 and this is nothing, but equal to k c that equilibrium constant this is the equilibrium constant how we can calculate.

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Now, here in this equation also you can say that the equation is this is very simple the rate of formation rate of formation of odd, equal to rate of degradation of a this is can be represented like this. How this this can be represented we have shown you then what is C A? C A equal to C A 0 into X A what is X A? The fraction of X A that is no this is sorry this is not the right thing this is I can cancel this is this will be 1 minus X A. X A is the fraction converted what is the fraction remaining that is 1 minus X A that is faction remaining that is equal to C A.

Now if you do C A; this will be what minus this will be constant. So, I can write C A 0 into d X A. So, this equation if you differentiate this is constant. So, this equation I can write in this form d X A by d t and this is equal to same and what is C A? C A equal to C A 0 into fraction that is converted and what is the C R? C R is the this is equal to usually 0 and this is the fraction that remain how much things has been converted to C A 0 into x n. So, at the at equilibrium condition this should be equal to 0. So, we can write this and each transport the equilibrium concentration. So, we can just change this nth terms of equilibrium concentration we can write this equation like this.

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Now finally we found this previous equation if you look at this equation I can take C A common all this equation. So, I can take out the C A out.

And this is equal to 0 now the ratio of this that M plus X A e divided by this equal to k 1 by k 2 and that is nothing, but equal to the K c what do you call your equilibrium constant. Now the rearranging this equation we can write in this form and then.

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Then we go we can elaborate this equation in this form, this is very simple we can do the take this common and we write this equation like this.

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And finally, we have the expression like this when we have this expression, then we can plot this ln 1 minus X A, this is versus this t if you plot the slope will give you the value of this one slope will give you the value of this one.

So, this is M equal to C B 0 by C A 0 that is constant and X A is the; that conversion of a under equilibrium condition. So, if you put that value we can easily find out the value of k 1. So, this is how you can find out the rate constant value. So, in conclusion I what I want to tell that today I try to discuss that two type of reactions that is largely in operation in the biochemical system one is the chain reaction, and there is the reversible reaction and chain reaction we consider very simple chain reaction A to B, B to C and reversible reaction A to B how reversibly converted, only one thing I forgot to mention that that in case of reversible reaction, that we can increase the product formation by two different approach either you as soon as your k c equal to concentration of product divided by concentration of substrate.

Now, if you want to increase the product formation as soon as product form if you take it out, more substrate will converted into product or there is a another approach we can have if we add more substrate to the system, you will get more product because k c remain constant. And the in the chain reaction we try to find out the time the expression for the all the different component present in the chain reaction, and major thing is that we are interested to find out that what time you will get the maximum intermediate product formation.

Thank you very much.