Chemical Reaction Engineering
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Lecture No. #15
Catalytic reactions - Kinetics

Friends let us continue our discussion on kinetics of catalytic reactions and to refresh our memory, our reaction is let us say A going to B. In this reaction, there are two adsorption and desorption steps which we discussed last time.

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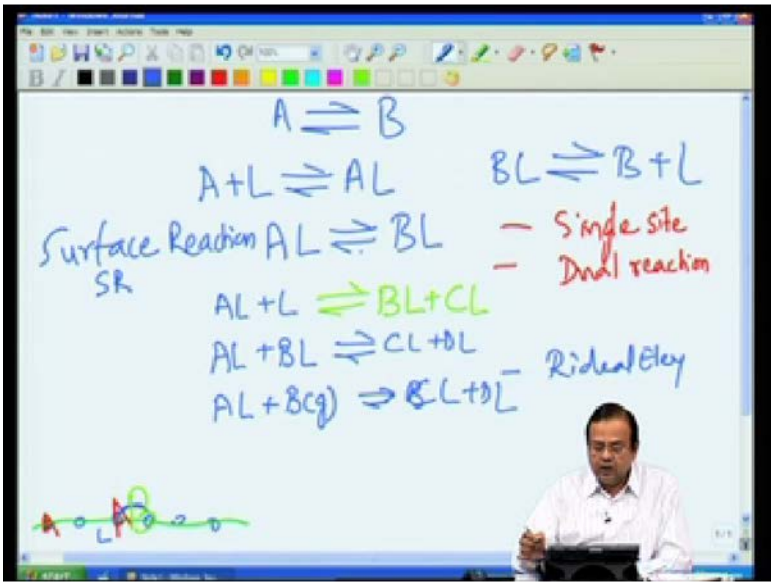

$A \rightleftharpoons B$

$A + L \rightleftharpoons AL$ $BL \rightleftharpoons B + L$

Surface Reaction $AL \rightleftharpoons BL$ – Single site

SR – Dual reaction

$AL + L \rightleftharpoons BL + CL$

$AL + BL \rightleftharpoons CL + DL$ – Rideal Eley

$AL + B(g) \rightleftharpoons CL + DL$

And now we need to connect this two this two reactions by bringing in surface chemical reaction, where the actual transformation of species A to species B in the adsorbed state takes place. So, this is our surface reaction - SR for short. Now, when there are surface reactions there are various different possibilities. For example, we talked about this is my active sites, some of which are occupied by A, and during the course of reaction this A is now going to change to B. That is my surface surface reaction.

Now, when it comes to surface reaction we could have a single site reaction. That is A A adsorbed over here on to this site becomes B. So that is one type of reaction. So, these are single site reactions. But more common or the dual site reactions, and this could take place of various different forms, for example AL, so this AL could interact with a vacant site L, this two together and this gives raise to product B. So, AL plus L gives raise to let us say a product BL plus CL that is one type of type of surface reaction - dual site reaction.

Another possibility of course is one type of adsorbed species combining with another type of adsorbed species giving raise to CL plus DL. So, if the overall reaction is A plus B will be giving raise to C plus D, we could have this kind of kind of reaction. There is also in possibility that an adsorbed species interacts directly with the reactant molecule. So, B is not strongly adsorbed or its adsorption on the active site is not required, and it directly interacts with AL, and we get our desired product let us say CL plus DL. These are what are called as Rideal Eley mechanisms Rideal Eley mechanism. So, adsorption of B is very weak and B it directly interacts. Whichever may be the may be the adsorption or surface reaction step we have to write an equivalent equivalent rate form for this.

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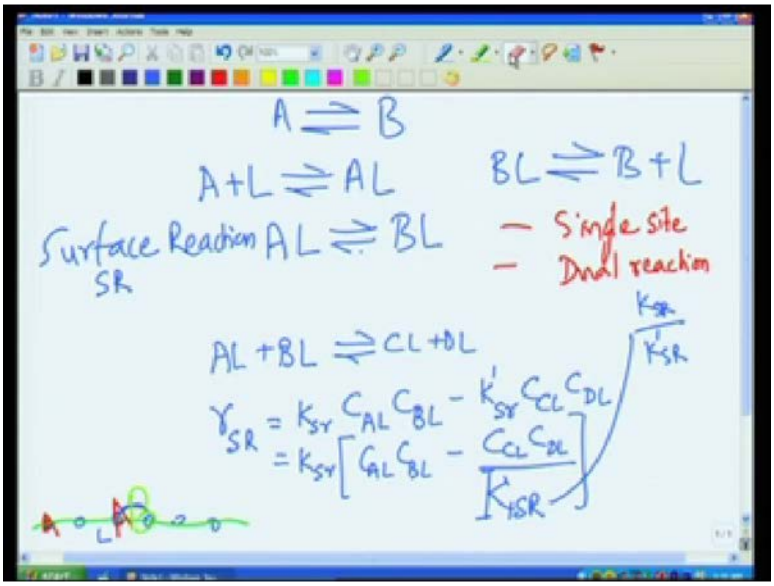

$$A \rightleftharpoons B$$

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Surface Reaction $AL \rightleftharpoons BL$ – Single site

SR – Dual reaction

$$AL + BL \rightleftharpoons CL + DL$$

$$r_{SR} = k_{sr} C_{AL} C_{BL} - k'_{sr} C_{CL} C_{DL}$$

$$= k_{sr}\left[C_{AL} C_{BL} - \frac{C_{CL} C_{DL}}{K_{SR}}\right]$$

$$\frac{k_{SR}}{k'_{SR}}$$

And let us let us look at this particular dual site reaction and write an rate of surface reaction as k sr the forward reaction rate constant, times concentration of C AL times concentration of C BL minus k prime sr the reverse reaction rate times C CL times C DL. So, this now becomes our our reaction rate as far as the surface reaction is concerned. This is still not the reaction rate of this overall reaction, but we are talking rate of individual individual reaction. So, we can also write this as taking k sr out C AL C BL minus C CL C DL capital K SR, where capital K SR is nothing but K SR, this is this is nothing but K SR divided by K prime SR. The small k(s) are indicated as a kinetic rate constant, capital K let us make it somewhat different; capital K as indication of equilibrium constant. So, this is a equilibrium constant for this surface chemical chemical reaction.

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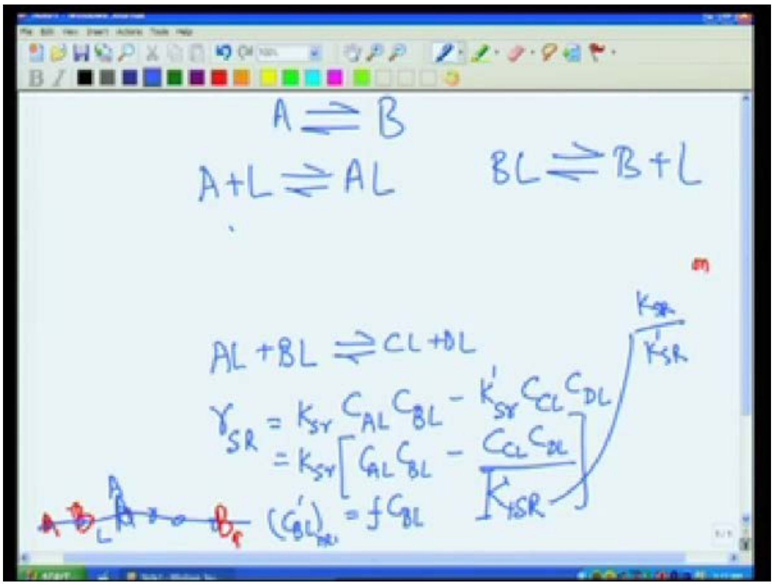

$$A \rightleftharpoons B$$

$$A + L \rightleftharpoons AL \qquad BL \rightleftharpoons B + L$$

$$AL + BL \rightleftharpoons CL + DL$$

$$r_{SR} = k_{sr} C_{AL} C_{BL} - k'_{sr} C_{CL} C_{DL}$$

$$= k_{sr}\left[C_{AL} C_{BL} - \frac{C_{CL} C_{DL}}{K_{SR}}\right] \qquad \frac{k_{SR}}{k'_{SR}}$$

$$(C'_{BL})_{AL} = f C_{BL}$$

Few additional points for example, if you consider this this particular reaction and let us say that we have A adsorbed over here. Now, for this reaction to take place there could be B adsorbed at different locations and so on. But for this reaction to take place the interaction will be with the closest neighbor. So, AL and closest BL will interact. This AL for example is unlikely to interact with this BL, this BL over here which is which is far away from from from the AL species. So, when we to write C BL the idea essentially is, it is actually C BL prime or C BL in the neighborhood of AL, and if we assume that there is no favorable distribution. So, probability that the fraction of the total concentration C BL is this nearing neighbor, then this f for example, will get adsorbed into this rate constant.

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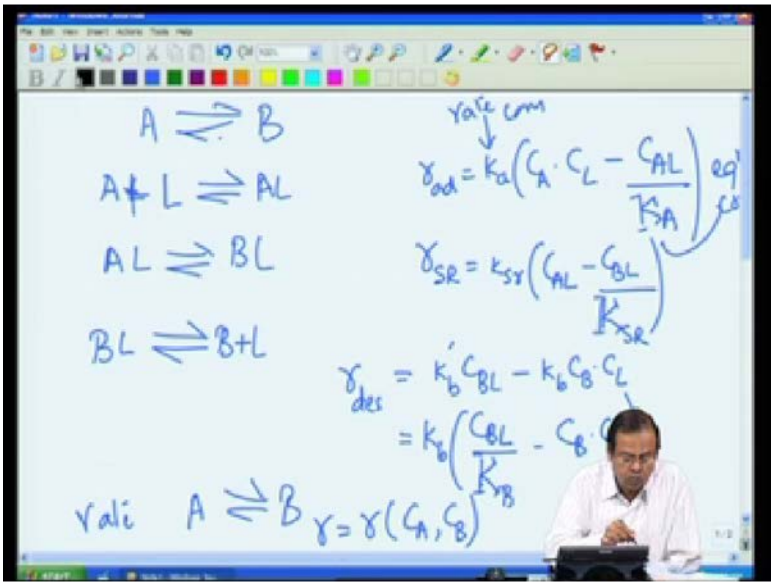

So, now let us complete our go back to go back to this reaction and complete our our kinetic description, so that we can now develop the rate of reaction. So, let us let us write AL going to BL as as the as the third step. So, this is actually 3, 4, 5; the steps 3, 4, 5 of our overall schematic that we that we talked about. So, now let us let us write down the rates of individual steps, so that we we then put together the idea of determining the determining the rate. So, let me let me rearrange this, so that we are...

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Our overall reaction is A going to B, our adsorption stage is A plus L giving raise to AL with the rate of this adsorption step. Now, I am going to write it in a simplified manner, where k a - this is a rate constant kinetic rate constant, and this is the equilibrium constant. So, we will follow the same terminology for all the rates. So, let us say that our surface reaction is AL going to BL, so we have we have rate of surface reaction which we just now wrote.

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Same terminology. And let us write down the rate of desorption, rate of desorption which will be in this case following the same terminology that is adsorption term we will use as k A or k B in this case. So, direction of adsorption k B reverse as k prime, so this for example will be strictly speaking k prime b C BL minus k b C B C L, which if we take out k b can be written as C BL by K B minus C B C L. So, so that K B, K A are still the adsorption constants to keep the terminology consistent.

So, we have these three steps and our interest is to find what is the rate of A going to B that is our interest. So, since this concentration such as C L, C AL, C BL are not easily measurable, concentrations of A and B are easily measurable. So, what we want to do is actually get the rate expression which is function of C A and C B by eliminating all the other other species. Now, how do we do that? Simplify this whole scenario. So, let us let us try to simplify this by saying that by doing the following. So, we have these rate expressions. So, let us let us try to simplify this. So, what is the what is the way in which we are going to we are going to simplify this.

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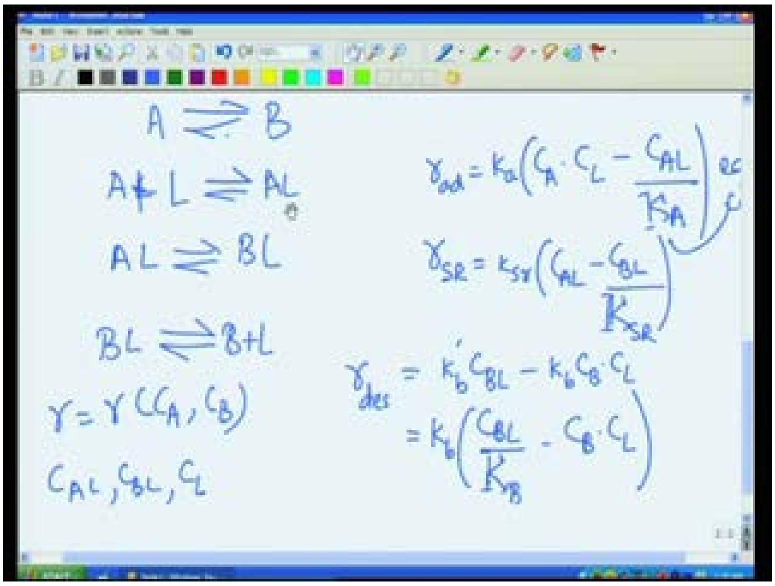

$$A \rightleftharpoons B$$

$$A + L \rightleftharpoons AL$$

$$AL \rightleftharpoons BL$$

$$BL \rightleftharpoons B + L$$

$$r = r(C_A, C_B)$$

$$C_{AL}, C_{BL}, C_L$$

$$r_{ad} = k_a\left(C_A \cdot C_L - \frac{C_{AL}}{K_A}\right)$$

$$r_{SR} = k_{SR}\left(C_{AL} - \frac{C_{BL}}{K_{SR}}\right)$$

$$r_{des} = k_b' C_{BL} - k_b C_B \cdot C_L$$
$$= k_b\left(\frac{C_{BL}}{K_B} - C_B \cdot C_L\right)$$

Now, we earlier talked about two different approaches of simplifying it. There is what we want to do is we want to develop the rate which is a function of C A and C B. So that means I have to eliminate, if you examine these if you examine these rate expressions we have C A no problem, but we have C L which we do not know, we have C A L we do not know and also we have C B L. So, we need to eliminate C A L, C B L and C L somehow from this from this rate expression. So, in order to do that we are now going to invoke one of the two approaches and we will start with adsorption or quasi equilibrium approach, because that is easier to deal with and therefore, naturally more common or more widely used approach.

If you recall what does this approach say? If this approach says that if we have series of reactions as we have over here. The slowest of all these reactions is the rate determining rate determining step. So, the rate of my overall reaction rate of my overall reaction is the rate of the slowest step and because compare to a slow step such as the surface reaction, adsorption and desorption are very rapid and therefore, they reach equilibrium very fast. So, reaction 1 and reaction 1 and reaction 3 are equilibrium almost reached equilibrium, whereas reaction 2 is the is the slow slow steps that that as compare to as compare to other reaction.

So, let us let us therefore say let us therefore say the rate of my reaction of this reaction is the rate of my surface reaction. So, I am going to say that rate of my reaction is my surface reaction rate. This is my reaction reaction rate. So, let me let me remove this and that is the rate of my overall overall reaction.

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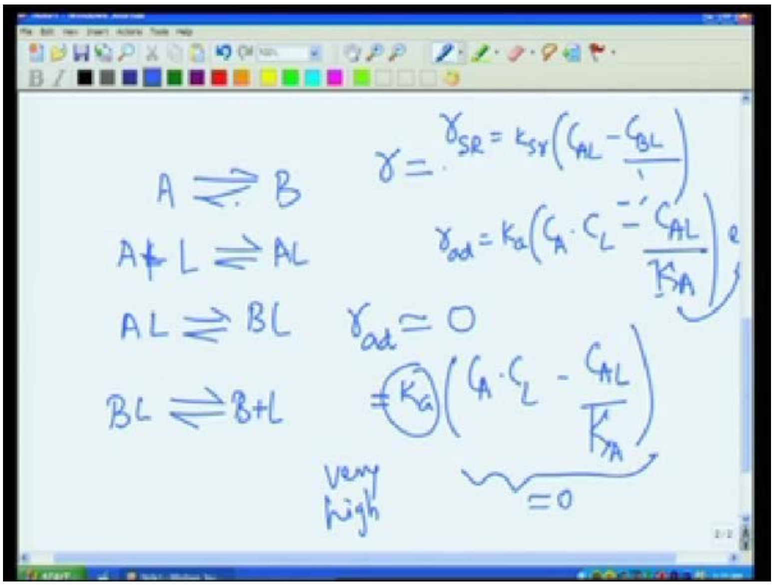

$$A \rightleftharpoons B$$

$$A + L \rightleftharpoons AL$$

$$AL \rightleftharpoons BL$$

$$BL \rightleftharpoons B + L$$

$$\gamma = \gamma_{SR} = k_{Sr}\left(C_{AL} - \frac{C_{BL}}{}\right)$$

$$\gamma_{ad} = k_a\left(C_A \cdot C_L - \frac{C_{AL}}{K_A}\right)$$

$$\gamma_{ad} \simeq 0$$

$$= \boxed{k_a}\underbrace{\left(C_A \cdot C_L - \frac{C_{AL}}{K_A}\right)}_{\simeq 0}$$

very high

Now, we are going to say that adsorption desorption are at equilibrium. So, let me let me simplify now. The the this rate expression and write my r adsorption is 0 - rate of adsorption is 0. Notice here I used the sign approximately and there is a reason for that. Because if you say that your adsorption rate is 0, the process has reached complete equilibrium, then the reaction rate itself will be 0, because no reaction can proceed if one of the reactions has reached equilibrium. So, then what is the meaning of equilibrium or quasi equilibrium? The quasi equilibrium means the following. As we wrote here…

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What we are seeing is the adsorption step is very large. So, value of this K A is very high very high. So for us to have the value of value of this adsorption rate to a finite small value if K is extremely large would require that this is close to 0 - the bracketed quantity. And therefore, this process has reached almost equilibrium.

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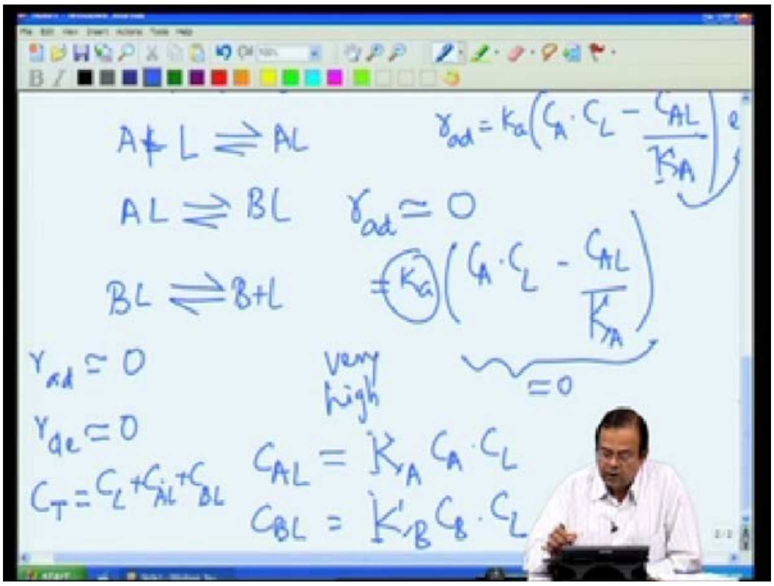

$A + L \rightleftharpoons AL$

$AL \rightleftharpoons BL$

$BL \rightleftharpoons B + L$

$r_{ad} = k_a\left(C_A \cdot C_L - \frac{C_{AL}}{K_A}\right)$

$r_{ad} \simeq 0$

$= \boxed{k_a}\underbrace{\left(C_A \cdot C_L - \frac{C_{AL}}{K_A}\right)}_{\simeq 0}$

very high

$r_{ad} \simeq 0$

$r_{de} \simeq 0$

$C_T = C_L + C_{AL} + C_{BL}$

$C_{AL} = K_A C_A \cdot C_L$

$C_{BL} = K_B' C_B \cdot C_L$

So, if we do that what it what it means is what it means is that my C AL is equal to K A adsorption constant C A into C L. So, this is the implication of quasi equilibrium. If I apply the same thing for the third reaction I will get C BL equal to equilibrium constant K B C B C L. Two quantities C AL, C BL related to C L. So, if we have third relationship… So, we had r ad approximately equal to 0, r desorption approximately equal to 0, remember we had three unknown quantities C AL, C BL, C L. We know two relationships; we know we need third relationship. And the third relationship is provided by the total active catalyst catalyst sites must be C A plus C L plus C BL. So, what it this is what all I have done is of the total sites on the catalyst surface C T; some are vacant, some are some are occupied by A, some are occupied by B. So, this gives me my required third relationship and if we now if we now substitute this if you now substitute this for C CL and C AL into this into this surface reaction rate, so I will get the following.

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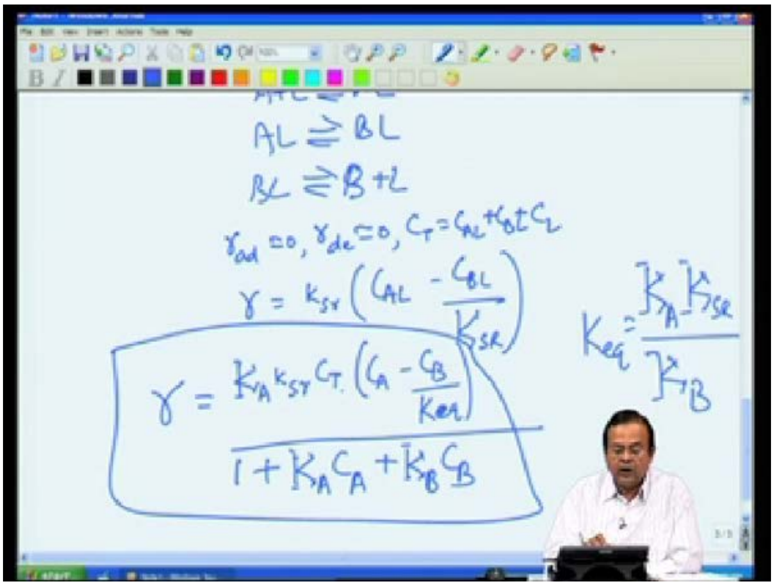

$AL \rightleftharpoons BL$

$BL \rightleftharpoons B + L$

$r_{ad} \simeq 0, \; r_{de} \simeq 0, \; C_T = C_{AL} + C_{BL} + C_L$

$r = k_{sr}\left(C_{AL} - \frac{C_{BL}}{K_{SR}}\right)$

$$\boxed{r = \frac{K_A k_{sr} C_T \left(C_A - \frac{C_B}{K_{eq}}\right)}{1 + K_A C_A + K_B C_B}}$$

$K_{eq} = \frac{K_A K_{SR}}{K_B}$

So, let me… Overall reaction mechanism…

(No audio from 20:27 to 20:40)

Quasi equilibrium approximation and total active sites, and my rate of reaction with the assumption that…

(No audio from 21:02 to 21:12)

So, I solve for C A C L, C BL, C AL using these three relationships and substitute those values I will get r equal to…

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This is my kinetic rate expression. What is it? K A k sr C T into C A minus C B divided by K equilibrium, what is K equilibrium? K equilibrium here is actually the product of the three steps in the reaction. The equilibrium constant K A for adsorption step multiplied by the equilibrium constant k sr for the surface reaction divided by the equilibrium constant of the adsorption of B. That is that is my equilibrium, and this is our thermodynamic property - K equilibrium, delta G 0 is equal to minus RT l n K equilibrium that K equilibrium.

So, now if we look at look at this particular particular rate expression, we find there are both equilibrium constants as well as as well as the kinetic rate constants. Now, if we if we if we examine this more carefully, we find that there is a term C T that is the total active sites and if that also is not very easy to measure, so that is typically typically adsorbed into the rate constant. And write this whole expression, I will write this whole expression as for the reaction A going to B, the rate is the constant K times C A minus C B divided by K equilibrium, the whole thing divided by 1 plus K A C A plus K B C B.

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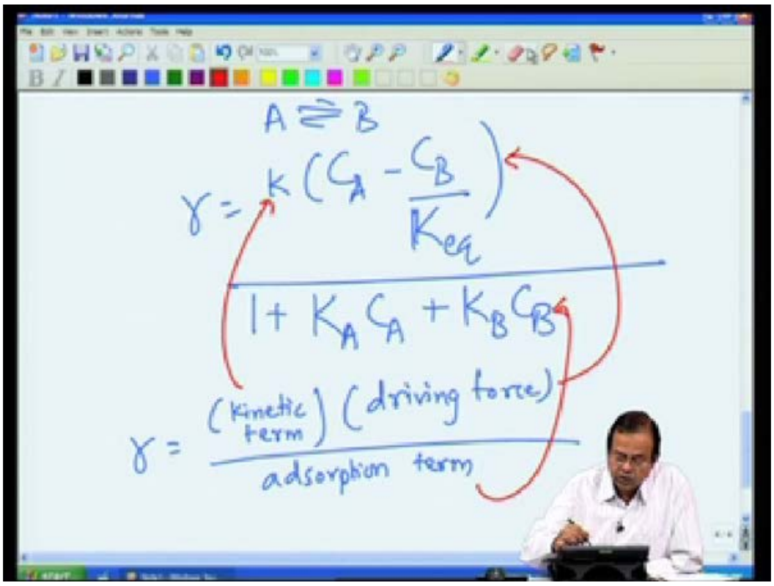

$$A \rightleftharpoons B$$

$$r = \frac{k\left(C_A - \frac{C_B}{K_{eq}}\right)}{1 + K_A C_A + K_B C_B}$$

$$r = \frac{(\text{kinetic term})\,(\text{driving force})}{\text{adsorption term}}$$

Now, if we if we examine this particular relationship and you will find for other kinetic catalytic kinetics as well. The following structure emerges for the rate, rate equal to some kinetic term multiplied by driving force divided by adsorption term; kinetic term K, driving force C A minus C B by K equilibrium; why is it called driving force? Because at equilibrium this term is 0 that is K equilibrium is C A C B by C A. So, for this reaction to take place the driving force is the difference between C A minus C B divided by K equilibrium. And when the driving force goes to 0 reaction reaches equilibrium, the rate becomes 0. And this adsorption term is this whole term in the denominator, why is it called as adsorption term, if you recall when we talked about adsorption and desorption phenomena we had this term which arises from A A plus L giving AL and so on. So so, we have we have this kind of rate expression for for…

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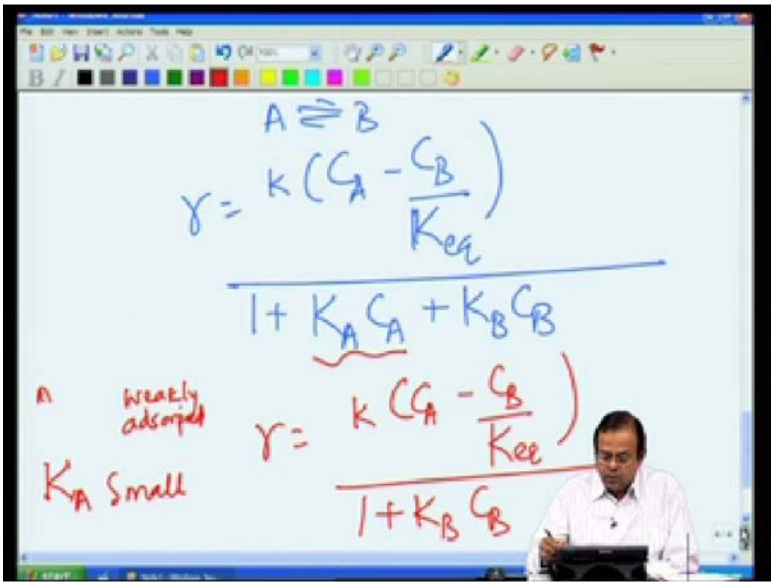

$$A \rightleftharpoons B$$

$$\gamma = \frac{k\left(C_A - \frac{C_B}{K_{eq}}\right)}{1 + \underbrace{K_A C_A} + K_B C_B}$$

A weakly adsorbed

K_A Small

$$\gamma = \frac{k\left(C_A - \frac{C_B}{K_{eq}}\right)}{1 + K_B C_B}$$

Now, before we go to the second approach, let us just look at what are the simplified forms of this rate expression. If the reaction, for example is irreversible for all practical purposes; what does it mean? This means that K equilibrium is infinitely large, which means that my rate will be if I substitute it over here K A K C A by K A C A plus K B C B. That is that is one kind of kind of simplification possible. What is the other simplification possible? So, this is when reaction is irreversible.

The other kind of simplification for example, would would be if A and B are weakly adsorbed. What does it what does it mean? This means that K A value - our equilibrium constant and K B value are small. If that is the case, then denominator terms are relatively small compare to 1, and we can simplify this as simply C A minus C B by K equilibrium. So, if the gases are weakly adsorbed on to the active site we get this kind of kind of… Another simplification that is that is often done is that let us say that only A is weakly adsorbed, A is weakly adsorbed so K A is small, so that is this term is negligible compare to the K B term, so rate will simplify to K into C A minus C B by K equilibrium divided by 1 plus K B C B. These are all various different simplifications that are possible, if we if we simplify the overall overall rate expression.

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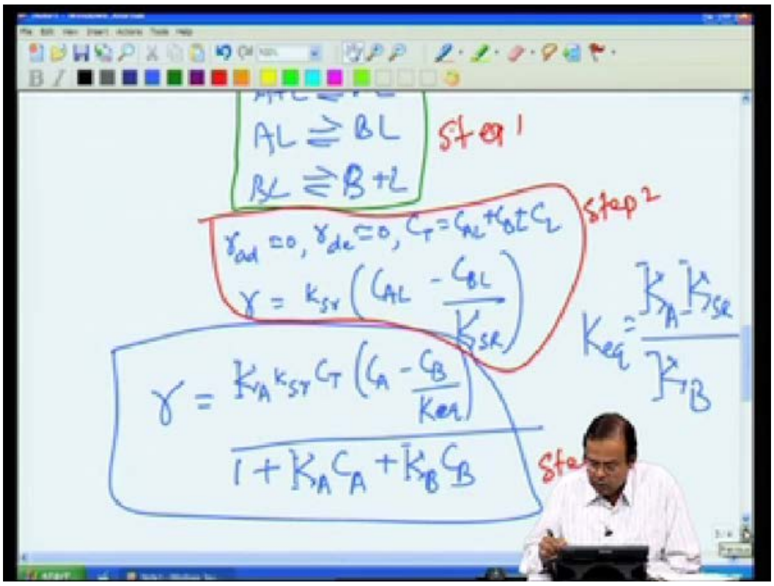

$$AL \rightleftharpoons BL$$

$$BL \rightleftharpoons B + L$$

$$r_{ad} \simeq 0, \; r_{de} \simeq 0, \; C_T = C_{AL} + C_{BL} + C_L$$

$$r = k_{sr}\left(C_{AL} - \frac{C_{BL}}{K_{SR}}\right)$$

$$r = \frac{K_A k_{sr} C_T \left(C_A - \frac{C_B}{K_{eq}}\right)}{1 + K_A C_A + K_B C_B}$$

$$K_{eq} = \frac{K_A K_{SR}}{K_B}$$

So, to recap what what did we what did we do. We had a we had a overall reaction, we wrote the mechanism for this reaction, so mechanism. We identified the rate determining step and used quasi equilibrium approximation. So, we had adsorption rate 0 almost 0, desorption rate almost 0, total site balance and the rate determining step giving us the rate of reaction, and simplified this little bit and got our overall rate reaction. So, three steps: step 1, step 2, step 3. Of course, the next challenge will be to experimentally verify this reaction rate whether does it indeed follow this kind of form; if it is yes, then our mechanism is correct, step one we are not made any error. But if not then we have made some error somewhere, so we have to rework this entire exercise by assuming the different mechanism making perhaps may be different simplifications and so on and so forth.

Now, it could very well happen that surface reaction is also fast compare to adsorption, so desorption is the rate determining. If that is the case then we will say r ad, r sr are almost equal to 0, and r de is not equal to 0, and we will get a different kind of kind of rate expression.

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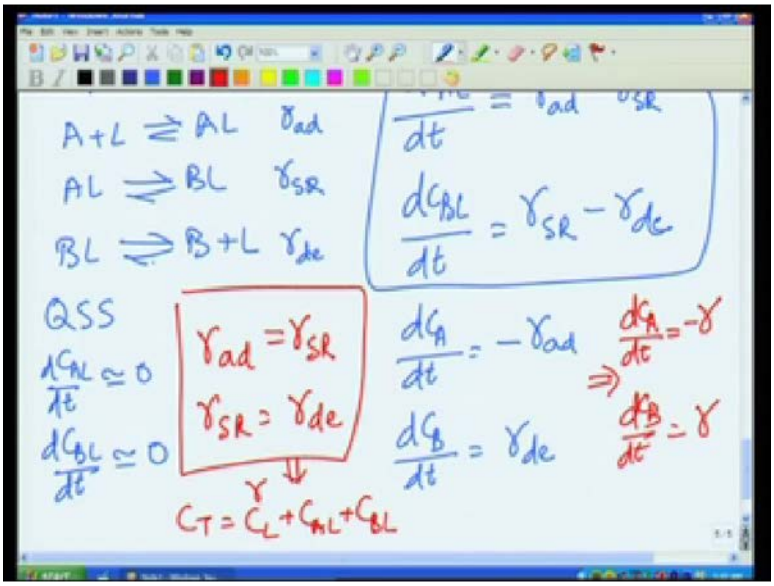

$A + L \rightleftharpoons AL \quad r_{ad}$

$AL \rightleftharpoons BL \quad r_{SR}$

$BL \rightleftharpoons B + L \quad r_{de}$

$\frac{\quad}{dt} = r_{ad} \quad r_{SR}$

$\frac{dC_{BL}}{dt} = r_{SR} - r_{de}$

QSS

$\frac{dC_{AL}}{dt} \simeq 0$

$\frac{dC_{BL}}{dt} \simeq 0$

$\boxed{\begin{matrix} r_{ad} = r_{SR} \\ r_{SR} = r_{de} \end{matrix}} \Downarrow r$

$C_T = C_L + C_{AL} + C_{BL}$

$\frac{dC_A}{dt} = -r_{ad} \qquad \frac{dC_B}{dt} = r_{de}$

$\Rightarrow \frac{dC_A}{dt} = -r \qquad \frac{dC_B}{dt} = r$

Let us let us look at the second approach that that we we could also also follow. This is of course, quasi steady state approximation. So, what is this this approach? Let us let me let me write my reaction once again, A going to B overall action, the mechanism…

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And now we are going to use quasi steady state approach. Our rate of this reaction is r ad, this is r SR and this is r desorption. So, we are going to now use quasi equilibrium quasi steady state approximation to to write the write derive the rate expression. So, our objective is still to get r as a function of C A C B.

So, to use quasi steady state approximation, what is this approximation? It says that some of this species in my reactions scheme are highly reactive. So, their formation and their appearance and disappearance are very rapid, and therefore, their dynamics is almost negligible. They have reached a steady state, not the whole system has reached the steady state, but few of this species have reached the steady state. So, which are the species in this scheme of things? Yes, you guessed it right; AL plus AL and BL, because these are active species, so they get formed and get disappeared also very rapidly. So, we can write the balances for this, so let us write C AL, closed system once again. And we can write in terms of these rates of these three reactions as r ad, because it is getting formed in the first reaction minus r SR. You could actually write the stoichiometric matrix and then write the entire set, if you want to verify you will get the same thing. r

SR minus r desorption for the species species B. What is the rate of consumption of A? Minus r adsorption; what is the rate of formation of B? r desorption. So, the entire set of mass balances for this for this species.

So, now we are going to make a quasi steady state approximation which says that d CL dt is close to 0, dynamics is very slow; d C BL dt is also very low value, so C L, C BL have reached steady state that is species A L and species B L. If we do this with this two this set of relationships, what do we get? We get r ad equal to r SR, and from second one r SR equal to r desorption. Or in other words quasi steady state approach tells us that the rate of adsorption is equal to rate of surface reaction is equal to rate of desorption. And then naturally you can see this would this this approximation together with this would imply d C A dt is what is our rate of reaction and that is, so this is equal to r, let us call this each of these rate as r, then we will get what we expect. The rate of disappearance of A is r, the rate of appearance of B is r. I mean that is what that is what we we we expect anyway.

Now, if we now our next step is to get actually that r in terms of C A and C B. So, if you want to do that again once again C L, C AL, C BL are unknown quantities, so we need to solve for them. And if you see here we already have two relationships, all we need is the total balance. So, we have three relationships that is same active site balance that we used. We have three relationships and three unknown quantities, so we can eliminate those.

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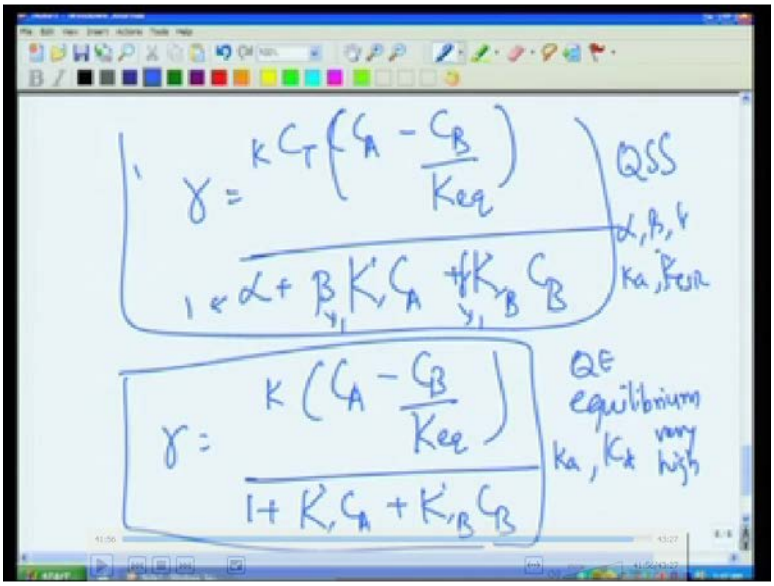

$$r = \frac{k C_T \left(C_A - \frac{C_B}{K_{eq}}\right)}{1 + \alpha + \beta K'_{1} C_A + \gamma K_{1B} C_B}$$

QSS

α, β, γ

K_a, K_{SR}

$$r = \frac{k \left(C_A - \frac{C_B}{K_{eq}}\right)}{1 + K_1 C_A + K'_{1B} C_B}$$

QE

equilibrium

K_a, K_d very high

And if you do that for this particular reaction, we will get r equal to…

(No audio from 37:07 to 37:28)

What did we get for equilibrium approach if we used? Equilibrium approached if we use then we get (( )) constant. So, K…

(No audio from 37:41 to 37:56)

This is what equilibrium approach gives us for quasi equilibrium. This is what this is what quasi steady state approximation gives us.

If you look at these two relationships they are almost same. Why almost same? They are the qualitatively exactly identical. Look at the driving force term, look at the adsorption term, functionally they are same and then there is a kinetic kinetic term. So, both these approaches give us the same functional form for the rate expression. But I must also caution you that that is not always the case. It was only for this reaction C A and C B or rather just A going to B that we got both forms to be same.

In general, quasi steady state form and quasi equilibrium approaches need not give you the same functional form. But if that is that is the that is the case here, at least they are functionally same, which also tells us that somehow quasi steady state approximation and quasi equilibrium approximation are related to related to each other. By the way what is this alpha, beta and gamma of course, what are they? This alpha, beta, gamma are contains this terms such as rate constants or equilibrium constant SR and so on, combination of that. It is a little complicated so I am not reproducing it here. You can see that in any standard text book.

So, what happens, so what is a link between quasi steady state and quasi equilibrium equilibrium approximation? Quasi steady state approximation as you can see here is a more generalized approach. We do not have to assume that individual steps or reactions are fast or slow and so on. We do not have to even assume that there is a rate determining step. Always said was the species are reactive. So, it is a more general approach compared to quasi equilibrium approximation.

Now, what is a connection between the two? So, this is a simplified form of this particular rate expression. What did we assume in quasi equilibrium? In quasi equilibrium we assume that K a and K d - the kinetic rate constants of adsorption and desorption reactions are very high. So, if we make that assumption and put it into the quasi steady state approximation that is this alpha, beta, gamma are all these functions of K a, K d. It turns out that we get alpha to be 1, beta to be 1, gamma to be 1 or in other words quasi steady state approximation general form reduces to quasi equilibrium approximation. If you make an assumption that K a and K d are very large compare to compare to K SR. And that is that is the connection between the two - quasi steady state approximation and quasi equilibrium equilibrium approximation. So, this in short is how we get the kinetics of the catalytic reactions. Let it be let it be homogeneous catalysis, heterogeneous catalysis, right now it is only the reaction, so we are not worried about whether there are one phase or more phases present in the system.

So, to summarize for a catalytic reaction, we get rate expressions which have kinetic term multiplied by driving force divided by the adsorption term. The adsorption, desorption terms denote the strength of how strong or weak is the adsorption of A on to the or the reactants and products on to the on to the surface; surface reaction term determined by what kind of reaction that is taking place, whether it is a single site, dual site or reaction of Rideal Eley mechanism, such as adsorbed species and gas molecule for example.

So, we will we will conclude our session on kinetics of catalytic reaction. And in the next class, we will look at last set of complex reaction namely, a case where we do not have precise idea of what these reactants and products are, and so how we deal with such situations, how do we determine their kinetics. Thank you.