Chemical Reaction Engineering
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Lecture No. #14
Catalytic reactions - Adsorption and Desorption

Friends, let us continue our discussion on the kinetics of catalytic reactions. And in the last class, we discussed about why catalysis is so important or catalyst is rather so important, not just for enhancing the rate of reaction, but also for increasing the yields, and selectivity's reducing the energy as well. So let us now, try to look at how we define the kinetics or how we derive the kinetic expressions - rate expressions for catalytic reactions. Let me let me recap the number of steps that are essential for a catalysis reaction to occur, and we are talking mainly in terms of gas-solid or liquid-solid catalysis.

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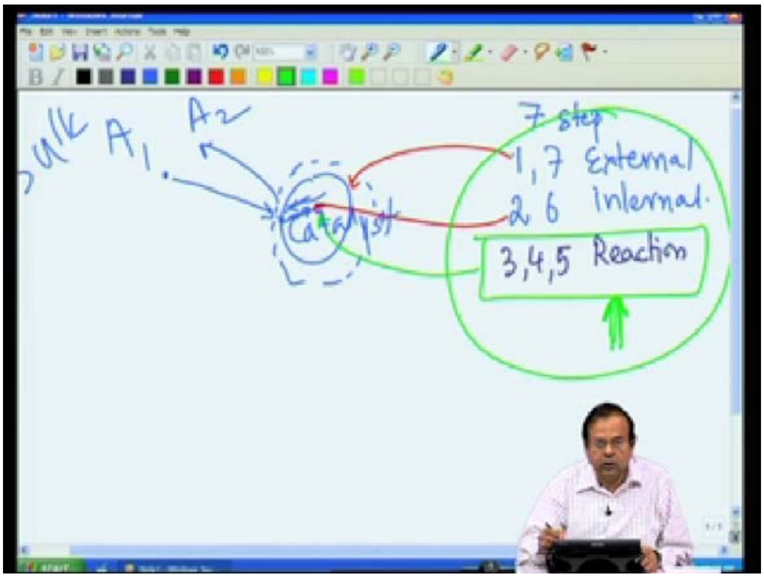

So you have a solid particle. Let us say catalyst, so this is my catalyst, and surrounding this are my reactants. Let us say A 1, A 2, and so on. So, what must happen first is that, the gas reactant molecule from the bulk phase; so, this is all my bulk phase. And this is my, the circle is my catalyst catalyst phase. So, what must what must happen is that, the gaseous reactant molecule should should come to the come to the catalyst surface, and in order to simplify the analysis, we assume that all the resistance to mass transfer is located in a thin film which surrounds this catalyst surface.

So, from bulk to the end to the edge of this thin film, shown by this dotted line, there is no resistance. All the resistance to mass transfer is mass transfer is located, located in this in this thin film. Now, one important point that I mentioned last time also, that is when you have heterogeneous system. There is when you have more than one phase. Like gas, and solid over here; there are boundaries between this two phases. So, there is a gas phase, there is a solid phase, and there is a boundary between the two phase.

Moment we have boundaries, there is a resistance to transfer. And it is this resistance which actually influences at what rate, the reaction will take place. That is whether the reaction will be kinetically controlled or the kinetics that plays a role or it is mass transfer control, will be determined by what kind of resistances, we encounter when there is a transfer across the boundary.

So, to begin with we say that, the resistance is localized in this thin film over here, thin film over here. This surrounding the surrounding the catalyst surface. So, once the gaseous molecule reaches the surface of the catalyst, since the catalyst is porous it has to defuse inside, it has to defuse inside get adsorbed onto to the active component. Undergo chemical reaction get desorbed from the from the surface of the catalyst; flow backward in this channel to the external boundary, from external boundary to this edge of this resistance boundary or film boundary; and from there back to the bulk phase. So, there were total 7 steps that we talked about.

First and 7 step external mass transfer, number 2 and 6 internal mass transfer. That is external mass transfer relates to transfer across this boundary, internal mass transfer relates to how the transfer is taking place in the pores, and then steps 3, 4 and 5 reaction steps. That is adsorption onto this, adsorption onto this material then surface reaction, and then desorption. So these are all three reaction steps. So, kinetically speaking, we are right now concerned with only this step. We will bring in these external, and internal mass transfer may be few sessions down the line. And how they influence the rate of reaction. So, when we talk about the kinetics, we are interested in finding out what is the rate of a reaction - which is a result of this three steps: adsorption, desorption, and surface surface reaction.

That is what we call true kinetic rate, and if this rate is what is controlling. Now, what is idea of controlling - we have kinetic rate. Similarly, we will have external mass transfer rate, we will have internal mass transfer rate. So, depending upon which of these three processes is slow, that will determine the overall rate of this reaction. So, if the reaction rate is is the slowest step; the reaction is the slowest step compared to the diffusion, then we say that this reaction is kinetically control. On the other hand, if the external mass transfer is the slowest, we say it is external mass transfer control.

Similarly, internal mass transfer control - if internal mass transfer is one of the one of the slowest step in the in the reaction. So, let us start looking at what happens when this adsorption, desorption or how do we characterize these these reactions.

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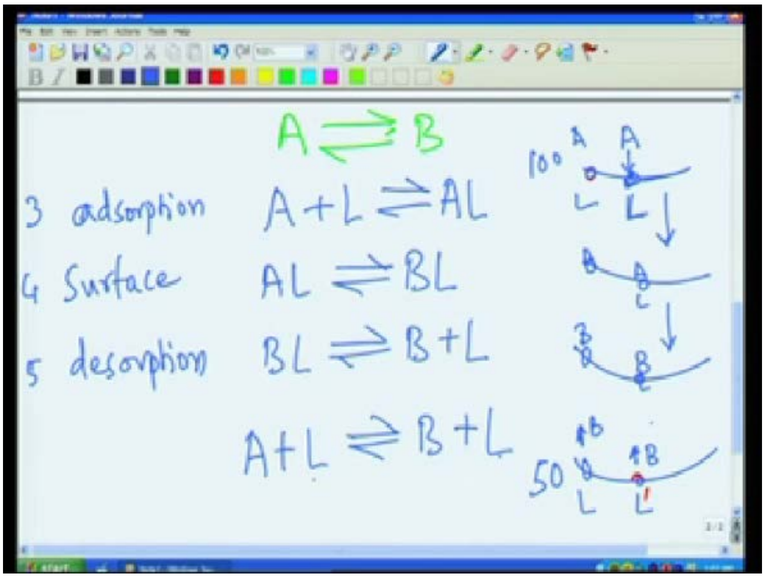

And to do that, let us start with reaction. Let us say that we have a reaction A going to B. We can consider a reversible reaction; A going to A going to B. So, now we will start our analysis by considering the first step - the adsorption step. So, the mechanism that we talked about, can be represented in the following form; we have now, let me just say that this is my catalyst surface now. And this is a location where the the the active material is there. Recall that we talked about the catalyst is not entirely made up of the material, which will bring about this transformation, because if you are making a porous catalyst, at least you need something to hold this porous structure together.

And many times that is that is not feasible with the catalytic material itself. When besides if you have for example, using a catalyst like platinum, having a platinum ball as a catalyst is a will be a disaster, because the cost of that catalyst itself, will will be more than any profit that, you can probably make from making this product.

So what is done is, you have a support material onto which this platinum is deposited. So, this is let us say one of those sites where the platinum is deposited. We will call this site as L; we will call this site as L, that is the lag end. And my A is going to interact with this active site L. So, my first step is A plus L gives raise to AL. I will call this AL, as AL; A sitting onto the active active site. So, this is if you recall my third step in the description or adsorption.

Now, what happens when when this this catalyst acts for variety of different reasons, and we we it is not in our scope to go into the mechanism; the the that is the chemical mechanism of this catalysis. You will require a full course on chemical kinetics or catalytic kinetics to understand that. But let let just say, that it undergoes a transformation. So from here, it becomes my product B, but still attached to this active site. So, let me write my surface reaction; so called, because it is occurring on the surface of the catalyst. So, AL becomes BL, but if this B is attached to this catalyst surface forever, that is once it is bound, it is there forever then obviously we cannot cannot have our product, back into our bulk phase.

So, what must happen next is the B is detached from the from the catalyst site or desorbed from the catalyst site, and moves back into the bulk. So, this step we call desorption- we call this step as desorption. And we can write this as B plus L, and this is what is what is happening when the catalytic reaction is taking place. Notice here, that we started with an free active site, and then we ended up with free active site. That is B have the active side back, after A got converted to B, A got converted to B. So that, the next molecule of A can come back interact with this L, and go through this go through this cycle.

So, regeneration of this active site or catalyst is is crucial. And this is the reason why many definitions of early definitions of catalysis catalysis, where put forward in the following manner. One of them said that, catalyst is a material which does not appear on reactant and product side. So, if you look at this overall reaction, I do not have my catalyst actively participating in the reaction; so, we have A going to B as as a general general reaction. But another definition also said, that it is a material which appears on both reactant side and product side. So that means, A plus L gives raise to B plus L; if you add up all these three reactions, we will end up with this. So, my catalyst appears on both sides of the reaction, the reactant side as well as product side. And hence various different different definitions.

But it is important to realize, that the catalyst site that we are generating must be same as the catalyst site, we started this cycle with; that is there should not be any chemical change in the structure of this catalyst site. For example, to give you an example suppose and it does happen indeed for some catalytic reactions, suppose while this (( )) chemical transformation is taking place and desorption is taking place. If this catalyst site is coated with carbon let us say; coated with carbon.

Then we can no longer say that the catalyst site that is regenerated over here is same as the, what we what we started out with. So, this will be the catalyst site which which got regenerated will be will be something something different than the catalyst site, we started out with. In which case, the second molecule of the gas molecule cannot come and effectively bind.

Now, if all sites on this surface happen like this. Then of course, we have lost the catalyst for ever. But what is more common is for example, there are various different, various different sites; this is not one, so these are all our L's and everywhere A is trying to interact and so on. So, it is possible that some sites carbon is deposited, some sites carbon is not deposited. So, when the catalyst was in the initial stages of reaction; let us say that it was fresh. We had mini catalytic sites, but in such scenarios at the end of these reactions, we are not able to retrieve all those active sites, but some of them have been lost.

So, we say that catalyst has lost its activity or is partially deactivated, because of because of some chemical transformations or other things temperature for example, may also play A role. So, because of that the catalyst has activity has decayed or catalyst has deactivated, does not mean that it has lost its activity fully. But to put hypothetical number, if 100 was the activity of the fresh catalyst, over a period of time we may end up the only 50 percent of those catalyst being active.

Now, one of the motivations for using catalyst is to keep on using it, because if you see, if all these 100 were indeed regenerated; then we could indefinitely use this catalyst. And that is one of the motivations for using catalyst. But if only 50 are are remaining after some sometime, then you may have to think of replacing the catalyst. There is throw away this old catalyst, and start with the fresh catalyst. And periodically keep on refreshing your catalyst stock - replenishing the catalyst stock. So, that is all that also becomes an crucial step in in deciding on a catalytic reactor design.

There is how long are we going to use this catalyst. (( )) what is a good time to replace, because on one hand replacing the catalyst involves cost, on the other hand not replacing the catalyst means loss of activity. And therefore lower productivity, lower yields, and so on; so, one has to then strike A balance between the cost of the catalyst, and loss in loss in productivity. And decide upon when to replace that replace that catalyst.

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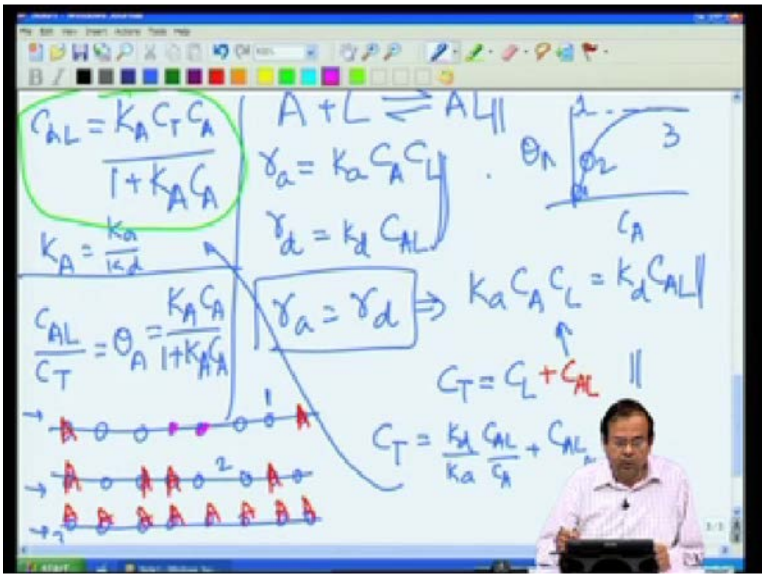

$$C_{AL} = \frac{K_A C_T C_A}{1+K_A C_A}$$

$$K_A = \frac{k_a}{k_d}$$

$$\frac{C_{AL}}{C_T} = \theta_A = \frac{K_A C_A}{1+K_A C_A}$$

$$A + L \rightleftharpoons AL$$

$$r_a = k_a C_A C_L$$

$$r_d = k_d C_{AL}$$

$$\boxed{r_a = r_d} \Rightarrow k_a C_A C_L = k_d C_{AL}$$

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

$$C_T = \frac{k_d}{k_a}\frac{C_{AL}}{C_A} + C_{AL}$$

But now, let us let us go back to our kinetics; and we will start with this adsorption adsorption, reaction. And write it simply A plus L going to AL. Now, you would have noticed, even though my last step is BL going to B plus L; this is actually nothing but reverse of my adsorption process of BL. So, whatever discussion we we can apply to the adsorption step, the same discussion in the reverse manner applies to desorption. So, we will not be discussing desorption step separately, but it is understood that one is the converse or reverse of reverse of other.

So, we we let us let us now start writing the kinetic rate expressions. So let us say that our attachment rate, that is adsorption rate A adsorbing onto L, is it is a law of mass action kinetics; so let us say, it is some kinetic rate constant K a, concentration of my reactant A, and it will also depend on the concentration of the active sides C L. So that is a adsorption rate, I can similarly, write the rate of AL going to A plus L; that is desorption as K d, d denoting desorption, a denoting adsorption over here into C AL. So, I am right now, focusing only on single step adsorption, I have not even brought in desorption, I mean I have not even brought in surface reaction, and then couple it with desorption.

But let us look at what happens when we have adsorption. And how do we develop adsorption isotherms. So this is my rate of, this is my rate of rate of adsorption, this is my rate of rate of desorption, and what happens at equilibrium. So, I will consider adsorption as an equilibrium process. At equilibrium, r a that is the rate at which A is adsorbing onto L, and the rate at which AL is desorbing must be same or in other words or in other words, r a must be equal to r d. So, this is at equilibrium; some of you may be wondering that we are trying to define the kinetic of a reaction, and we already got equilibrium.

Where did the kinetics go, but believe me, we will come to the kinetics very shortly. So, equilibrium r a must be equal to r d. What does this imply, this implies that K a into C A into C L is K d into C AL, from definition of our adsorption and desorption desorption rate. Now, what is it that we are trying to determine here; we are trying to find out that given concentration of A CA. what is the fraction of A that is at equilibrium with the catalyst. So, that means what is the concentration C AL.

Now, if you look at these balance we have one relationship, we will we will say that C A is the concentration, which is present in the system. So, we know that; so this is an this is an input, this is an output. And we have a relationship between input and output in which K a, K d are adsorption, desorption rate constants, but there is another quantity C AL which we do not know. Knowing C AL would require, that if suppose let us say this is my catalyst, and these are all my active active sites; and when the A is there some of them have A sitting on it.

So, on my catalyst surface what do I have, I have vacant site L on which no A is sitting and an occupied site AL on which the reactant molecule has has spread. What I am interested in C AL is this concentration. So, what are the difficulties in knowing that, difficulties are to know this first we have to know, what is the total number of sites here, 5 as illustrated 6 as illustrated in this example; it is just an an illustration. But how do I know that our priory; it is very difficult, we do not know really.

And on top of it, we also do not know how many are occupied, because that is what we are trying to find out. So, what do we do with these vacant sites. And this is what we do with the calculation of vacant site. And this is an important important concept which is commonly commonly used.

So let me let me, go back to my catalyst. And let us say that we were some active sites - some active sites, some of them have been occupied by A. And some are free, as we as we talked about. But we also realize by looking at this cartoon that whatever it is, whether it is occupied red or unoccupied blue; the total number of sites on the catalyst are same. That is in one scenario in one scenario, I am trying to replicate the same active site, in one scenario there may be 4 A molecules occupying 4 sites. In another scenario there may be only two occupying; that may vary that will vary depending on what is the concentration of A in the bulk, but whatever it is, the concentration or the total sites are same.

So if I say that, my total sites on the catalyst is C T, then this must be same as C L the blue ones plus C AL occupied, and unoccupied, but this number is constant; that is that is wonderful. Because if this also now is a constant, then we can we can say that C T must be, we can put for for C L. For example, C L we can use these use these relationship or or other, let us let us use that relationship; namely k d by k a, C L by C A; k d by k a C A

A plus C AL is is my C T.

So now, if we now in this expression, all I need to do is to rearrange this equation. And if I do that, I end up with the following relationship. That is if I rearrange this I end up with C AL equal to K A, I will talk about what is K A, C T, C A divided by 1 plus K A C A. What is my K A? K A k capital A is nothing but the rate constant k a divided by the rate constant k d. So, k a is actually nothing but an equilibrium constant. k a is nothing but the equilibrium constant. Ratio of the adsorption rate constant to a desorption rate constant; and that you can see from here itself.

k a by k d will be c AL by c A into C L and that is nothing but our equilibrium constant. So that is that that is that k A. Now, we know my fraction or rather the total sites which are which are adsorbed are C AL C A L equal to K A, C T, C A by 1 plus K A, C A or I can also I can also, express the same relationship as the fractional coverage C AL by C T which we call as theta A. The fraction of this surface which is occupied by this catalyst. It is for example, two by eight in this cartoon, in the first case; it is 4 by eight in the second case; so, 50 percent. Here it is only 25 percent and so on.

So this is nothing but K A, C A by 1 plus K A, C A. And that is my adsorption isotherm, you probably also will know it as Langmuir adsorption adsorption isotherm. What is a characteristic of these isotherm - the characteristic of this isotherm is if I plot C A verses theta A, C A verses theta A, it will be an an hyperbolic curve like this.

There is when C A is small, concentrations are small; the number of occupied sides will be also small. So this is a situation where C A is C A is small. It go on increasing increasing C A more and more A molecules will occupy; so this is that intermediate intermediate steps. So let me say that, this is the scenario at step one - so this is my step one. This will be something at step two, so this is my two, but then what happens if I keep on increasing the concentration of A.

So let us consider a third case, that these are my same active sites. And I am increasing my concentration of A; so more and more A are available, there will come a time when all the sites are occupied by A, all the sites are occupied by A; so this will be my situation three which is what is happening over here.

So, once all the sites are occupied, even if you increase the concentration of A, no more active sites available on the catalyst. And therefore, the coverage cannot increase or in other words this fractional coverage if you are looking at, will reach A value theta will reach A value one. So, let me let me recap this adsorption step. What we said was, we have A binding to L, step number one this is my overall reaction, this is my adsorption, desorption desorption rates. I assume equilibrium; then I say that total sites are either free or occupied, and do some algebraic manipulation to get my final adsorption isotherm.

So these are the steps, that we we follow for any adsorption isotherm. Important thing to remember, that when we say that the total number of sites is constant, we are considering the case when this catalytic cycle is going on there is no deactivation. So, there is no loss of catalyst, because if suppose these are deactivated as shown in the violet color over here. If they are deactivated then our C T is not constant; so, the key assumption here is that the total number of active sites are constant. That means the when the catalytic cycle is completed of adsorption surface reaction desorption, the vacant site we regenerate is same as the fresh site. If there is any difference, we have lost the catalyst. So now let us, quickly look at look at what happens other situation, this is the simplest situation, but remember that we have…

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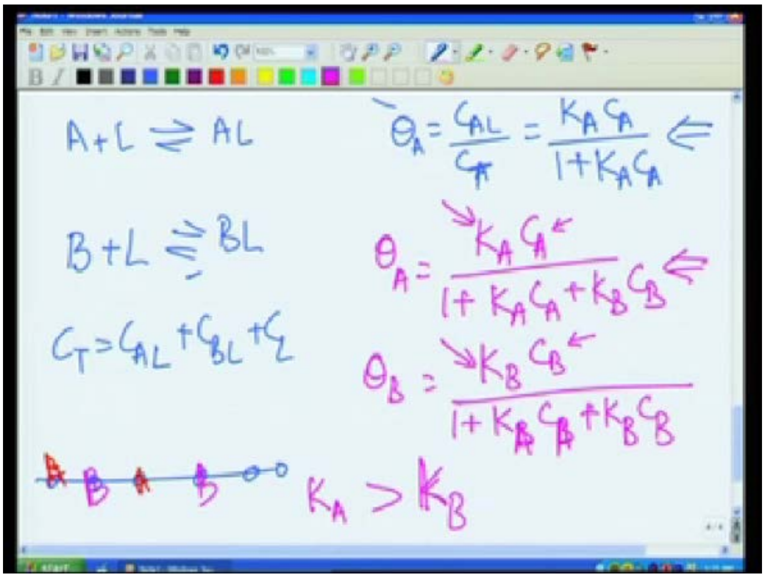

$$A + L \rightleftharpoons AL$$

$$\theta_A = \frac{C_{AL}}{C_T} = \frac{K_A C_A}{1 + K_A C_A} \Leftarrow$$

$$B + L \rightleftharpoons BL$$

$$\theta_A = \frac{K_A C_A}{1 + K_A C_A + K_B C_B} \Leftarrow$$

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

$$\theta_B = \frac{K_B C_B}{1 + K_A C_A + K_B C_B}$$

$$K_A > K_B$$

So let me let me erase all this or let us start a fresh by saying, that we just now considered A plus L or let me let me we considered we considered A plus L goes to AL, and we saw that we get fractional coverage theta A as C AL by C A, C T as K A C A by 1 plus K A C A. But in our gaseous reactant we have product B also, so we could have B plus L giving rise to BL; so, both this things happening simultaneously. So, if you once again go through the same exercise, so what we are essentially saying is these are the catalyst active sites. And some of which are occupied by A, some are occupied by B. So, what do what do you expect will happen.

Now, there is a competition for these active site between A and B, which means that the adsorption coverage of A will now be lower, there is if B was not there, we would have got certain coverage, because there was no competition. A A binding to the active site, moment B is present, there is a competition from B. So, the available sites for A now has gone down. So, if we if we if we carry out the same analysis by saying that same; adsorption, desorption rates of first reaction are same, second reaction are same, and using that equilibrium.

And now we will have to of course, use C T equal to C AL plus C BL plus C L. So if you do all that, we will get for the for the second case theta A equal to K A C A by 1 plus K A C A plus K B C B. And similarly, theta B will be K B C B divided by 1 plus K B C B 1 plus K A C A plus K B C B. Look at what has what has happened here. That is, let us compare this expression theta A with this when B was present. What does competition do. Competition has reduced the coverage of theta A, because we have A additional term in the denominator.

So for computational competition has reduce the coverage of coverage of A, what else has competition done. We can also argue in the following manner, which one of the two will be more; will B be adsorb more or A be adsorb adsorb more. What will it depend on obviously, it will depend on the concentration of A and B; that is if concentration of A is more than that of B, you expect coverage of A will be more than that of B. No surprise there, but it also depends on the relative values of K A and K B.

What is K A? K A is the adsorption constant for A - what is K B? K B is the adsorption constant for B. So, whosever has higher value wins. For example, if K A value is greater than K B, then you can expect higher coverage of A compared to B. In fact, why you can expect. If concentrations of A and B are same, and K A is greater than K B, then we can easily see theta A has to be greater than theta B. What does adsorption constant high value means, that means the affinity of A for the catalytic site is much higher than the affinity of B. So, A adsorbs more compared to compared to B.

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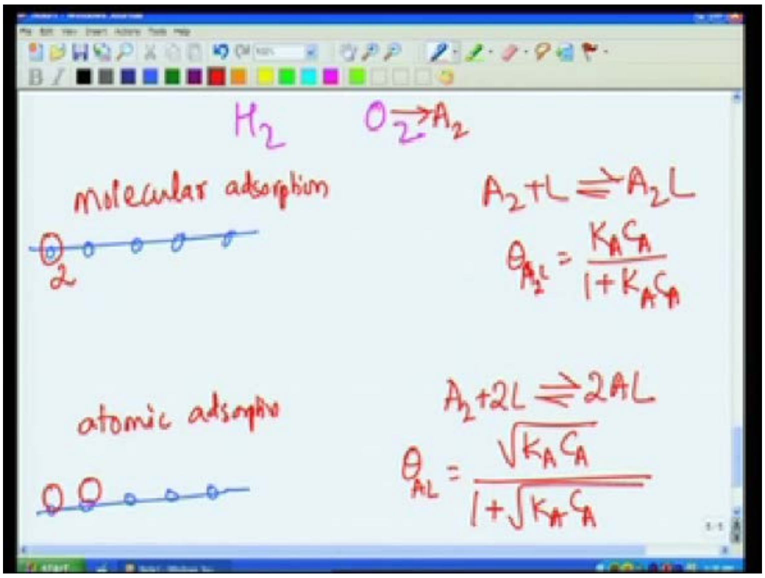

Let us consider few other scenarios. Now, many as I said many of these reactions are gaseous, and many of the gaseous involved in this catalytic reactions are diatomic gases - like H 2, like O 2, and so on. Now, there are two possibilities when this gaseous adsorbed onto the active sites. So, let us say that, we have let us put it over here, we have these active sites; one possibility is that this oxygen this oxygen simply adsorbs as a oxygen molecule. So, molecular adsorption...

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So, if I call molecule of A O 2 as as A, then this is same as A plus L giving rise to AL. So, entire discussion that we had earlier applies equally well. But quite often, oxygen or diatomic molecule - undergoes disassociation and the adsorption is now, as a atomic oxygen on two sites as an atomic adsorption, on two sites. So, what happens in in this particular case, and let me let me for sake of clarity, let us call this gas as A 2, not as species A 1, A 2, A 3, but just atom A twice - diatomic A 2. So, if I say this is A 2, then I need two active sites to give 2AL for for this case. Atomic adsorption; so let me let me let me rewrite this, I think I should have written it separately; so, for the molecular adsorption my A 2 plus L A 2 L only single site.

For atomic adsorption A 2 plus 2L 2 A L, A is my oxygen atom; I mean it can be nitrogen, it can be hydrogen or it can be even other diatomic gases. So now here, you will get same as before; theta A that is my fractional adsorption, it will be for theta 2 A A A 2 L here, will be K A C A by 1 plus K A C A. But if you go through the exercise for atomic adsorption, the same thing that we talked about, then we will get theta AL as theta AL as root K A C A by 1 plus square root K A C A.

I leave it to you as an exercise, where did this half came from or square root came from. If you know this reaction will be K A C A 2 concentration of A C A into C L square equal to k d into C AL square. So, if you do that exercise, you will get this rate expression. So here, K A C A root K A K A C A. So, this is this is as far as the adsorption is concerned. This is the simplest kind of adsorption adsorption isotherm.

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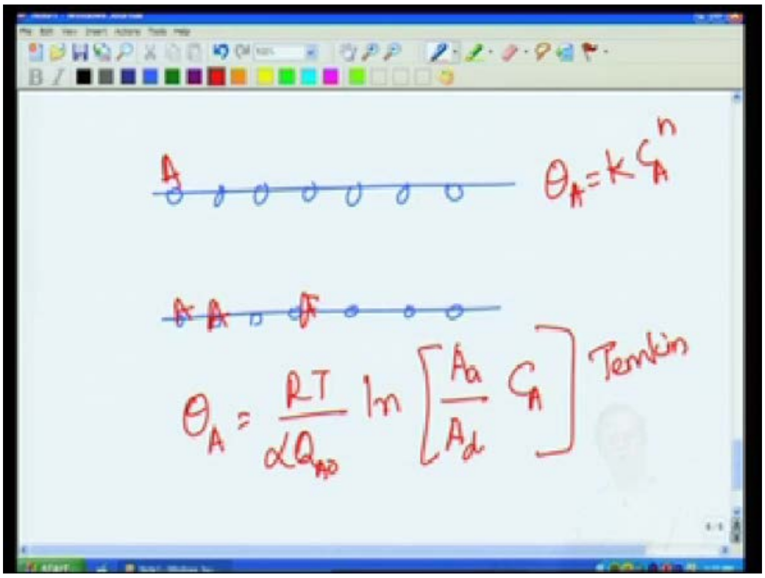

$$\theta_A = k C_A^n$$

$$\theta_A = \frac{RT}{\alpha Q_{A0}} \ln\left[\frac{A_a}{A_d} C_A\right]$$

Now, there are other types in the c adsorption isotherm, we assumed that we assume that, if if these are my if these are my active sites. Langmuir adsorption isotherm is that, all these sites are same energetically active. They are identical, there is no way to distinguish between the between the two. Now, another approach is to say that not all sites are same. So, I am going to just put some different symbol, I mean it differs. And in fact many times, it depends depends upon they are energetically different, so it depends on how many are occupied.

So, this may be the case when there are only few occupied, this may become the case when more are occupied. So, that means the nature of this active site, depends on the fractional coverage coverage itself. So, if if one looks at such approach, we end up with theta A as…

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This is what is called as Temkin isotherm. That is these are energetically non uniform. So this is, this is as far as adsorption is concerned. In fact, we can we can also get what we call Freundlich adsorption isotherm, under this assumptions. Where n and K are are are constants. So, we get Freundlich isotherm or Temkin; this is in fact Temkin isotherm is used in ammonia synthesis reaction. Freundlich isotherm is quite widely widely used, but most common is of course, Langmuir adsorption isotherm approach. And this is what we will be carrying forward in our next session, where we now bring in surface reactions, and see how these two interact to give us the kinetics of the of the process. So, that will be the topic of discussion in our next session, thank you.