

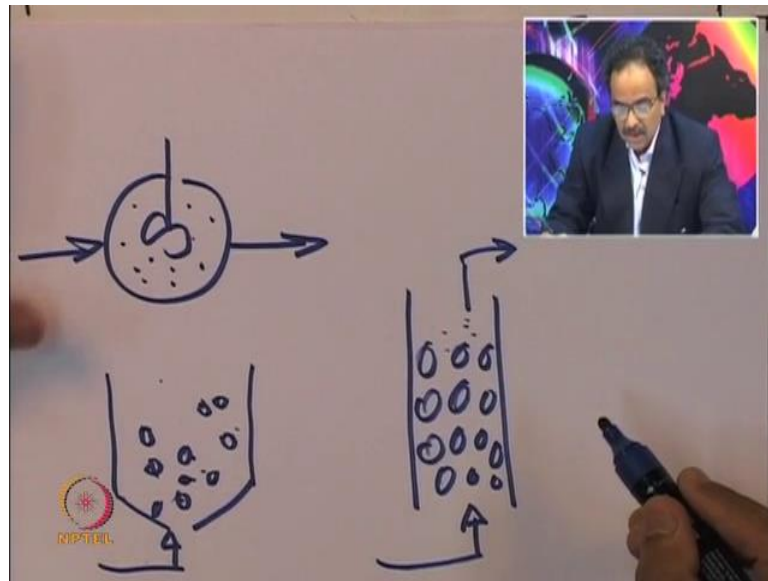
**Chemical Reaction Engineering II**  
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**Lecture - 2**  
**Step in Catalytic Reaction Adsorption, Reaction and Desorption**

Good morning. Will quickly review what we learned in last section. I told about what is catalytic, it reduces activation energy. The 2 types of catalytic used industry homogenizes and heterogeneous. Homogenizes catalytic are quit common because of the engineering benefits, they can is a break at very easily problem are less and that a main reason like most of the reactions are catalytic by the solid catalysts. Now, how to deal with catalysis, because the red expressions are different they are many other aspects like mass trams very facts, because we have multiple faces involved in the reactor and there is the possibility that you have different kind of radic expression depending on how the reaction take place of the catalysis surface.

Now, today we are going to look at different steps involved in catalysis. So, when a reaction takes place, is not as simple as like a is getting in contact with b in the presence of catalytic reaction takes place. Because here in this case, catalyst is or other catalytic is present in the solid fakes and the most of the time are the reacting product are in liquid or gas filled.

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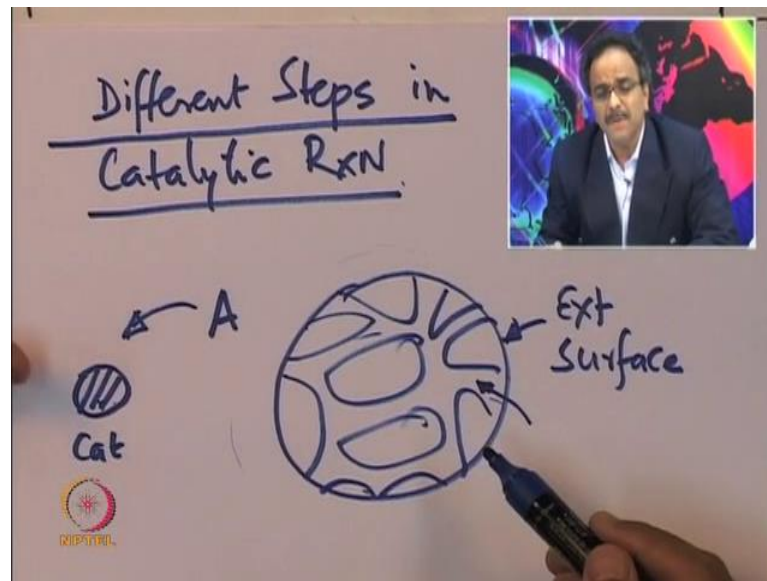


So, if you have reactors for a example, CSTR; in which, there is the reaction taking in the present of solid catalytic. So, it is like a slurry for example or it be give fluidized reactor, were the catalysis fluidize perform and the reactor both form the bottom and fluidize catalytic can be gas reaction or other gas faces liquid surface reaction mixer or it can be fixed based, were the catalysis part in the cattle in the tube and then you have flow taking place either the bottom to top or it can tip to bottom.

So, there is many possibilities, we good look at the catalysis reactor the detail and the relater and the design, but than just together in ideal as to what react molecular as due and the product molecular due, as well as reaction of the catalysis surface consult. So, we have the reactors sitting in the bulk, where is the catalysis present in the solid form on which the present. So, now the reactant has to go to the catalysis surface and the reaction as take the place there, now why deriving the rate equation or coming with the estimation of a the rate of reaction we need to understand all this steps.

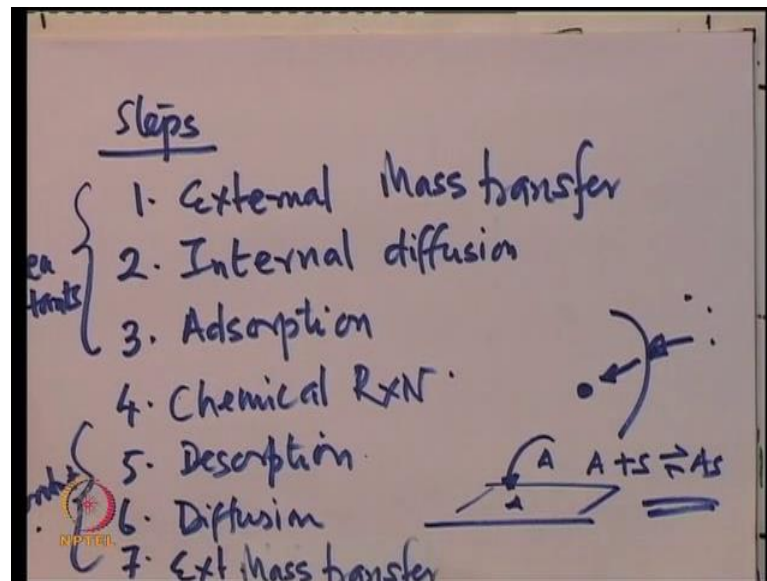
Because of this must of the time this steps, they take place in series, and because of that like one of them, if it control over all them in minutes to really concentrate on that ways. So, let look at deference steps involved in catalyses all a catalytic action to take place.

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So, I have a catalytic article and I have a reacted sitting in a bulk, further semi article like this. We just looking at 1 catalytic part of article and A that is the reactant go to go and react on the catalytic surface. As a told before, like inside the catalytic you have force. So, most of the times, we talking about force on which, much are the surface area is there. So, A as go to the catalytic surface first and then travel to the force and get access to the catalytic sides. So, has I said in the before lecture before or earlier lecture. You have this force presents and through is the travel. So, what it needs do first is, it as overcome the resistance offered by then environment, near the external surface of the catalytic. This is the external surface catalyses. So, that resistance needs to be overcome and after that a molecule as to travel to the pole. So, there is the different type of resistance offer by the particle. So, there are 2 different resistance is offered by this particular system for the reactant to go to the catalysis surface and reactor. And then subsequently I take place and then force your reaction and the same think happen case a product.

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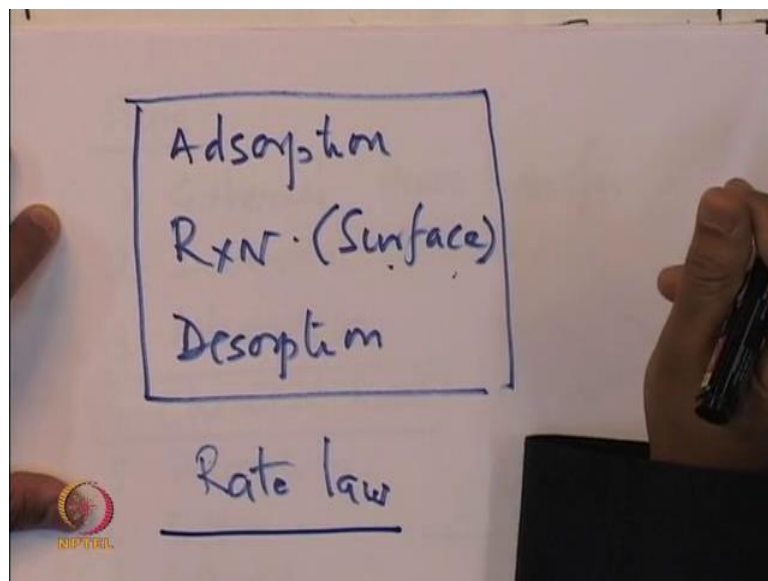
So, what are the different steps the steps are, External mass transfer from the bulk to the catalytic surface, than internal diffusion; that means, to the component or the reactant has to travel inside the particle through the force, environment is different that for the resistance off ward by particle, will depend on its own properties and off course the reactant. After that, suppose there is catalytic side present on the internal surface, then we have the actual reaction taking place, that put you yesterday, told you are last class I told you that, the component of the reaction, will not directly react because catalytic specie or the active side will be presence a surface though the reactant has to go 1 at saw on the surface first.

So, if have the surface on which the catalytic side is there. A as to gone adsorb, an form complex which he make called is as A plus S giving AS; we go deal with this latter in detail. So, so this adsorption has to take place and all this is the happens for the reacted first. It can be a reaction with multiple molecules, can the A plus B giving C or it can the A getting as well as B. So, it can the single molecular reaction can the bias molecular reaction. So, all this is going to happen for reactants, then once adsorption take place reaction will happen on the surface between the adsorptions or one of the reactant can be adsorption and the other reactant can the gas face.

So, actual chemical reaction will take place, for once the reaction takes place the same thing will happen for the products. What is that, the product has to desorb from the surface, because the reaction is taken place on the surface product at been that soft state. It as to desorption, then diffusion through the particle and then it should come out from the film. So, again the external mass transfers for the product. So, this is for product; so, this are the difference step are the taking place, when a many catalytic reaction on solid take place. So, we in order to standers understand the overall rate we need to understand each and every step, what it is depending on.

Because, most of the times the rate is governed by 1 or multiple of the steps of depending on what kind of condition, you are doing the reaction. So, there are 6 or 7 important steps, 7 important steps; main chemical reaction is 1 of them and rest all are mass transfer, diffusion side of particle, adsorption and desorption diffusion external diffusion again for the product. So, look at individual steps in detail, off course, to start with lets concentrate first on this steps that of the adsorption reaction and desorption. We will talk about, internal diffusion or same time it is also called as inter part diffusion and external mass transfer, in detail later and how to deface of these steps in overall rate.

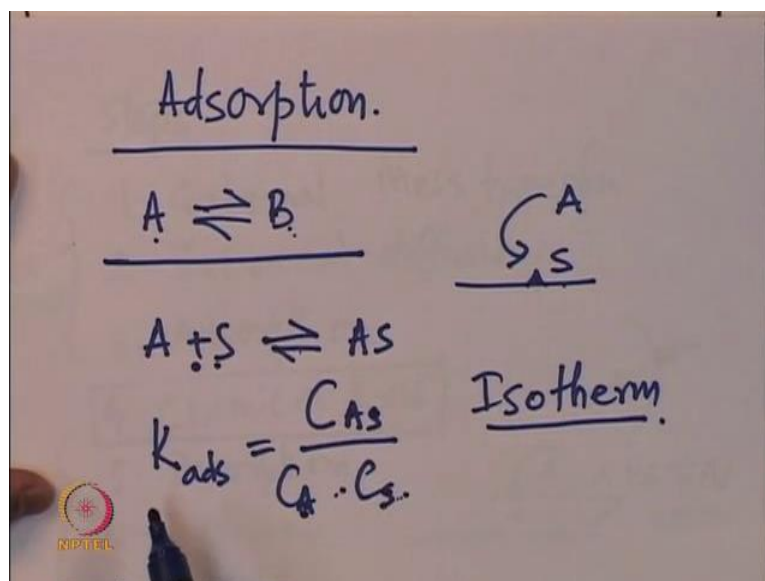
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So, let first concentrate on 3, 4 and 5 that is adsorption, reaction or some time called surface reaction and desorption. Way we want should study to this together, because this 3 steps with the late that, the overall rate of the reaction or actually the rate of the reaction, with the concentration in the liquid and at just in to a liquid or gas and just in to the solid surface. These 3 steps are going to gives the rate law.

So, in a normal case I have only the reaction taking place, were as in the case of heterogeneous catalyses a long with a reaction we have to adsorption and desorption both taking place simultaneous. So, the rate law is going to come up or going to be derived out of this, will depend on these 3 steps. Definition and intraparticle, external mass we detail with as the separate s side.

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So, let us talk about adsorption. Let us give mathematical treatment to this process, as you know, adsorption can give 2 types physical adsorption and chemical adsorption, out of which as a same before chemical adsorption is quit relevant here, will most of the time a reactant they formic kind of bond with active side and this bond or this particular complex is something that corresponds to at a transition state or a intermediate, which is at a peak of that a energy carve. Now, this particular adsorption can be treated as a reaction. So, let right, I have a suppose I have a reaction that is taking place, which is A

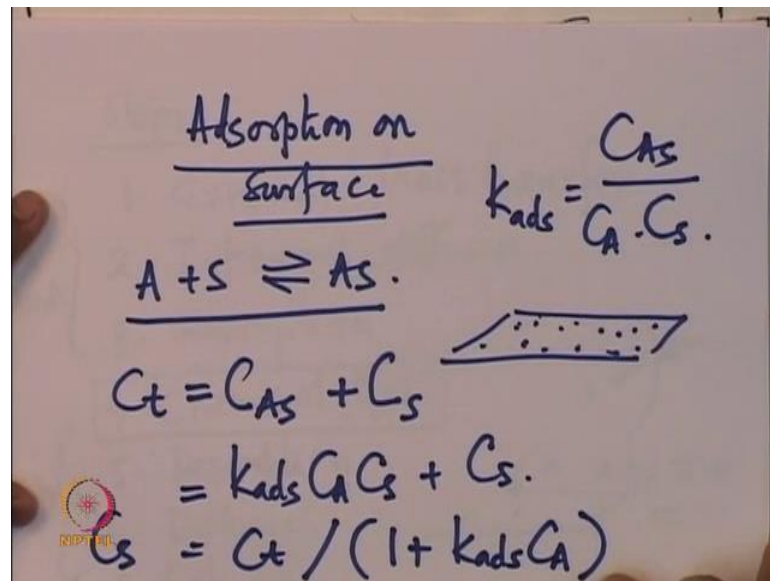
goes to B see say simple reaction as hum rations reaction, that is a overall reaction that is happening. So, this is A which is present in the reacting swings getting converted to B. Now, what is rate law of a this reaction, if the reaction take places on the solid surface, see in order to derived rate law we need to understand the different steps and we looking at the first steps that is the adsorption now you have at active side S. On which A is go on to adsorption.

So, let me write this as a reaction A plus S. So, this is a overall reaction and this is an individual adsorption steps were A plus S gives AS, this also is reversible process. So, that I have a reversible sing here. Now I am writing this a reaction. So, it may have its own rate, adsorption as an individual steps will have its own rate. Now, if the adsorption step is intense here, at any given time this equilibrium satisfied; that means, in the reaction very fogy equilibrium satisfaction. And what do we calls equilibrium as, in languages of adsorption it is called as Adsorption Isotherm.

So, can be come off with the expression for a adsorption as isotherm. So, that writes law of mass section. So, this reaction say K adsorption is equal to CAS divided by CA into CS. So, this is the law mass section; now in this, what do have, you have this as the concentration of adsorption psi AS. This as a concentration waken sides, what is S? S is a side. So, CS in a concentration waken sides and this is the concentration of the A in the bulk; now, the units can the different, this can be per unit the rate of catalytic of per unit surface area of the catalytic this would be per unit volume of a react can be anything and the according in the unit of K will get as this term, but this is a something I do not know waken side.

So, can I express waken side in terms of adsorption? So, when I do is permanent the laboratory for adsorption what I would determine is the concentration of adsorption side and concentration of A in the bulk. I when determine that is let I can explain this is in terms of other compotes. So, let us not vary about reaction right now, let us talk about only adsorption; that means, this only A present in bulk a part from inward, which is not getting adsorb probably yes and lets stand write the expiration for it, so adsorption of A on the catalytic surface.

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Adsorptions on surface and I am writing it is A plus S giving AS for which, I have, suppose I do a side balance; that means, on a catalytic surface, I have different sides. So, the total concentration of the sides  $C_t$  is equal to  $C_{AS}$ ; that means, there are some size on which is A adsorb of plus  $C_S$ , that there is some size on which no A is ads of all are the vacant sides. Please remember, the here we not considering reactional any other only A presents and off course in art. So, is getting adsorption and there are some side which can vacant. So, we just to trying to understand adsorption at the movement, we try to connect it with reaction bet later.

Now, you already return law of mass section for this reaction. What is that, it says K adsorption is equal to  $C_{AS}$  divided by  $C_A$  in to  $C_S$ ? If you calculate  $C_S$ , if you calculate  $C_{AS}$  from this, an substitute here and what you get?  $K_{ads}$  adsorption into  $C_A C_S$  plus  $C_S$ , when derives  $C_S$  expression  $C_S$  from this;  $C_S$  is equal to  $C_t$  divided by  $1 + K_{ads} C_A$  that is it. So, this is the expression for  $C_S$  if a substitute for this here, and then I get the relationship between  $C_{AS}$  and  $C_A$ .



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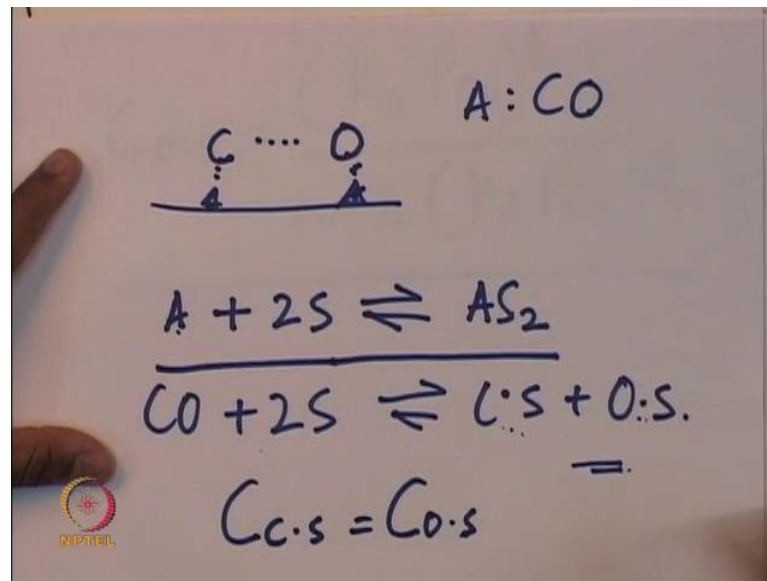
$$k_{ads} = \frac{C_{As}}{C_A \left( \frac{C_t}{1 + k_{ads} C_A} \right)}$$
$$C_{As} = \frac{k_{ads} C_A C_t}{1 + k_{ads} C_A}$$

Ads. Isotherm.

So, let do that. So, K adsorption is equal to  $C_{As}$  divided by  $C_A$  in to  $C_t$  divided by 1 plus K adsorption  $C_A$ . So, this is nothing by, the relationship between  $C_{As}$  and  $C_A$  and rests all that is K adsorption  $C_t$  they are constant. So, in other word  $C_{As}$  is equal to K adsorption  $C_A$  in to  $C_t$  divided by 1 plus K adsorption  $C_A$ . So, this nothing but the adsorption as isotherm, it relates  $C_{As}$  with  $C_A$ . Now, how to the know, it is adsorption as isotherm correct, this all based on over assumption that, A goes an adsorption on a single side, which flow the reversible reaction between A and S. If that assumption is correct, then in that case this expression is ok.

So, what we do to understand or to know whether this expression is correct or not, we do experiment in the laboratory. This is only adsorption time talking about; I am not talking about reaction here. So, just take A in sub a minute, if recurred and contacted with catalytic and look at how it behaves or a what kind of adsorption relation I get. We generate that I laboratory and relate the data with this, if you date fits very well in this particulate equation, then your assumption is correct and this adsorption as correct, but there is the possibility, that is not getting adsorpt or this single site, it quite possible that a gets adsorpt site at 2 sides at a time.

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So, for an example you have a surface on which we have 2 sites and A is a molecule. So, suppose A is carbon monoxide. So, what is likely to happen is that CA, the molecule for carbon monoxide will get adsorption on the 1 site and oxygen will get adsorbed on the other side. So, that the different possible ways. So, what kind of expression on reaction I can write in this particular case, because the 2 sites participating in adsorption, you have A plus 2S giving AS<sub>2</sub>. This is 1 possibility, if you want to write it in terms of actual components like for example, carbon monoxide, I can write it as CO plus 2S giving C.S plus O.S.

So, if you start from here the expression the time to get later, for an adsorption isotherm would be quite different. It will not be as simple as what we have derived just now, by considering A plus S giving AS; now, it is A plus 2S giving AS<sub>2</sub>. So, we can follow the same steps and then come out with an equation for an adsorption isotherm, it will have a very different form, if of course these 2 are again different. So, if I start with this and try to eliminate the vacant site concentration, in terms of CSA adsorption concentration and the bulk concentration. He will get an expression, which is quite different on the other side from the earlier one. In this particular case C.S is the same as O.S, the concentration of CS is the same concentration of OS.

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$$C_{O.S} = \frac{(K_A P_{CO})^{\frac{1}{2}} C_t}{1 + 2(K_A P_{CO})^{\frac{1}{2}}}$$


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$$\frac{(P_{CO})^{\frac{1}{2}}}{C_{O.S}}$$

=

$\frac{1}{C_t (K_A)^{\frac{1}{2}}}$

+

$\frac{2 (P_{CO})^{\frac{1}{2}}}{C_t}$

So, I give an expression, we can try to derive it. So, for example, if it starts with this particular case, the expression given goes to get of this particular nature say CO.S is equal to  $K_A P_{CO}$  raised to 1/2,  $C_t$  divided by 1 plus 2 into  $K_A P_{CO}$  raised to 1/2. So, trying to derive this equation based on this reaction as the adsorption mechanism and 1 more assumption that in a one more think, we remember deriving this is that  $C_{CO.S}$  is equal to CO.S. And that is quite understandable; because it comes they both O and S, O and C they come from same molecule. Now, let look at this expression.

So, I have given in then expression in the form of  $P_{CO}$ . What is  $P_{CO}$ ?  $P_{CO}$  is partial pressure is carbon monoxide, and now like if I am dealing with gas phase component, these are based on the better weight to express concentration that is nothing but partial pressure. So, concentration and partial pressure their interchangeable. So,  $P$  by alt is  $C$  and  $P_{CO}$  by alt is equal to  $C_{CO}$ . So, earlier we were dealing with concentrations. Now, that a talking about the gas phase component CO, I am expressing a in term to the  $P_{CO}$ .

So, do not get confuse if we are seeing in expression in terms of partial pressure in side of concentrations. We can derive this trace  $C$ , by following the same steps that what we are done, but taking the side balance as an all, we are able to derive. Now, why we are doing all this, because now I have got is different expression (( )), and then again and

generate data and the laboratory. And see, whether this fits well in the as a isotherm and if it fits well, then this is my isotherm equation and this is the adsorption mechanism that is, that 2 sides participating. So, as automatic level adsorption thing place, see is getting adsorption 1 side and O is getting adsorption other sides.

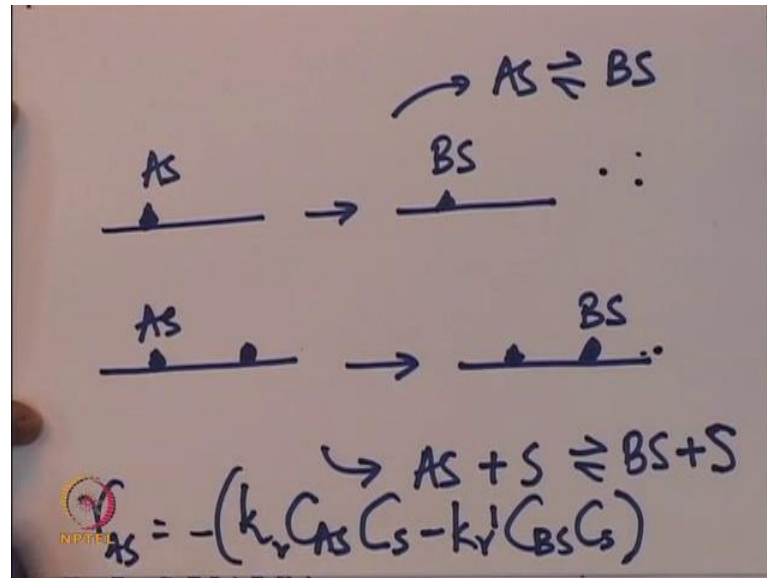
So, because of this we have different types of adsorption equation that a possible and the to see, which 1 is correct. So, we know the mechanism also and you get a right adsorption equation that you go to use latter, in deriving the rate law. So, in this particular case, if a have been talking about fitting isotherm data, you can give different forms to this particular equation. So, this particular equation can be written in the form  $\frac{P_0}{C_0} \text{ re se to half divided by } C_0.S \text{ is equal to } 1 \text{ divided by } C_t K_A \text{ re se to half plus } 2 \frac{P_0}{C_0} \text{ re se to half divided by } C_t$ .

So, this is nothing but or this is same as this, but I given a form which looks like a linear plot between this say this is y and this as x. And If I plot this, than I am go to get this a and this slow. So, I will go to generate the data  $C_0.S$  verses  $P_0$  in the laboratory and put them the form like this, and if I getting linear relationship between this 2 than, I am suave that this expression volts good. So, this is the way to know to how adsorption take place and what is a right kind of a adsorption isotherm, that is applicable the particular the case. It may very form component to component, if a very from a adsorbent to adsorbent. So, if it ways batter that we do this exercise, before we go head and time fine out how the adsorption take place and what is the adsorption isotherm equation applicable in that particular case.



am say here, that on a catalytic side A is getting adsorb. So, I have AS here and I am the same side its getting transforms to be that mans this.

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So, you have AS, you have this saturation it gets convert in to BS on the same side, this is called single side mechanism. Now, this is a possibility that another side may be involved in this, it may be like this, you have AS there is a site here, in order for A is to get convert in to BS, if needs help of this side. How off course not, if do not know, if should not go in to that must detail, but let assume that, this side is required for conversion invest to AS. So, it may you after the reaction you may something like this.

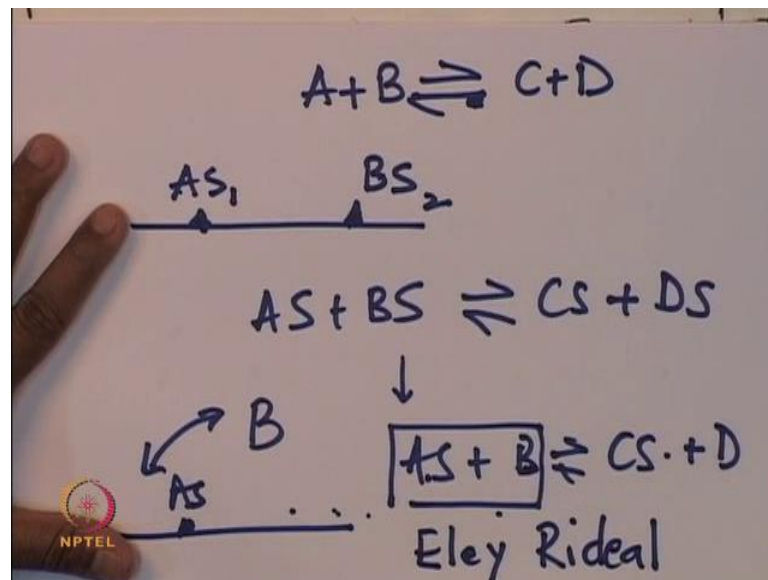
So here, the question is, a in this case, the question is equilibrium BS here, it is A as plus S is an equilibrium BS plus S; you may have 3 sides required. So, it all depends; so, not necessary that, you always need 1 side for conversion, so, that different mechanism. So, that how the reaction on solid surface, is different from what happens in normal homogeneous medium. Because we have discrete catalytic sides available on the surface at several, at different positions, divisions. So, there is a possibilities that you may this particular situation, you may have 2S here we may need 1 more side.

So, there many possibilities accordingly your equation will change. Now, in ordered for

this reaction to take place, I have 2 sites in world. So, its rate is equal to this particular reaction  $r_{AS}$  is equal to  $k_f C_A C_B$  minus  $k_r C_C C_D$ . You may say,  $C_A C_B$  common you can between these known, because  $C_A C_B$  change it 2 times. It is in equilibrium, it at adsorption is passed it is in equilibrium with adsorption easiest. So, accordingly rate equation will change.

So, there are different methods that can be used possible, the first one is single site, second one is called as dual site. It is dual site mechanism, the scientist in who have come of with these are and of course, these are the kind consists of the initial would applied them to get this equations that is why it is this is called a. So, this is the in the single site mechanism, a single site kinetics and this is Langmuir initial would dual site. So, now, I am talking about just 1 as adsorption reaction. Let us take an example of a Bio molecular reaction or 2 different reactions reactive, in that case again the several possibilities look at this.

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We have a site, we have  $AS$  and we have another site, where another reaction of adsorption, I am talking about a multiple reactant case  $A$  plus  $B$ . Now,  $B$  is reactant not a product, so  $A$  plus  $B$  giving  $C$  plus  $D$  or  $C$  whatever; so  $AS$ . So,  $A$  will get adsorption this and  $b$  will get adsorption on other site  $BS$  and reaction will take this place between

this, is the AS plus BS giving possibly CS plus DS and then we can derive the rate equation. So, so this in again several possibility, if you want to further complicated, this 1, this side is of 1 nature. So, S and this side is on other nature.

So, on a catalytic surface you may have sites of different nature, which are selective towards particular reactant. Many possibilities and that case again, we can imagine things will change. So, all this exercise give this is nice platform to come of with the right kind of rate equation, for a particular steps in heterogeneous catalytic. We want to as a I am be saying, all the time we go to put all this things are gather at latest stage to derive the single rate equation for a give reaction taking place of solid surface. Now, we just looking at individual steps first; understand them properly, and then trend put them together later.

Now, this is the dual site mechanism there is another possibility that you have AS and it is go to react with, but B is not getting adsorp. We there sites present here, is not gather adsorpt B remain in the bulk and the reaction take place between AS and B giving, say CS plus D or whatever or it can be DS all so. Some S will participate or no; what is more important here is that, here the reaction is in between adsorp psi and the component present in the bulk. And this is going to give another rate equation, which is not same as 1 that we it all if he it how we it write the reactions and finally, which equation as. So, many expressions, that we got which equation is correct, who will decided that? It the experimental data in laboratory.

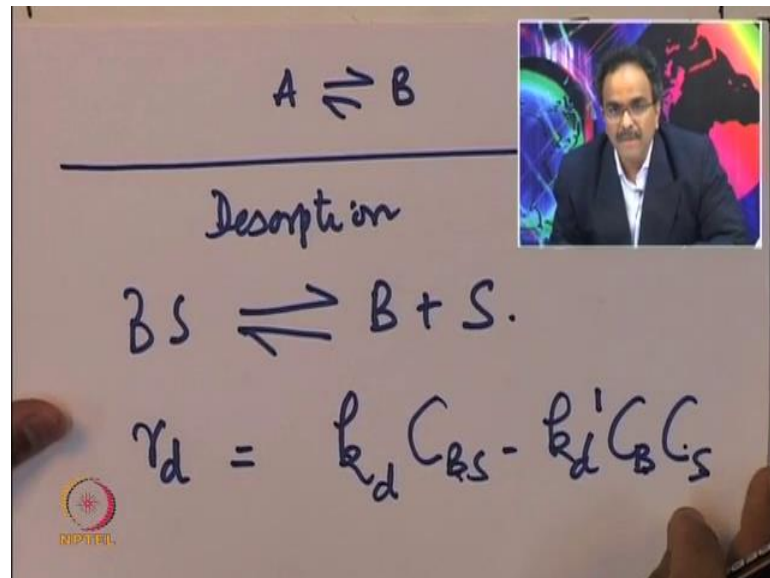
So, that experimental data which fits that equation well or in other words, the equation that fits the experimental data well, is the right equation and that of kind of mechanism for the reaction. So, this exercise helps in knowing the mechanism of the reaction at the same time coming with a right kind of equation for the chemical reaction and is happening on the solid surface. And this mechanism is called as Eley Rideal, where the reaction taking place between adsorption component or adsorptions and the bulk gas phase component.

Now, the last steps or other the third steps, which is nothing but desorption. Now, that is a just similar, but opposite of adsorption. So, it the need much or other with the we can



give same treatment to desorption as what we done for adsorption.

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So, again let us go back to reaction over all reaction A giving B; in that case, suppose B is adsorpt or A is adsorpt and the if in forms in B in B adsorp. Then desorption is BS, which is the formed the ter reactions gives B plus S; again, same think this is the opposite of adsorption. So, in order to know the adsorption isotherm, we are to do the similar experiment A at we did, before for a an understand. Weather it is single site or the 2 side participating weather it is automatic level or molecular level.

So, all this thinks are quits similar to what we done for adsorption. Now, intra D of A you have and B here at the desorption is exactly opposite to adsorption, now that is for isotherm and for the rate of desorption again 3 this are reaction. So, rate of desorption is equal to k desorption CBS mains k d dais CB CS. So, this is rate of desorption now in this rate equation we have this fashions is BS and C, this are the concentrations on the solid surface, which is the difficult to match us during the curse of the reaction. This is something that, again nature that is CB.

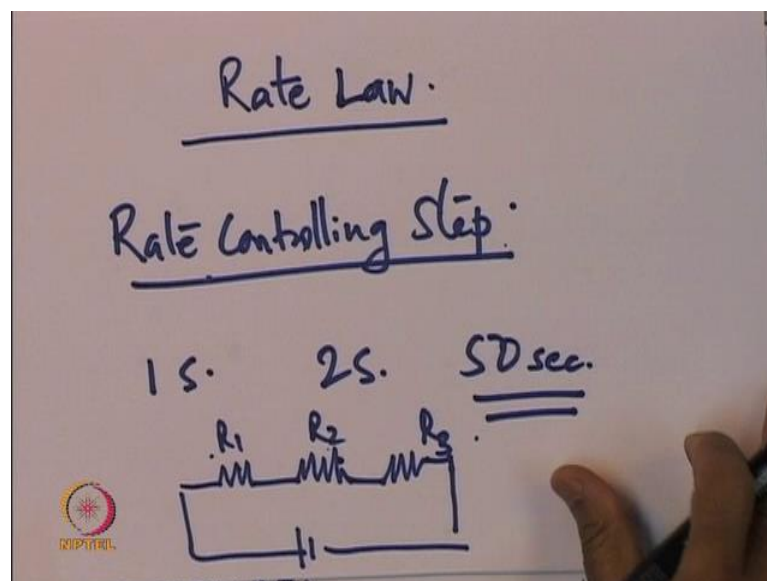
So, the next step is how to deal with this concentration, this will aspire even in the case of adsorption reaction. So, all the rate expression that we are seeing, so for are having

this concentrations, concentration adsorp as well; that difficulty to measure. So, I will get rid of them or other we have to substitute them, in terms of the bulk concentrations and that a nick a next excise. So, let me summarize what we learn so, for. We are look at 3 different steps adsorption, reaction and desorption. Adsorption can take place on single side; it can take place 2 sides and depending on that, will having different Isothermic equation.

How do you verify the Isothermic correct or not, we generate data in laboratory for adsorption and see, whether it false in line the expression that we have do on. And from that, identify the mechanism and officious the rate expression or isotherm expression for the adsorption. Reaction it is a again similar, we have to right expression like what we do for reaction, but again it can be single site, it can be duel site or it can be Eleradlle mechanism. Were the adsorp psi can react with the monocular the gas fields. And accordingly will have the rate equations and if at all the reaction is assistance, we can the right equilibrium reaction also the reactions. And same treatment holed good for desorption as well.

Were again, like we can right expression for isotherm, if the desorption is a instance or and off course, this are weight verify whether the isotherms correct or not. We can write the rate equation as well, depending on what is the mechanism desorption how many. So, if a there we can sides taking in part how whatever. So, as we just looked at base giving B plus as again expression for that. So, 3 steps; we look that individually now, we go to put together and see, how the rate law can be derived for a particular reaction that is taking place on the catalytic surface reaction.

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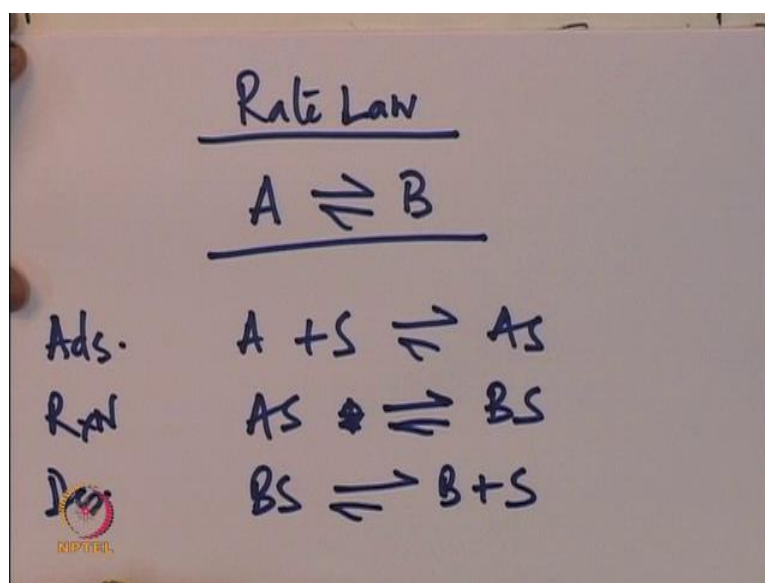


So, let start with the same reaction and derive the rate law depending on which 1 is the slowest step or in other ward which 1 is the rate controlling steps. So, we need to understand, what is a rate controlling step? So, let us spends some time to understand what is rate controlling is easy to understand, It quit logical that you have us process taking place in series. So, we have process taking place in series than, the overall rate is governed by the slowest tafule. So, let us talk about rate controlling steps. So, I have 3 steps; let a taking place in a series. This more likes the real race. So, that 3 steps 3 participants 2 of them are very fast and 1 is relatively slow, the time taken by first participant is a 1 second, time take by second participant is 2 second and time take by third participant is 50 second.

So, who is the rate controlling person this 1, because he can slow as a fall and need to take more efforts on this. So, that the overall time required can the reduce, what the total time it is about 53 seconds. So, if I efforts this people, I am not going to reduce the time much, were as this fellow needs attention. So, what this fellow is doing is the rate or other. This is a rate controlling step, as simple as that, this is analogy between electric circuit and chemical steps as wells, we have these assistance in sires. So, this assistance are nothing but steps. And the total assistancy the addition of are total of all these assistancy it is like this.

You have so, haven't R2 R3; if R2 is much higher than R3 and R1 and need to reduce this. So, that the current net flowing in a circuit can be increased significantly, that is nothing but rate controlling steps. Now, let us come back to our reaction and in reaction you have these 3 steps that are taking place. Adsorption, Chemical reaction, desorption. The overall rate will be governed by 1 of these and time with can be 2 or all 3 of them can be governed, but that is quite a rate. So, the 1st controls the overall rate, that is called as rate controlling steps. So, you will use this concept later to come off with the rate laws.

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So, we are going to derive the rate law for a reaction taking place on a solid surface, it goes back to equation A giving B, this is the overall equation and overall reaction as a summarized reaction. Now, if I want to know the rate for this reaction and need to come off with a mechanism. So, I have adsorption taking place, A plus S giving AS, then the reaction AS giving BS and then the desorption that is, BS giving B plus S. This is a single side mechanism for A going to B, but it is quite possible as said before that there are 2 sides involved in the rate determining steps. In that case, the derivation will change. So, these 3 steps, they are going to take place simultaneously and the overall rate will be governed by the steps, which is the slowest of all intrinsically slowest. So, that is going to govern the overall rate and we are going to write an expression for

the rate for individual steps, the 1 which is slowest, we are going to retain that expression and rest of, we are going to treat them of equilibrium steps and come off with the rate law. So, will continue this discussion in the next lecture.

Thank you.