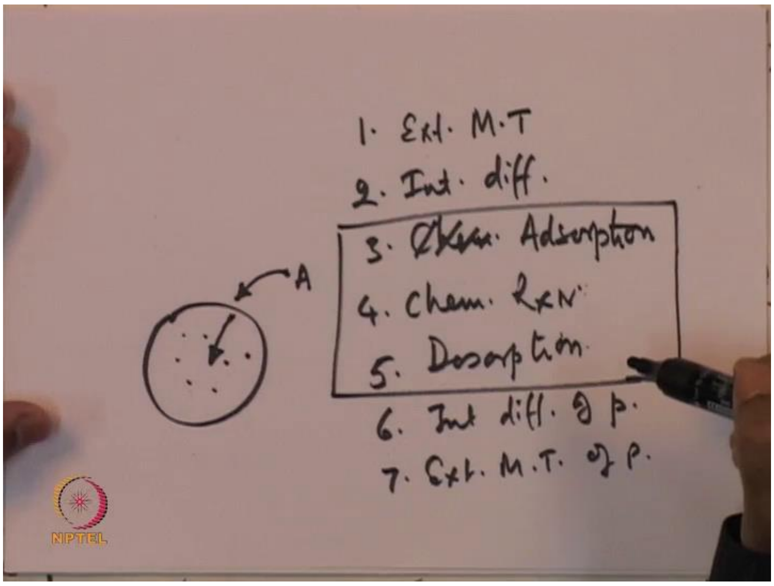
Chemical Reactions Engineering II
Prof. Sanjay Mahajani
Department of Chemical Engineering
Indian Institute of Technology, Bombay

Lecture - 3
Derivation for the Rate equation

Good morning. So, let us continue on discussion last lecture we looked at different steps involved in a catalytic reaction.

(Refer Slide Time: 00:31)

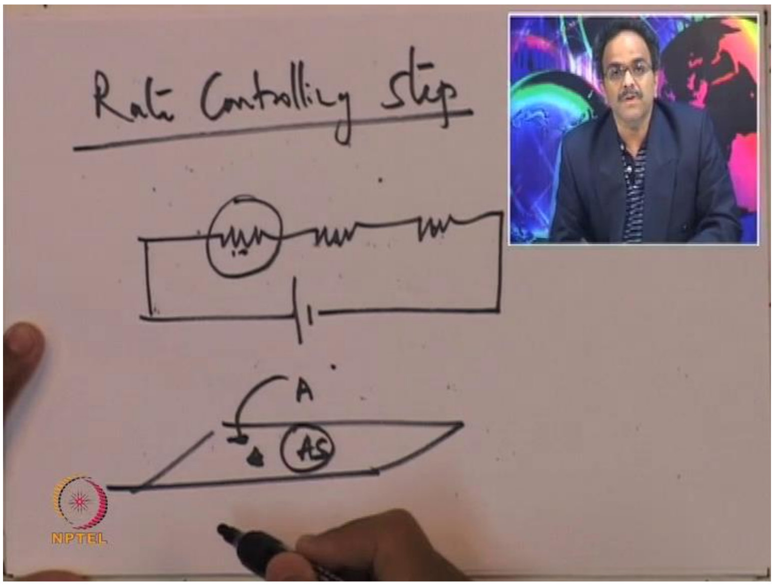


So, if you have a catalyst typically the catalytic site will be present inside and a reactant will be there in the bulk and this reactant has to diffuse or rather first overcome the external mass transfer resistance will reach at the external surface of the catalyst. Then, inside a catalyst it has to defuse through the pores and reach the catalytic sites. So, the steps involved, I will just do a quick review external mass transfer, then internal diffusion, third chemical reaction on the surface before that you have adsorption, then chemical reaction on the surface, desorption of the product or products.

Then again the bad diffusion internal diffusion of the products and last step is external mass transfer back to the bulk of the products. So, these are the different steps and then we concentrated more or you focused your attention more on these three steps; why because these are the three steps that take place when the reactant molecule is very close to the catalytic site. So, these three steps together will give us the rate equation for intrinsic other reaction to take place. Of course, after like if you include the effect of external mass transfer and internal diffusion, and then we get overall rate equation for reaction that is taking place on the surface of the catalyst.

So, in the last lecture we looked at these three steps and the equations associated with these three steps for the rate of the particular step. So, adsorption chemical reaction and desorption. Today, what we are going to look at is how to come up with the rate law for a particular reaction if one of these steps is the rate controlling step. So, what is rate controlling step; concept of rate controlling step is very important if you have multiple steps occurring when a reaction takes place.

(Refer Slide Time: 03:02)



So, rate controlling step, this is also called as rate determining step. So, R C S or R D S. What is it, if you have many reactions or many steps taking place for example, in our case; we have adsorption, chemical reaction on the surface and desorption. So, these three steps are taking place in series. Now, the overall rate of the reaction of course, not considering diffusion external mass transfer now, but adsorption, desorption and reaction the overall rate will be determined by the slowest step intrinsically slowest step.

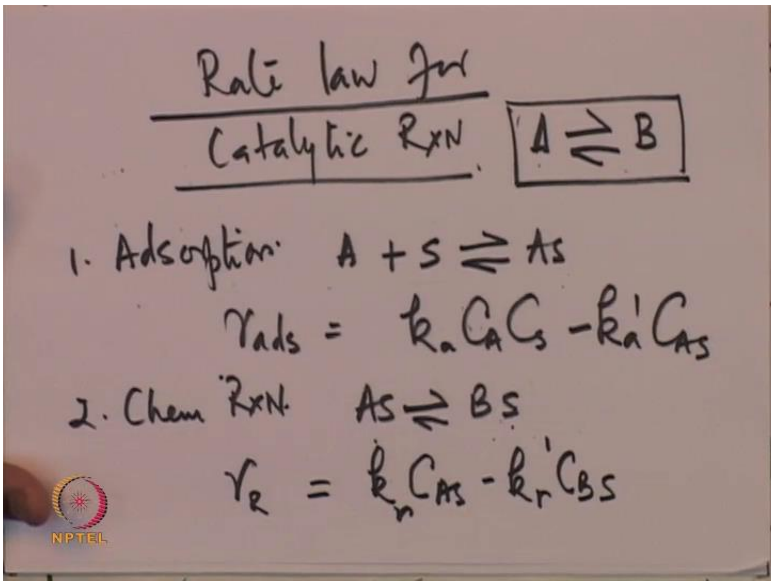
So, it is very similar to what happens in an electrical circuit for example, there are three resistances in series. So, you have a circuit the current that flows to the circuit will be dependent on this magnitude of these resistances; if one of these resistances is very large; that means that resistance controls overall flow of the current in the process. If I want to increase the current flow I will concentrate more on this, which is the largest resistance than the other two. So, for example, this is fifty this is two and this is one; then I will try and reduce fifty that will make much more impact on the rate compare to the other two.

So, in short the rate controlling or rate determining step is the step, which is intrinsically very slow. Now, who decides whether the step is slow or not then the rate constants involved net process. So, the rate constant for the reaction is very small that case the chemical reaction on the surface controls overall rate; if the rate constant for the adsorption is very small in that case, it that is adsorption that controls overall rate or is desorption rate intrinsically rate constant is very small. In that case, it desorption that controls the overall rate.

Now, how is this important because after all I want to get the rate equation, which combines the effect of all these three steps? Now, why do I need to combine these steps; because I want to get a rate equation in terms of the concentration or the partial pressure of the reactance in the bulk? Now, it is very important that you have the surface reaction taking place and A is getting adsorbed and A will have certain concentration on the surface in the form of say AS. Now, this concentration I cannot measure this concentration. So, if I want to design a reactor I know the concentration in the bulk.

I know the concentration of a coming in the feed I know the concentration of a going out of the reactor I know the concentration inside a reactor. But that is in the bulk in the sense in the liquid or gas mixture, which surrounds the catalyst. But I do not know the concentration on the surface. So, that is a problem. So, I need to somehow do read of all these concentrations, which are unknown and come up with the rate equation that is in the form of the bulk concentration that is what we are going to do now.

(Refer Slide Time: 06:55)



Rate law for Catalytic RxN

$\boxed{A \rightleftharpoons B}$

1. Adsorption: $A + S \rightleftharpoons AS$

$r_{ads} = k_a C_A C_S - k_a' C_{AS}$

2. Chem RxN. $AS \rightleftharpoons BS$

$r_R = k_r C_{AS} - k_r' C_{BS}$

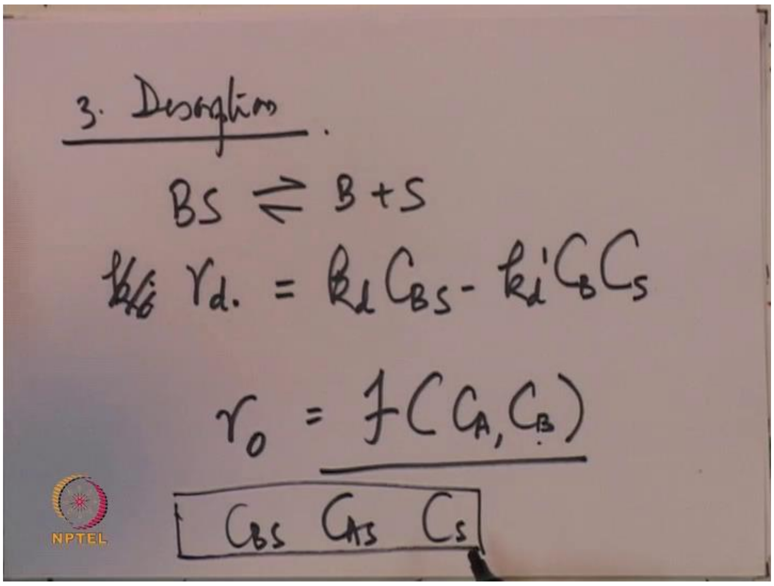
Rate law for catalytic reaction; remember when I say catalytic reaction it is the solid catalyst reaction, where adsorption takes place and in the chemical reaction in desorption. In a normal homogeneous reaction that we have studied before in the first of part of reaction engineering; there we just looked that chemical reaction no adsorption and no desorption. Now, I want to combine the effect of these three steps and come up with the rate equation. So, first step adsorption we have looked at this adsorption A. So, let me say I have a reaction A reversible with B overall reaction. So, if I am setting outside a reactor not reactor outside catalyst, then I am seeing conversion of A to B and this is the overall reaction.

Here, it is assumed that external mass transfer and internal diffusion are, so fast that the concentration of fluid inside pores in contact with those active sites is equal to the measurable bulk concentration. Actually, this reaction will take place in different steps. So, adsorption A first A adsorbs in catalytic site, which is present on the surface then this is in equal to equilibrium with AS. So, this is adsorption we already looked at it. The rate of adsorption, the rate of adsorption is equal to k a C A C s minus k a dash that is the d that is the reversible step or the reverse step C A s; this is a rate of adsorption.

Now, this step may be rate controlling or may not be rate controlling we will look at that separately in later on. Now, I am just looking writing rate equations then the chemical reaction AS on the site gets converted to BS this is my hypothesis. Remember, this is my hypothesis I told you like that can be different ways; I can write these steps and accordingly my rate equation will change later, which one just rate equation that will decide based on the experiment experimental data you are going to we are going to look at it later. But right now I am just assuming this and seeing whether I will get a right kind of rate equation or not.

So, the reaction that is taking place isomerization reaction on the surface this site AS gets transformed to BS and this is the reversible reaction. It has to be reversible reaction because overall reaction is reversible. So, I am not quite sure whether, so let me write it as reversible reactions and then we will see what happens;, so chemical reaction the rate of chemical reaction. So, I am let me write the rate of chemical reaction is r R, see whether I get r A then it will be negative sign. So, I have to consider the sign whether it is reactant or product and all that I am just writing general equation. This is k r C A s minus k r dash C B s simple, then we will move to desorption.

(Refer Slide Time: 10:42)



3. Desorption.

$$BS \rightleftharpoons B + S$$

$$r_d. = k_d C_{BS} - k_d' C_B C_s$$

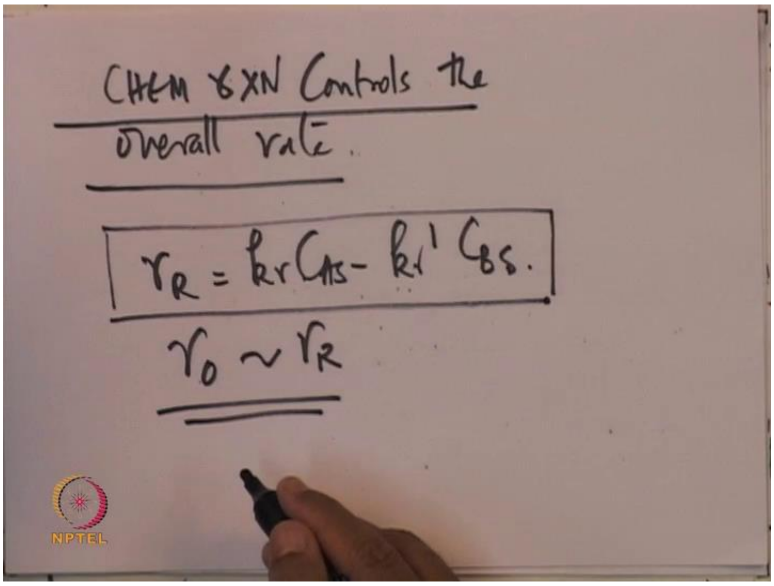
$$r_0 = \underline{f(C_A, C_B)}$$

$$\boxed{C_{BS} \quad C_{AS} \quad C_s}$$

Third step, BS is going to get converted B plus S that is desorption and you wants to go to bulk. So, now k desorption rate of desorption is equal to k d C B s minus k d dash C B C s. So, we have three rate equations we have three rate equations; I want to now combine these three rate equations of individual steps and get the rate the overall rate as you function of C A and C B very important. I do not want C A s here I do not want C B s here; I do not want C s here in this; because C B s C A s and C s these three concentrations, I do not know the values of these three then I cannot measure them that there.

But then I cannot go to the surface and actual measure this concentration. So, is always better that I get a rate equation in terms of bulk concentration, that is the aim of this exercise. So, how I get this now in order to get a rate equation for bulk catalytic reaction; I need to make assumption of that one of the steps is the rate controlling step. So, it can be either adsorption; it can be chemical reaction or it can be desorption depending on the activation energies of respective steps. Now, the way I have written all these reactions then the reaction form even if it is adsorptions; physical adsorption or it can be chemical adsorption of course, for the reactions it is chemical adsorption I am considering it as reaction. So, I am writing rate equations for these and one of these is the slowest depending on the activation energy all the rate constants of those steps.

(Refer Slide Time: 13:11)



CHEM RXN Controls the overall rate.

$$\boxed{r_R = k_r C_{AS} - k_r' C_{BS}.}$$

$$r_0 \sim r_R$$

So, let me make an assumption initially that the chemical reaction controls the overall rate what I mean by controls the overall rate. This again one more way of saying that chemical reaction is the rate determining step or rate controlling step. So, that is the slowest step, that is the slowest step. Now, if you remember when the chemical reaction controls I had written r R as k r into C A s minus k r dash into C B s. Now, in this equation C A s and C B s are unknowns. Now, if the overall reaction rate is controlled by this, I can make an assumption that r o is r R very, very important.

Because the rate of the reaction is very slow, this is intrinsic rate is very slow the other two steps are very fast. So, the overall rate is governed by the reaction. So, it is like a relay race at I was telling you about this that three people running in the relay race; the slowest of them will govern the overall time required to complete the race. So, the first fellow does it in five minutes; the second fellow does it in two minutes, but the third fellow takes normal does not happen, but if it takes say fifty minutes the total time is very close to fifty.

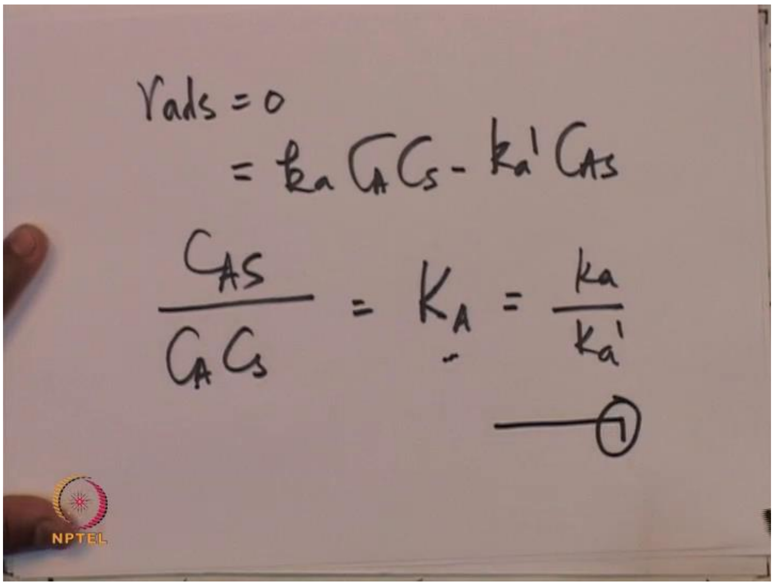
So, the rate of the third person is the rate of the overall process that is I am that is how I am looking it. So, rate of overall process is a rate of chemical reaction. So, this is a rate now can I just save at this is my rate equation and stop here I cannot do that. Because this concentration is not a bulk concentration; I need to express these concentrations in terms of the bulk concentrations. So, next step is again very important that I need to convert these we are going to list different steps; how to derive the rate law of catalytic reaction. I am just first explaining you how with help of example how to get to a rate equation then will systematically write different steps to be performed.

Now, this is the rate equation C A s and C B s are to be express in terms of bulk concentration. Now, how I do that now I take the help of the adsorption step and desorption step. Now, these two steps are instantaneous; they are very fast what does it mean. Just look at those steps I have this adsorption step; now I have this rate equation if this reaction is instantaneous if this this particular step is instantaneous; then it is always at equilibrium. I will repeat it is always at equilibrium. What does it mean? It means that A s is in equilibrium with A and S at any given time which reactions.

So, fast that the equilibrium is achieve what does it mean if the equilibrium is achieved; that means, the rate of adsorption once the equilibrium is achieved is zero; that means, this is equal to this. So, this is an equilibrium step because it is intrinsically very fast what about this; this is not an equilibrium step, because this is the slow step and the rate governs. So, I am still going to write same thing here where as in this case I am going to equate this rate to zero. Similarly for desorption for desorption this rate is going to be same as this rate.

Because r d is very fast; that means, this step is this term is equal to this term. The reaction of desorption is the equilibrium step. So, the rate controlling step is the slowest step and that is going on to govern though overall rate raise to r in equilibrium. They are instantaneous they are an equilibrium. So, let me write those expressions by setting those rates of those individual steps, which are intrinsically fast to be equal to zero. So, we have adsorption step I am going to set this rate equal to zero.

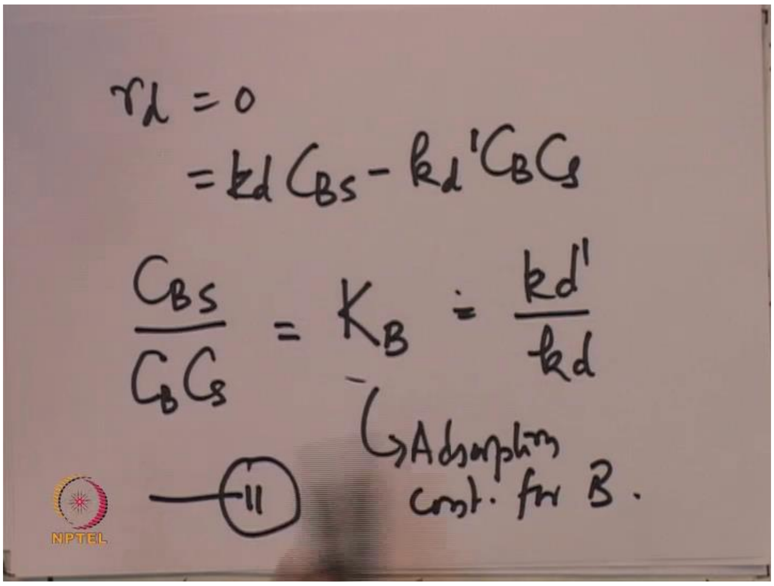
(Refer Slide Time: 18:20)



$$r_{ads} = 0$$
$$= k_a C_A C_s - k_a' C_{As}$$
$$\frac{C_{As}}{C_A C_s} = K_A = \frac{k_a}{k_a'} \quad \text{---} ①$$

So, what happens is r a d s is equal to zero which is nothing, but k a C a C s minus k a C A s is equal to zero. What it means, is that A s C A s divided by C A C s is equal to some constant capital K, which is equilibrium constant. This is nothing,, but in terms of small k a and k a dash it is k a divided by k a dash. What is this? This is adsorption equilibrium constant. So, I got one equation which relates C A s with a C A and C s. So, let me write let me remember this equation and get back to this later.

(Refer Slide Time: 19:29)



$$r_d = 0$$

$$= k_d C_{Bs} - k_d' C_B C_s$$

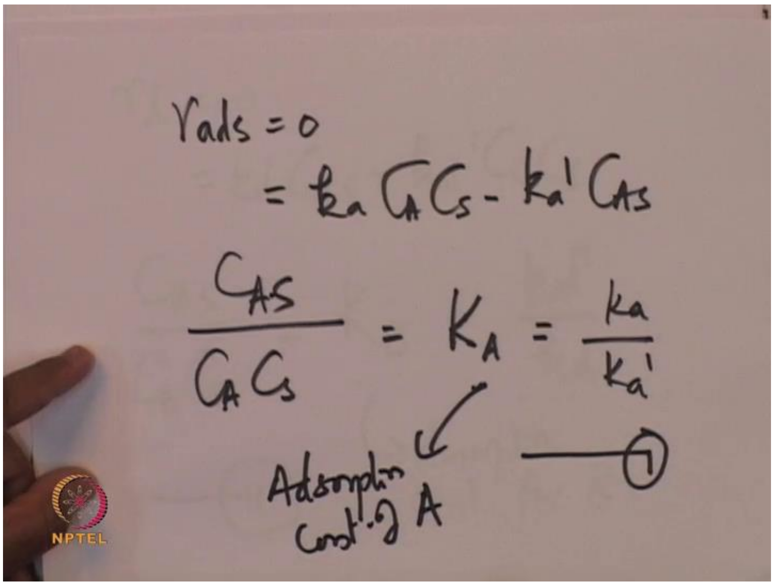
$$\frac{C_{Bs}}{C_B C_s} = K_B = \frac{k_d'}{k_d} \quad \text{— (11)}$$

↳ Adsorption const. for B.

Similarly for desorption for desorption I have R d equal to zero because rate of desorption is now zero equilibrium is achieved it is very fast step which is nothing, but k d C B s small k d. So, these are the rate constants for desorption. So, this gives me C B s divided by C B into C s is equal to some capital K B. So, this is adsorption equilibrium concentration, which is nothing, but k d dash divided by small k d dash divided by small k d; these are the rate constants.

But similar to normal reaction equilibrium or reversible reaction; this is adsorption equilibrium constant for and B similarly I had adsorption constant before. So, let me remember this equation and make use of it later. So, I have got two expressions C B s for C B s one equation from desorption step and for C A s one equation from adsorption step.

(Refer Slide Time: 20:46)



$$r_{ads} = 0$$

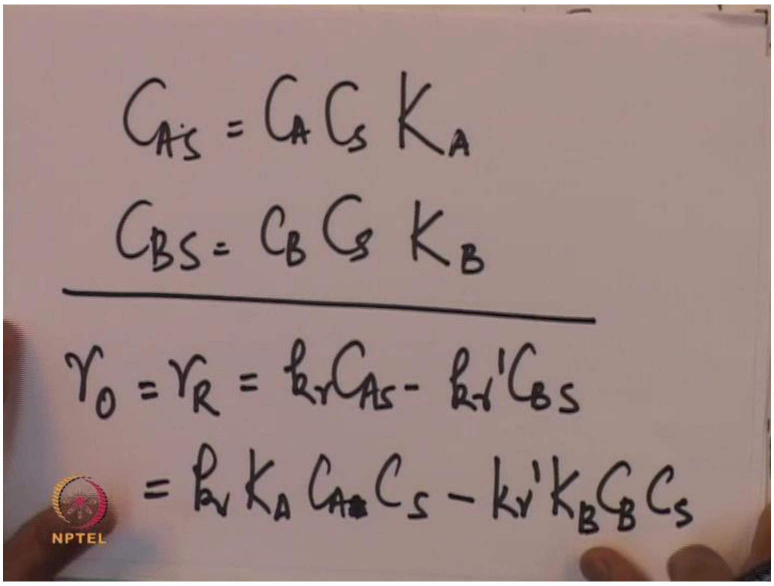
$$= k_a C_A C_s - k_a' C_{As}$$

$$\frac{C_{As}}{C_A C_s} = K_A = \frac{k_a}{k_a'} \quad \text{——} ①$$

Adsorption const. of A

This is adsorption constants. Now, I am going to make use of these two equations going to make use of these two equations and express C A s in terms of bulk concentrations. So, let me write it down.

(Refer Slide Time: 21:21)



$$C_{As} = C_A C_s K_A$$

$$C_{Bs} = C_B C_s K_B$$

$$r_0 = r_R = k_r C_{As} - k_r' C_{Bs}$$

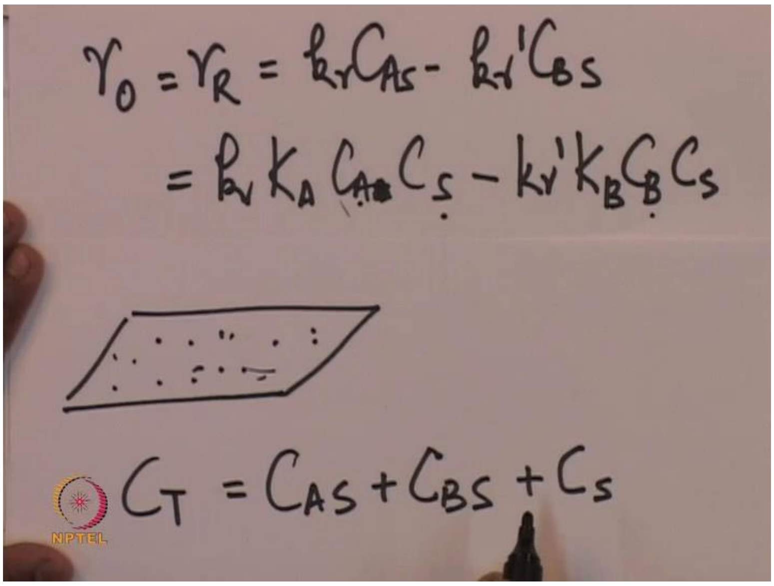
$$= k_r K_A C_A C_s - k_r' K_B C_B C_s$$

From equation one, C A s is equal to C A into C s into capital K A; from equation two C B s is equal to C B into C s into capital B. So, these are the two equations I have got for C A s and C B s. Let me get back to the rate equation the rate overall is equal to rate of reaction is equal to k r C A s minus k r dash C B s. Let me substitute for C A s in C B s, which gives me k r into C capital K A C A s into C s minus k r dash capital K B C B into C s. So, I have got a rate equation or the rate equation overall rate remember what I have done is I have just looked at the slowest step, which is the rate controlling step.

I have written its rate equation and whatever I do not know I am trying to substitute for it taking help of the equilibrium steps or the instantaneous steps, which are in this particular case adsorption and desorption. Now, r o is equal to this. So, do you know everything in on the right hand side? I know C A; I know C B; do I know C s, I do not know C s; I do not know the concentration of vacant sites empty sites on the catalytic surface. So, these concentrations are again needs replacement or rather I need to substitute for them such that right hand side is the function of only the bulk concentration.

Of course, there will be rate constants are adsorption constants, which are constants any way the parameters of the rate equation. But concentration should be the only bulk concentration measurable concentrations. So, let me do that how do I get C s. Now, I need to express C s in terms of the other concentration what are doing for that.

(Refer Slide Time: 23:57)



$$r_0 = r_R = k_r C_{AS} - k_r' C_{BS}$$

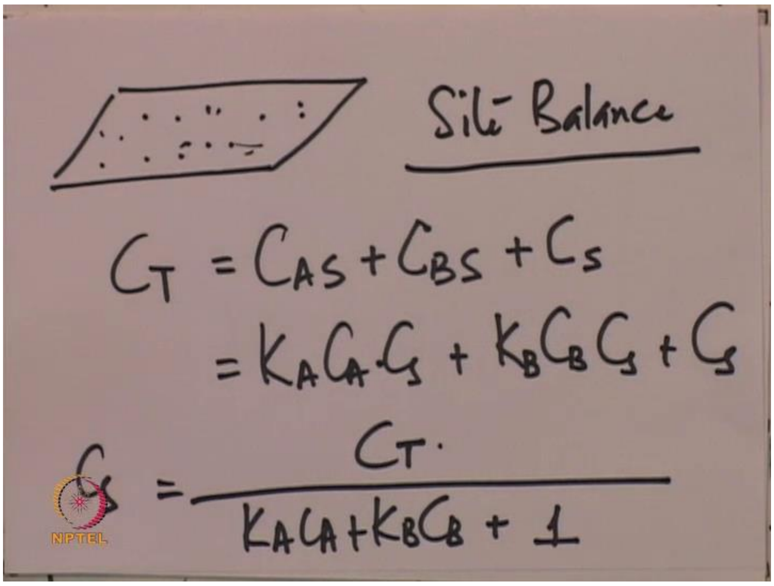
$$= k_r K_A C_A C_S - k_r' K_B C_B C_S$$

$$C_T = C_{AS} + C_{BS} + C_S$$

Now consider a catalytic surface, there are many sites of course, this is a very simple presentation of the surface. Actually, the surface is not in the form of sheet or plate most of the time it is there inside pores, but when I am just opening those pores and showing the surface as this and derive sites present. Now, these sites this is a fix concentration of these sites fixed number of these sites. So, the total concentration of the sites C T, which is a constant for the given catalyst this C T is the constant.

That is equal to at any given time C T is equal to there are some sites on which A is adsorbed; there are some sites on which B is adsorbed; what else there are some vacant sites. So, we have three different types of sites present on the catalytic surface. Now, this makes the site balance makes our job very easy now. Because in this expression C T is constant; C s is something that I need to find out C A s and C B s there also not known, but then I got an expression for them. What are those expressions for C A s and C B s? These are the expressions for C A s and C B s.

(Refer Slide Time: 25:54)



Site Balance

$$C_T = C_{AS} + C_{BS} + C_S$$

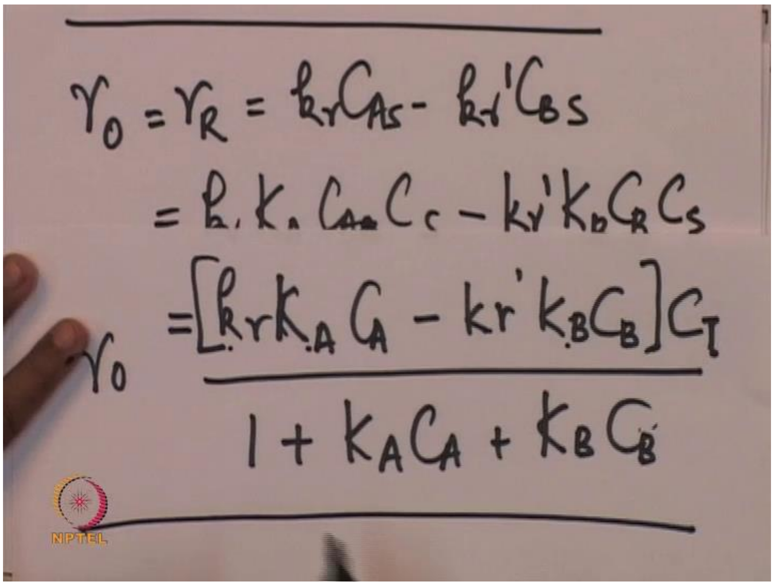
$$= K_A C_A C_S + K_B C_B C_S + C_S$$

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

So, let me go ahead C A s is nothing but capital K A C A into C s plus capital K B C B into C s plus C s. Now, this gives me the expression for C s in terms of C A and C B. If I take C s common, then I can write C s is equal to C T divided by capital K A C A plus capital K B C B plus one. What I have done here is the site balance very important step. So, remember what I have done, so far. I am looked at different steps; I have decided at one step is rate controlling that governs the overall rate. So, I have written rate equation for that step in that step there are some species concentrations unknown, unknown in the sense I cannot measure them they are in the adsorbed form or whatever.

See in order to replace those concentrations I have taken help of the equilibrium steps; the steps which are not rate controlling like adsorption and desorption and from those equations equilibrium equations; I have got the concentration of adsorbed sites and I have replace these concentrations in the form of the bulk concentrations. So, let me substitute for C s. Now, I have done site balance and got a concentration of empty sites or vacant sites in terms of the total concentration of the sites and the bulk concentrations. So, let me get back to my rate equation.

(Refer Slide Time: 27:44)



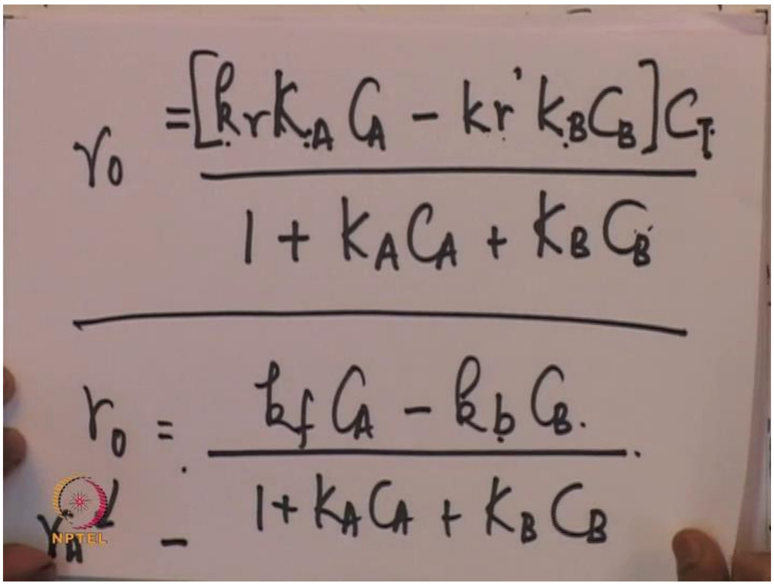
$$r_0 = r_R = k_r C_{AS} - k_r' C_{BS}$$

$$= k_r K_A C_A C_S - k_r' K_B C_B C_S$$

$$r_0 = \frac{[k_r K_A C_A - k_r' K_B C_B] C_T}{1 + K_A C_A + K_B C_B}$$

So, my rate equation is this I do not know C s. So, I have I am going to replace it with the help of the expression that I have got just now that is C T divided by 1 plus K A C A plus capital K B C B. This is the expression for the overall rate. Look at a right hand side is there something that I do not know see there are all constants k r K A capital K A k r dash capital K B C T; this is also constant and what is not constant or rather the other concentrations of A and B they are in the form of or they are the bulk concentration that is something I want. So, this is the final expression that I have got now of course, you can club this.

(Refer Slide Time: 29:00)



$$r_0 = \frac{[k_r K_A C_A - k_r' K_B C_B] C_T}{1 + K_A C_A + K_B C_B}$$

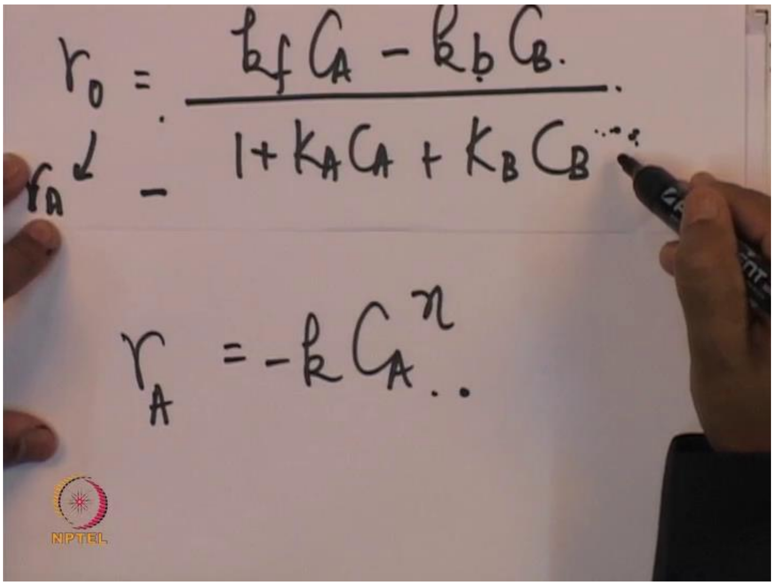
$$r_0 = \frac{k_f C_A - k_b C_B}{1 + K_A C_A + K_B C_B}$$

$$r_A \; -$$

Say, for that I have r o is equal to k of forward reactions k f C A minus k of backward reactions C B divided by 1 plus K A C A plus capital K B C B. What I have done is I have combined these C T k r and capital K A in k f and k r dash C T and capital K B. So, this is a form of equation now if I want to write it for k that is A instead of this I have r A then this will be negative. Because A is getting consumed r B this will be positive; like say same as positive done before in part one depending on the stoichiometric coefficient of the component I give the sign on to the right hand side.

So, k B can be expressed in terms of overall equilibrium constant of the reaction in that case the number of unknown parameters will be reduced by one. So, this is something which is equivalent to what we have done before like for example, a rate law power law rate equation.

(Refer Slide Time: 30:32)



$$r_0 = \frac{k_f C_A - k_b C_B}{1 + K_A C_A + K_B C_B \ldots}$$

$r_A \downarrow$ −

$$r_A = -k C_A^n \ldots$$

What is a power law rate equation? r is equal to minus r; r is equal to k C A raise to n; r is equal to k C A raise to n if it is r A then it is minus. So, this equation that we use, so far rate constant and then the order of reaction instead of that I have got this particular rate equation. So, this is for normal reaction normal in the sense homogeneous reaction, irreversible power law rate equation, where has this is the rate equation that I have got for a solid catalyzed reaction, which takes place on the surface as a result of adsorption chemical reaction and desorption.

But do not forget I got this rate equation by assuming that does chemical reaction is a rate controlling step. So, this is not a unique equation for any heterogeneous catalytic reaction it depends on the assumption that I have made. So, the assumption is reaction is rate controlling and other two steps are equilibrium steps. But what I am trying tell you is these are the, so this. So, what I have got is I have got something equivalent to what I used before here; now, then I what I did later with this rate equation in the first part that is designing CSTR plug flow reactor in which I have used this equation.

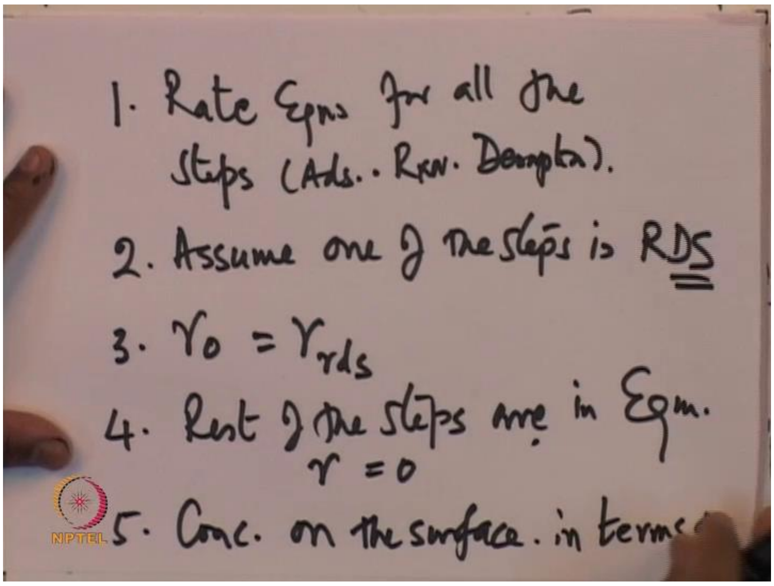
Now, what I going to do now like for a catalytic reactor instead of this rate equation I am going to use this rate equation that is the only difference. Of course, I need to consider external mass transfer; then inter particle diffusion and other steps, but at this movement if suppose for example, like these two steps external mass transfer and diffusion or the not controlling all then not there at all; in that case this is my rate equation. So, try understand difference between solid catalyze reaction and normal reaction homogeneous reaction, where the rate equation is in a very simple form whereas in this particular step or in this particular case like you have the rate equations slightly complicated and it again depends on the assumption that I am making.

Now the next obvious equation is that whatever assumption I have made whether it is correct or not. Who will tell me that assumption is correct? For that I need to do experiments in laboratory and see whether this rate equation fits my data very well. I hope it is clear rate equation is the validity of the rate equation that I have assumed is correct or not is decided only through experiments. Of course that are theories it is find out or all that, but the common practice is do a experiments in laboratory using the same type of reactors that I used the first part and differential reactors and all that.

A batch reactor laboratory or small CSTR and do experiments and see how the rate equation fits the data if it fits well then my assumption is correct; I go ahead and use that rate equation formality reactor design. If it does not fit a data well then what you do you go back to your assumption, change your assumption. Now, for example, in this particular case I have got this rate equation; I got this rate equation from by the assumption that is reaction is controlling.

Now, I make an assumption that the adsorption state controls. In that case the rate equation will change will see what change will be seeing in the rate equation? But before that let us try and summarize in write an algorithm step by step procedure to get a rate equation when a reaction takes place on the solid catalyst and the complete adsorption and desorption. So, what I have do I have already told you about and let me write it.

(Refer Slide Time: 34:27)

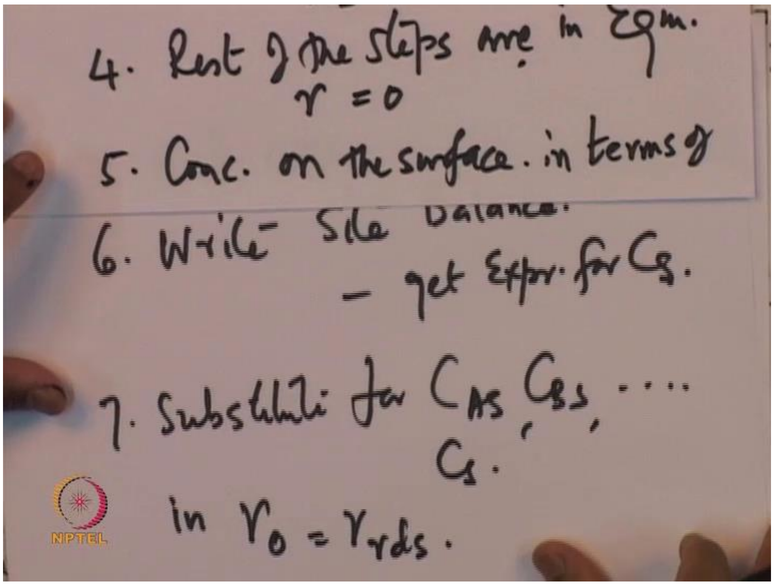


1. Rate Eqns for all the steps (Ads.. Rxn. Desorptn).
2. Assume one of the steps is RDS
3. $r_0 = r_{rds}$
4. Rest of the steps are in Eqm. $r = 0$
5. Conc. on the surface. in terms

Step one rate equation for all the steps we need to assume some stoichiometry here or the scheme here like A plus S giving A S and so on. For all the steps; that means, adsorption reaction and desorption. Second, assume one of the steps is rate determining step overall is equal to R D S. In the example it was a chemical reaction that we considered to be the rate determining step and this particular equation will have C A s C B s C s.

Now, all these concentrations are not known for that what I do is rests of the steps are in equilibrium. So, the rate for these steps said to be equal to zero. What next? What I get is all the unknown concentrations. So, a concentrations on the surface, so from this particular assumption what I get is the concentration on the surface in terms of bulk concentrations.

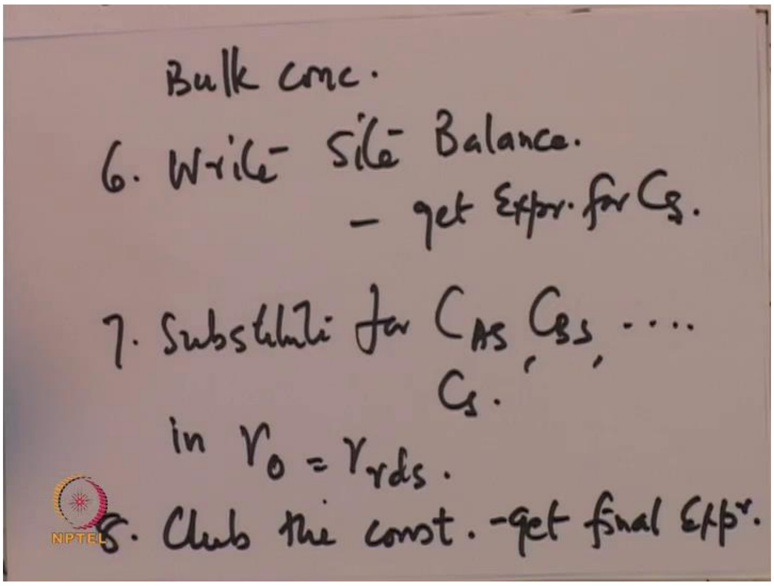
(Refer Slide Time: 36:29)



4. Rest of the steps are in Eqm.
$r = 0$
5. Conc. on the surface. in terms of
6. Write Site Balance.
– get Expr. for C_s.
7. Substitute for C_{As}, C_{Bs}, ...
C_s.
in $r_0 = r_{rds}$.

In terms of bulk concentrations, write site balance why because I need to get expression for C s. Substitute for surface concentration and C s; substitute for C A s C B s they can be many components, which are going to adsorbed and C s in r o is equal to r r d s. So, this is substitute for C A s C B s in C s in this particular equation.

(Refer Slide Time: 37:35)



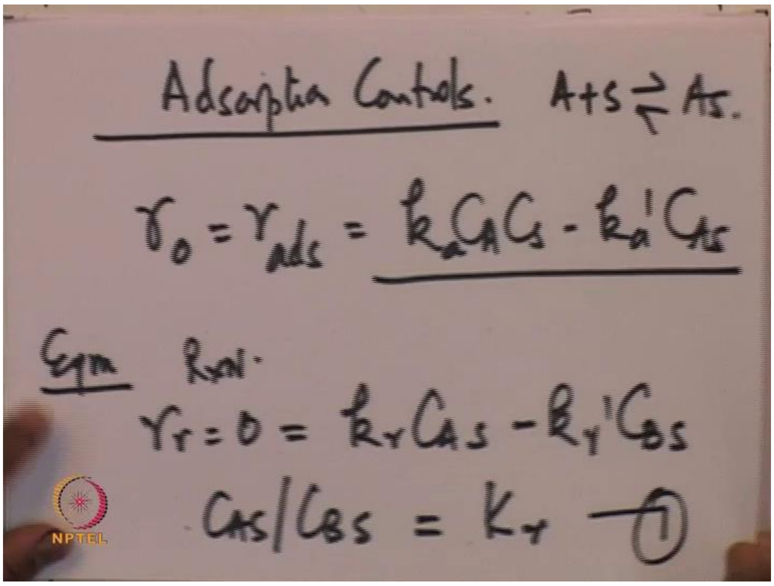
Bulk conc.
6. Write Site Balance.
– get Expr. for C_s.
7. Substitute for C_{As}, C_{Bs}, ...
C_s.
in $r_0 = r_{rds}$.
8. Club the const. -get final Expr.

Then, you have to just club the constants impossible and get a final rate equation expression. So, these are the steps involved in getting rate law for heterogeneous reactions or rather the reactions catalyzed by the solids in which adsorption and desorption are taking place. So, now I have shown you just one example very simple reaction A reversible with B; that means, isomerization reaction in that how to get a rate equation.

Then, they may be further complications that you may have a bimolecular reaction or you have A reacting with B giving C or C plus D order. How to get a rate equation for such cases? I have shown I have considered only chemical reactions to be controlling here, but there is a possibility that this rate equation does not fit a data where I can get back to my assumption for the same reaction A going to B; I can say that fine now adsorption is controlling it.

Now, let us say what will happen if we have adsorption. Let see what will happen with a adsorption controlling overall rate I am not going to derive the rate equation again, but so many things. So, many assumptions based on which every time will get a rate equation different rate equation, what you need to remember are the procedure? You do not need to by heart it is rate equation that you got finally, you need to understand how the rate equation is being derived.

(Refer Slide Time: 39:16)



Adsorption Controls. $A + S \rightleftharpoons AS$.

$$r_0 = r_{ads} = \underline{k_a C_A C_s - k_a' C_{As}}$$

Eqm Rxn.

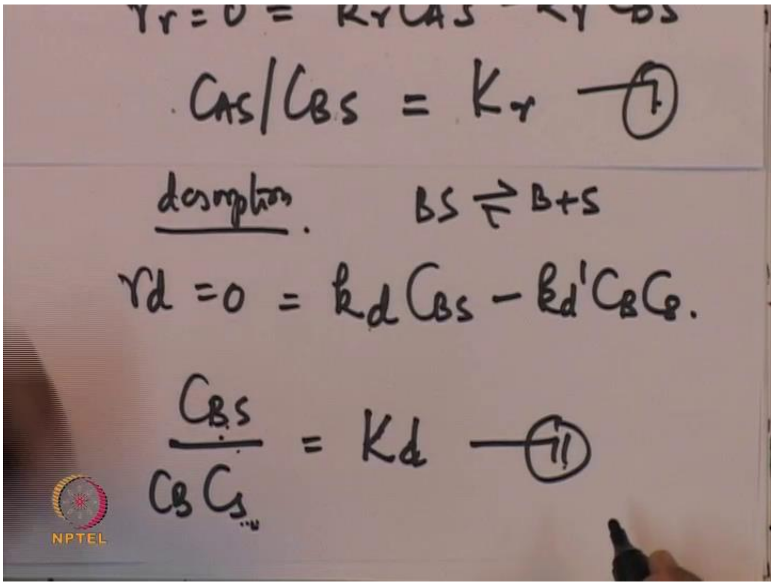
$$r_r = 0 = k_r C_{As} - k_r' C_{Bs}$$

$$C_{As}/C_{Bs} = K_r \quad ①$$

So, if adsorption controls the same procedure I will follow. In that, I will write rate equations for all steps I am not going to write all of that. But then the next step is the rate determining step that is adsorption. So, r overall is equal to r adsorption is equal to what is A adsorption A plus S giving A S. So, k a C A C s minus k a dash C A s this is my rate equation. Now, I am not going to set it to be equilibrium because it is a slowest step. Now, this A s is a unknown this C A s is unknown and it replace them how do I replace them by setting other two steps to be in equilibrium; that is the chemical reaction and desorption.

Now, chemical reaction is now equilibrium steps chemical reaction r r is equal to 0 is equal to k r C A s minus k r dash C B s. I am going to set it to be equal zero. So, C A s divided by C B s is equal to some equilibrium constant for the reaction capital K. This is capital K it is not small k this is equilibrium I got a relation between C A s and C B s. This is not enough this is one equation that I am going to use later.

(Refer Slide Time: 41:09)



$$r_r = 0 = k_r C_{As} - k_r' C_{Bs}$$

$$C_{As}/C_{Bs} = K_r \quad \text{— (I)}$$

desorption. $BS \rightleftharpoons B + S$

$$r_d = 0 = k_d C_{Bs} - k_d' C_B C_s .$$

$$\frac{C_{Bs}}{C_B C_s} = K_d \quad \text{— (II)}$$

In equilibrium, again I have desorption to be very fast. So, r desorption is equal to 0 is equal to what is that desorption step B S giving B plus S. So, desorption is very fast same as what you done before is equal to zero. So, k desorption C B s minus k d C B C s; this is zero. So, C B s divided by C B into C s is equal to K desorption capital K and this is number two. Now, these two equations together will give me C A s and C B s. Now, slightly different from what we have done this is not an explicit relationship for C s. C s because C B s appears here, but I have an expression for C B s I substitute it here and then I get C A s and C B s in terms of the bulk concentrations and site concentrations.

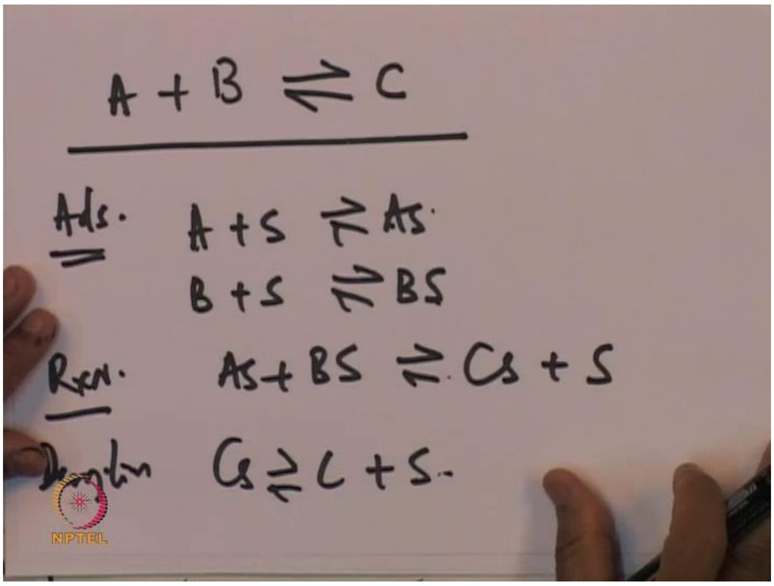
You know how to get rid of this this particular concentration that is by site balance. So, I am not going to continuous this exercise further and a final rate equation; you can do it on your own and will you get same rate equation that we have got before. You going to get different rate equation the form of the rate equation is going to be different from what we have got before by assuming the rate to be controlling that is before rate of the reaction to be controlling before surface reaction in this case it is adsorption that is controlling.

Similarly, you have desorption controlling the overall rate you will get a different rate equation all together. So, you got three rate equations three choices. So, your experimental data that you going to generate in laboratory see, where exactly this data falls other which equation that you got if it is data very well and this is not end of it. There are, so many other assumptions that I am assumption that I can make to get at different type of rate equation. So, that my data fits well in the rate equation. I have just looked I have just looked at possibility of single site adsorption if you remember in last lecture I told you that can at adsorb on two sites at a time.

So, I right now I have just taken rate equation rate for adsorption or the equation for adsorption as A plus S giving AS, but it can be a plus two s giving AS two. So, in that case the situation will be quite different my rate equation will be quite different and I have choice of rate equation. So, like this you can make many assumptions and come up with different rate equations and see whether it fits the data very well or not. There are independent ways to know the mechanism, but we will not get in to detail with that.

So, there are techniques to which we know whether the single site adsorption or double site adsorption is and so on. So, for a simple reaction of A being converted to B you have many possibilities of getting rate equation for a solid catalyzed reaction. Now, there is another possibility that you may have reaction, in which two molecules are involved; a reaction in which two molecules are involved where A is reacting with B.

(Refer Slide Time: 45:05)



$A + B \rightleftharpoons C$

Ads. $A + S \rightleftharpoons AS$

$B + S \rightleftharpoons BS$

Rxn. $AS + BS \rightleftharpoons Cs + S$

Desorptn $Cs \rightleftharpoons C + S$

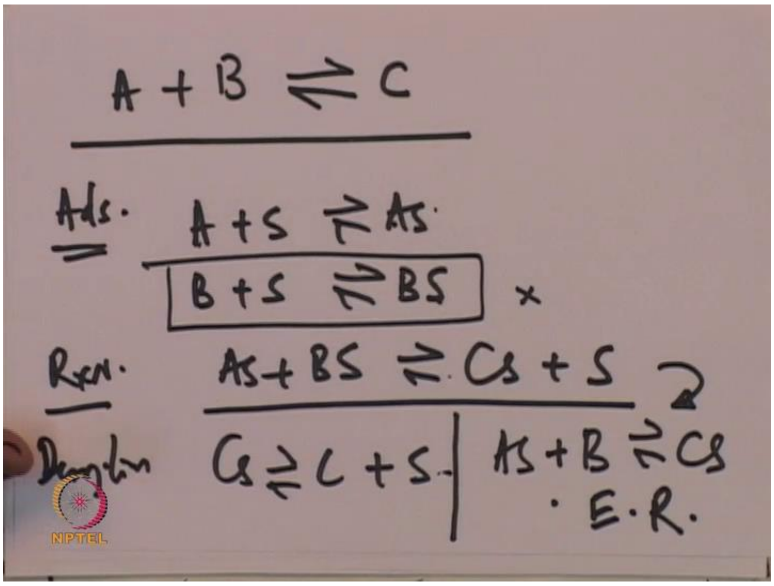
A plus B giving C this is my overall reaction overall reaction. Now, I am not looking at what happens on catalyst surface, but if I am sitting outside a catalyst in the reactor; then this is something I am seeing. Now, in this case again there is n number of or they are many possibilities and you can come with different mechanisms. So, let me just write down equations and look at possibilities I am not going to derive the rate equation, but see there is a possibility that adsorption A plus S giving AS. Now it is not only A being present there.

So, you have B plus S giving BS reaction; AS plus BS giving what C s, but one site is left out plus s. So, this is one possibility one can say that C is adsorbing on two sites. So, it becomes C s two instead of s. I am just telling you many possibilities and very possibilities going to give you a different rate equation. So, this is reaction desorption C s giving C plus s. This is one possibility from this you can get a rate equation assuming that one of the step s rate controlling.

Now, how many steps are there earlier you have three steps; now in this case you have four steps: one, two, three and four. So, any one of them can control overall reaction. It can be adsorption of A; it can be adsorption of B; it can be chemical reaction the surface it can desorption of C. So, these possibilities will give you different rate equations. Now, I have written this particular mechanism here, which is a language initial hood type mechanism.

Both the reactants are in a adsorb state giving the final product in the adsorb state itself, but we have discussed this before as well that there is no or rather this it is not necessary that A s should react with B s; A s can be on the catalyst surface and it will react with B which is sitting in the bulk.

(Refer Slide Time: 47:48)



$A + B \rightleftharpoons C$

Ads. $A + s \rightleftharpoons As$.

$\boxed{B + s \rightleftharpoons BS}$ ×

Rxn. $As + BS \rightleftharpoons Cs + S$

Desorption $Cs \rightleftharpoons C + s$. | $As + B \rightleftharpoons Cs$

· E.R.

So, get back to this A s plus B s giving C s plus s instead of that I may write A s plus B giving C s; instead of this I can write this; in that case this become is the irrelevant. So, I have three steps is A plus s giving A s A plus B giving C s and C s giving C plus there is no B adsorption surface. B remain kin the bulk it is adsorption is negligible I will get different rate equation. So, this is called as Euler riddle. We have discussed this before. So, this is one mechanism it will give another rate equation it will give another rate equation.

So, they are many possibilities and you will get many rate equations and because of which you have another when you get rate equation there is like we get. So, many rate equations you have to validate against the experimental data and in that case you see, which rate equation is fits data very well. So, in this case we have assumed that all sides are equal in terms of the activity in terms of their affinity towards the components. Now, there is another possibility that the sites on which A is adsorbed are different from the sites on which B is adsorbed.

So, on the catalytic surface I have two different sites. So, one species one component will get adsorbed on one type sites and other component will get adsorbed on the other type of sites and then the reaction will take place on the surface. Then, the site balance will change instead of one concentration of the empty site C s; I will have C s one and C s two; the two different types of sites.

It is difficult for me to derive equations for every case, but I am trying to tell you many possibilities here, which are likely to give rise to different rate equations and give the design engineer or reaction engineer or reactor engineer, a choice of rate equation that fits a data very well. So, these are all called as semi empirical rate equations, where I have taken help of theory to some extent, but I made some assumptions and I am going to do data fitting later. So, there are all semi empirical rate equations and most of the times they fit the data very well. That is why they are quite popular as per as the kinetics of solid catalyzed reaction is concerned.

Thank you.

We will discuss how to use the experimental data to validate its rate equations in the next lecture by taking some examples.

Thank you.