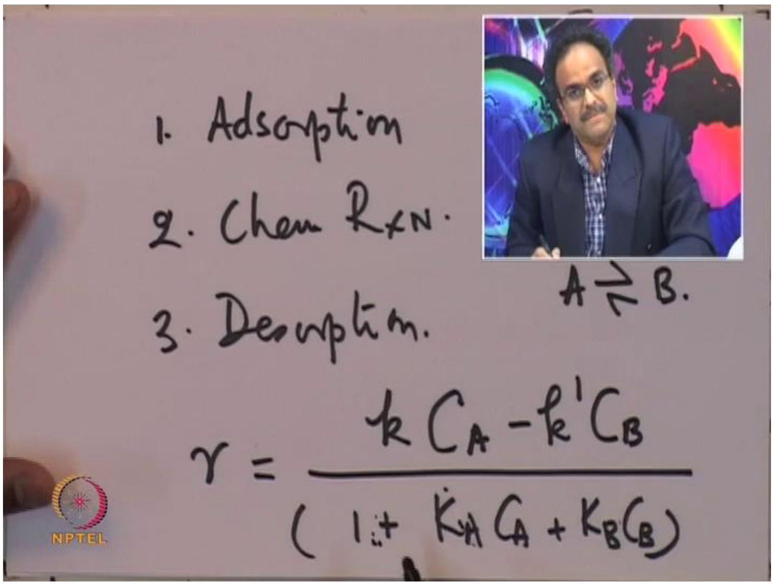
Chemical Reactions Engineering II
Prof. Sanjay Mahajani
Department of Chemical Engineering
Indian Institute of Technology, Bombay

Lecture - 8
Synthesize the rate equation

Good morning. So, in the last lecture we looked at different steps involved in catalysis and based on these steps we wrote down the equations and synthesized the rate equation. The overall rate equation depending on which step is rate controlling. So, it can be the chemical reaction which controls a rate or it can be that absorptions or it can be desorption.

(Refer Slide Time: 00:48)



1. Adsorption
2. Chem Rxn.
3. Desorption.

$A \rightleftharpoons B.$

$$r = \frac{k C_A - k' C_B}{(1 + K_A C_A + K_B C_B)}$$

So, there are 3 distinct steps which are nothing but adsorption, Chemical reaction surface reaction rather and the third one is Desorption's. And be the written down an algorithm as to which one of these steps like, controls overall rate and based on that how to derive the rate equation. Now, the adsorptions steps can be controlling, can be reaction that can control overall rate or it can be the desorption in that can control overall rate.

And the rate equation that we get is of the form say r is equal to some rate constants into concentration that bulk concentrations it can be k dash c b for a reaction in equilibrium with b right, and the denominator we are going to get an expression something like this.

This is one particular rate equation depending on what assumption and probably the rate reaction rate of reaction on the surface to be controlling.

So, this is 1 rate equation I am just showing with the form the rate equation, it can be slightly different depending on which step controls the overall rate. So, if we just closely observe this particular rate equation, what you see is in the numerator you have something similar to what you would you have otherwise gone when the reaction was not catalyze by the solid catalyst; that means, it was normal reaction taking place in homogeneous medium.

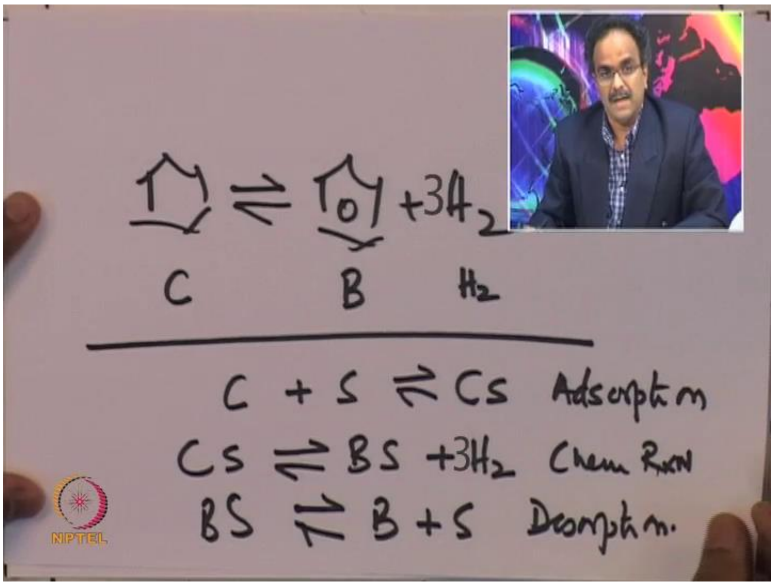
So, this is an additional thing that comes in and what you have here, these are the adsorption constant or probably desorption whatever something to do with that adsorption and desorption. So, the denominator that you have seen here is, because of the adsorption and desorption the spices or the components involving in the reaction. Because, there is a competition for the m t or active side for the reaction take place.

So, in a way this is adsorbed side or going to other already occupied sides or going to be unavailable available reaction to be take place. So, this is this is how we interpret overall rate equation that we get right. But then of course, this may change depending on the assumption that we make which step is a rate controlling step. So, we looked at differential steps to arrive at the it is particular rate equation, how to synthesize this rate equation.

But that is not enough, because once we get this rate equation what is guarantee that the rate equation is valid. So, in order to know whether the assumption that we made or correct or not or the equation you have got is right or not as I told you in the last lecture, we need to look at the experiment data; we need to generate a experimental data and laboratory and see whether the data fits very well in this rate equation.

If it does not then have to go back and make another assumption and come up with different rate equation and see whether the data fits or data falls in line with the rate equation that you have got. So, in this today’s lecture what we are going to do is, like we going to look at a simple example and you going to look at how the experimental data can be used to see the authenticity or validity rather of the rate equation that we have taking about. So, for that we going to consider 1 more example. So, let us go for real example where like for example.

(Refer Slide Time: 04:42)



$C + S \rightleftharpoons CS$ Adsorption

$CS \rightleftharpoons BS + 3H_2$ Chem Rxn

$BS \rightleftharpoons B + S$ Desorption.

For let us say for instance we have a dehydrogenation reaction say Cyclohexane dehydrogenate to give Benzene and Hydrogen. Now, this is Cyclohexane let me call this is C Benzene B and of course, Hydrogen. So, I am going o denote my concentration with C, B and H2 as a name as I mean go ahead. So, let’s first synthesize the rate law with certain assumption.

Then, we look at a possible experiment data and see how we select for either in rate equation fine. So, now, I am not going to any go through each and every sep quite systematically like what we have done before, but quickly come up with the rate equations for 3 different cases: when first that absorptions controls; secondly, that is the reaction control and the third is desorption control.

So, let me first start with adsorption controlling before that, let me right down the mechanism. So, I have c plus s giving c s right adsorption, then C s gives B s plus Hydrogen now is very important steps look at a way I have made an assumption in here. Chemical reaction what is happening here is the hydrogen is generated, but it is coming out immediately it is not occupying the sides, 1 can make some different assumption here saying that C s plus s gives Bs plus H2.

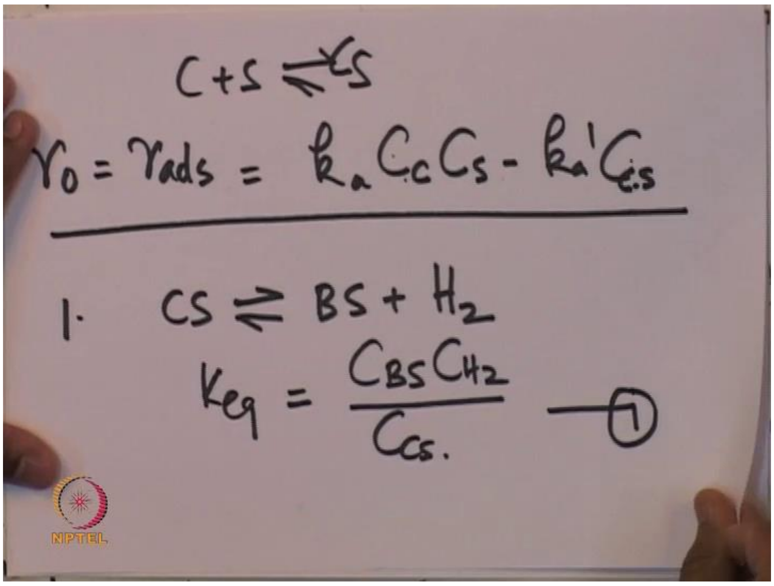
That means, H2 of a Hydrogen is on the in the adsorbed condition. Right now, I am making an assumption which is quite similar to Eley Rideal assumption where one of the component is not in an adsorbs state it does not have infinity for the catalyst as for the adsorption is concern and as infinity is form is go to the bulk. So, that is a meaning of this particular step chemical reaction. So, this particular component is always present in bulk is no adsorb Hydrogen.

Now you may ask me why I have made this assumption right now there is no bases for this adjust assumption I am going to go ahead and see whether this is valid or not based on the experiment. If it is not valid come back and make some other assumption. So, on possibilities are there right what happened I am just trying to tell you meaning of or significance of this particular step that is chemical reaction.

And then the desorption that is Bs gives B plus s right. Now you know how to derive the rate equation if 1 of the steps is rate controlling. So, in the last lecture will look at simple isomerisation reaction a giving b reversible and we said that chemical reaction was controlling and we looked that a rate equation. Today let us, derive the rate equation for adsorptions controlling and then quickly write equation for the chemical reaction and desorption.

And then look at a validity of these equations based on the experimental data. So, first we will spend some time deriving the equation for the case when adsorption controls.

(Refer Slide Time: 08:21)



$$C + S \rightleftharpoons CS$$

$$r_0 = r_{ads} = k_a C_C C_S - k_a' C_{C.S}$$

1. $$CS \rightleftharpoons BS + H_2$$

$$K_{eq} = \frac{C_{BS} C_{H_2}}{C_{CS}}. \quad \text{—} ①$$

So, C plus s giving cs all right, so rate of adsorption is equal to overall rate; that is my assumption rate determining step, rate controlling steps, flow step is equal to k adsorption right into Cc into Cs minus k a dash C cs right. So, this is the rate equation that I have got and depending on the stoichiometric coefficient I will have the sign here; like what you do writing an any normal rate equation.

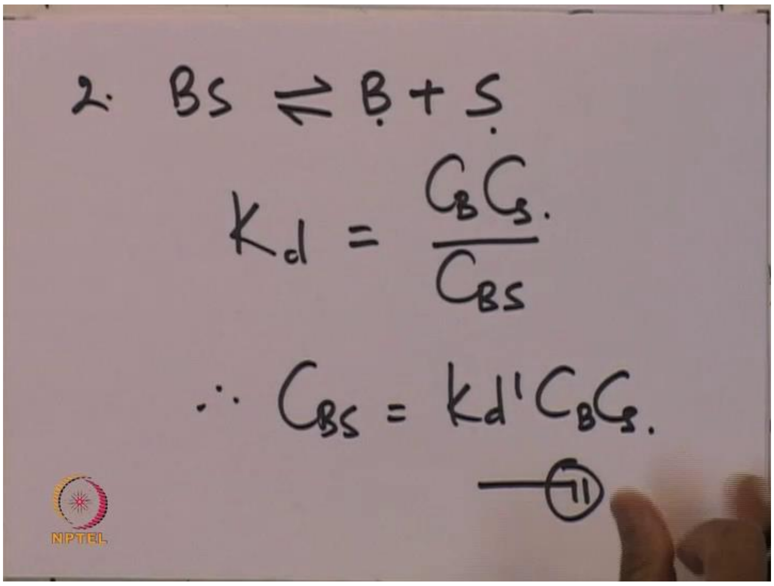
So, I am writing a general rate equation here, so let us go ahead now in this particular equation we have bulk concentration Cc, but apart from bulk concentration we have empty side concentration, vacant sides concentrations and concentration of adsorb spices. These are the concentration which are unknown and they will come from equilibrium steps.

Now, what are the equilibrium steps here, the first step is of course, the reaction now reaction is not the slowest steps like what we did before. In this particular case, adsorption is slowest steps desorption and reaction they are they are equilibrium control or they are equilibrium in instantaneous.

So, the reaction is Cs giving Bs plus Hydrogen, so adsorption controls overall rate and this concentration which are Cs and Ccs, which are which are the concentration below no they will be obtained from the equilibrium step, which are the equilibrium steps here? The reaction, chemical reaction which is now instantaneous earlier in an earlier example with considers reaction to be controlling here adsorption controls.

So, reaction is instantaneous which is that equilibrium? So, the reaction and desorption these 2 steps are going to give me, this bulk that adsorb spices concentration and empty side concentration. So, this is reaction equations Cs an equilibrium with Bs plus Hydrogen. Now, if you write equilibrium equation for this it is K eq: K eq is equal to C BSb CH2 divided by Ccs. Now with an express CBs in terms of Ccs here, so let me just write equation 1 here; use equation 1 later to get value of Ccs, right.

(Refer Slide Time: 11:16)



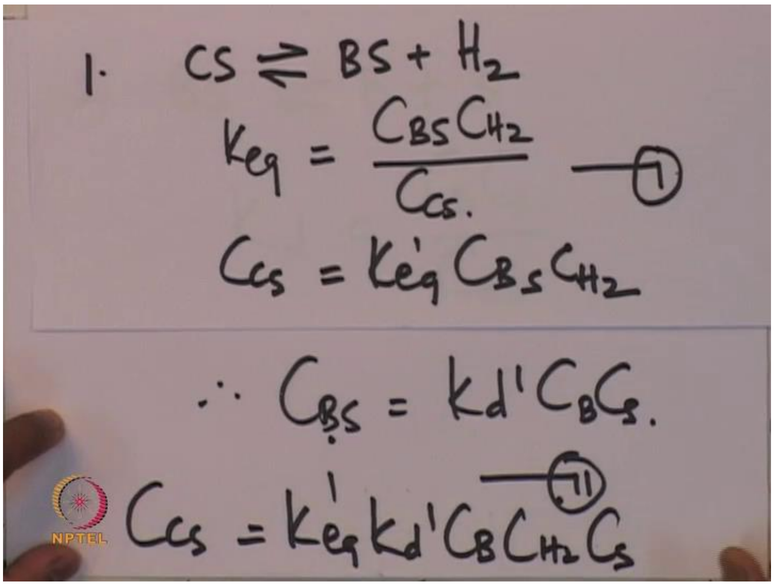
2. $BS \rightleftharpoons B + S$

$$K_d = \frac{C_B C_S}{C_{BS}}$$

$$\therefore C_{BS} = K_d' C_B C_S. \quad \text{—} ②$$

Similarly, I desorption which is again an instantaneous process where you have Bs that is Benzene is going to get desorbs right. So, this is top Benzene, Benzene in bulk and empty side. So, again the same thing I can write Kd is equal to CB Cs divided by CBs, so CBs is equal to Kd dash CB Cs equation 2. Now, using equation 1 and equation 2 I am going to substitute for CBs and C cs in the main equation that is obtained by adsorption to be the rate controlling step, right.

(Refer Slide Time: 12:10)



1. $CS \rightleftharpoons BS + H_2$

$$K_{eq} = \frac{C_{BS} C_{H_2}}{C_{CS}}. \quad \text{—} ①$$

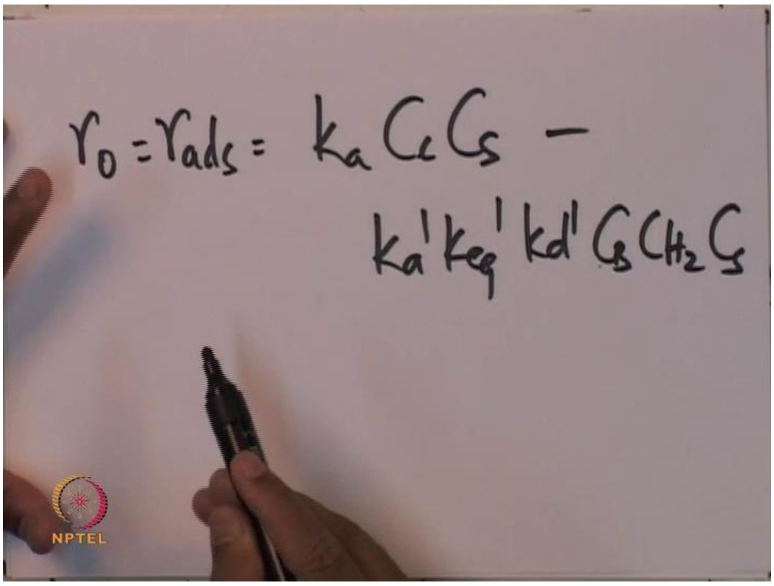
$$C_{CS} = K'_{eq} C_{BS} C_{H_2}$$

$$\therefore C_{BS} = K_d' C_B C_S. \quad \text{—} ②$$

$$C_{CS} = K'_{eq} K_d' C_B C_{H_2} C_S$$

So, what I need is C cs, now how do I get C cs from this equation C cs is equal to some constant into C Bs CH2 right and from equation 2 you C Bs is equal to this. So what it means, this C cs is equal to again K eq dash Kd dash CB CH2 Cs. So, I have got expression for C cs which is to be rate in the main rate equation the overall rate of the reaction. This is the 1 C cs this is where I need to substitute for it.

(Refer Slide Time: 13:18)

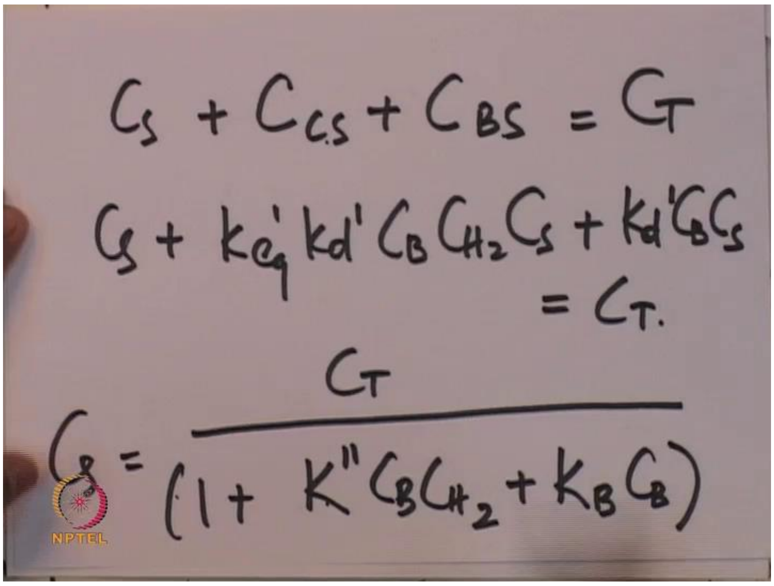


$$r_0 = r_{ads} = k_a C_c C_s - k_a' K_{eq}' k_d' C_B C_{H_2} C_s$$

So, if I do that what I get is r0 that is overall rate is equal to rate of adsorption is equal to Ka Cc Cs minus ka dash K eq dash Kd dash CB CS H2 Cs. Now in this I do not know only Cs rest of all are bunk concentrations. By the way now, it all depends on what kind of reaction that I am talking about the gas phase reaction or liquid phase reaction; for the gas phase reaction normally the concentration is expressed in terms of partial pressures for the liquid phase reaction it is concentration.

So, right now I am just express the all this in terms of concentrations, but if you’re talking about gas phase reaction, you can convert it into partial pressure. So, b by r t is equal to concentration fine all right now you this equation.

(Refer Slide Time: 14:20)



$$C_s + C_{cs} + C_{BS} = C_T$$

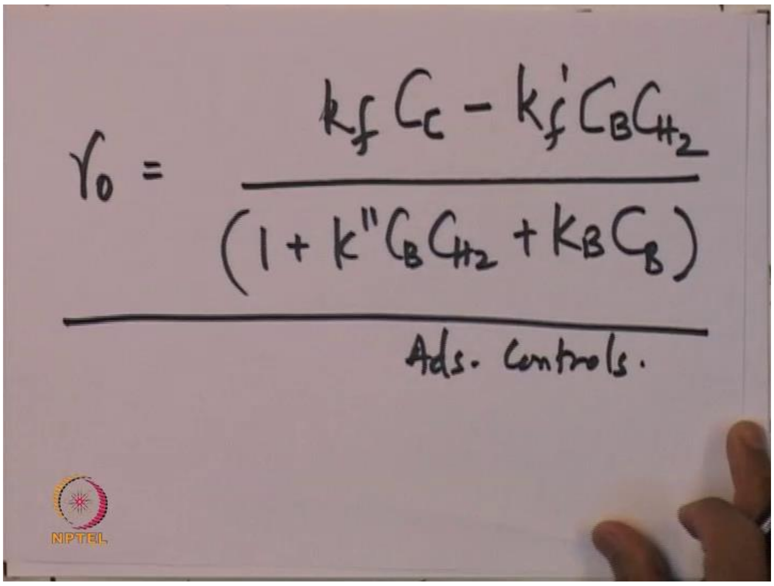
$$C_s + k_{eq}' k_d' C_B C_{H_2} C_s + k_d' C_B C_s = C_T.$$

$$C_s = \frac{C_T}{(1 + K'' C_B C_{H_2} + K_B C_B)}$$

Further side balance Cs plus C cs plus C Bs Cyclohexane adsorb, Benzene adsorb is equal to CT. Now, Cs what is C cs; C cs is equal to and C Bs is equal to which we have already derive is equal to CT right. So, Cs is equal to CT divided by 1 plus let me write, again some constant here CB CH2 plus KB CB right. So, this is I have just club all these individual constant in k double dash right.

So, I got expression for Cs look at a expression is slightly different look at this term which was not there before. Now, it is adsorption control in that is why you have different terms appearing in the denominator try and observe differences. Now, I have got the expression for Cs, I will substitute for Cs in the main rate equation that I have got.

(Refer Slide Time: 16:07)



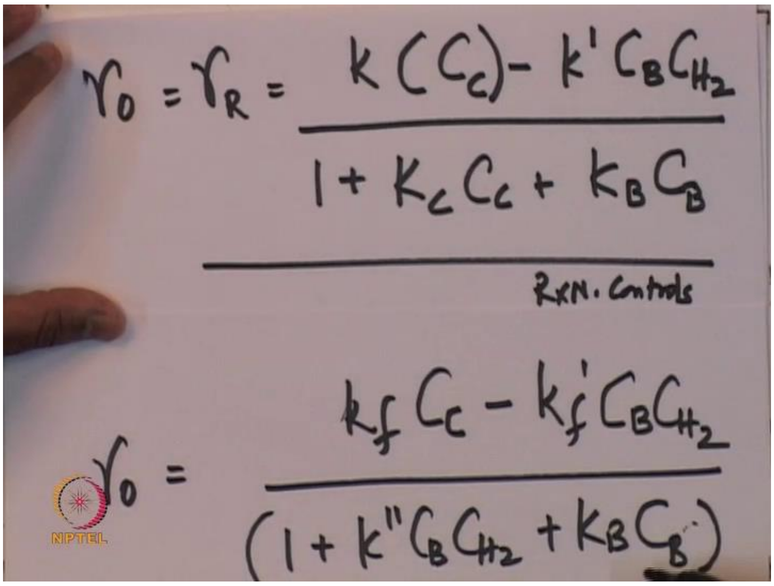
$$r_0 = \frac{k_f C_C - k_f' C_B C_{H_2}}{(1 + k'' C_B C_{H_2} + k_B C_B)}$$

Ads. Controls.

So, ro is equal to k forward now I am just giving you the for final form, you can this is all of obtained by clubbing all those constants right this kf which is function of Ka k and CT and so on Cc that is concentration of Cyclohexane minus kf dash or no one can say k reverse k backward k be rather CB CH2 divided by 1 plus right. So, this is a final expression when adsorption controls adsorption is a rate determine step.

Now, this is 1 expression that I have got suppose I do the same excise, but there now with reaction to be controlling. Then, I will get different rate equation and you can do the excise on your own as I gone to do it here, I will just write rate equation.

(Refer Slide Time: 17:40)



$$r_0 = r_R = \frac{k(C_c) - k' C_B C_{H_2}}{1 + K_c C_c + k_B C_B}$$

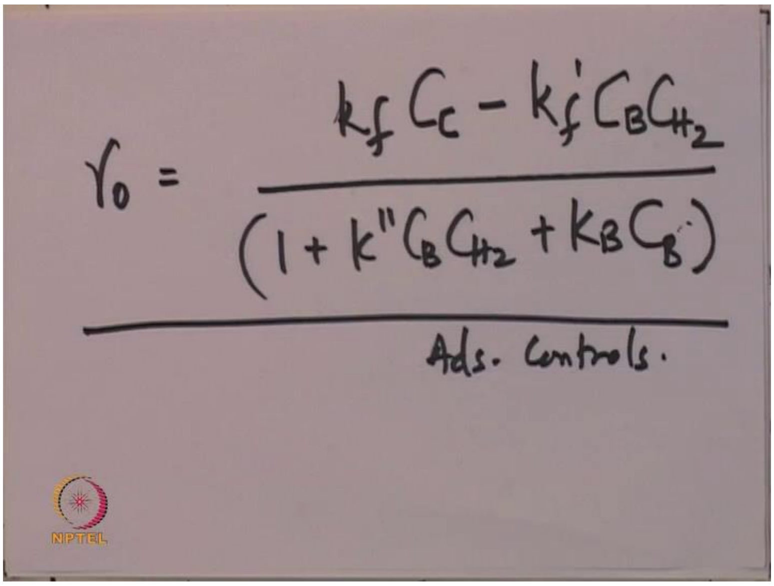
Rxn. Controls

$$r_0 = \frac{k_f C_c - k_f' C_B C_{H_2}}{(1 + k'' C_B C_{H_2} + k_B C_B)}$$

The form the equation it is going to be ro roll is going to be r reaction is equal to some K into Cc minus K dash CB into C Hydrogen divided by it is quite similar to what we have done before Kc Cc plus KB CB this is where the reaction controls. So, look at a difference, this was when adsorption controlling you can difference numerator is not changing much.

But the denominator this is a difference, there is a difference and I am going to explain that is difference no based on the experimental data which 1 is a right equation, but the is not get over. Now, I am going to that the case 1 desorption controls.

(Refer Slide Time: 18:57)



$$r_0 = \frac{k_f C_C - k_f' C_B C_{H_2}}{(1 + k'' C_B C_{H_2} + K_B C_B)}$$

Ads. Controls.

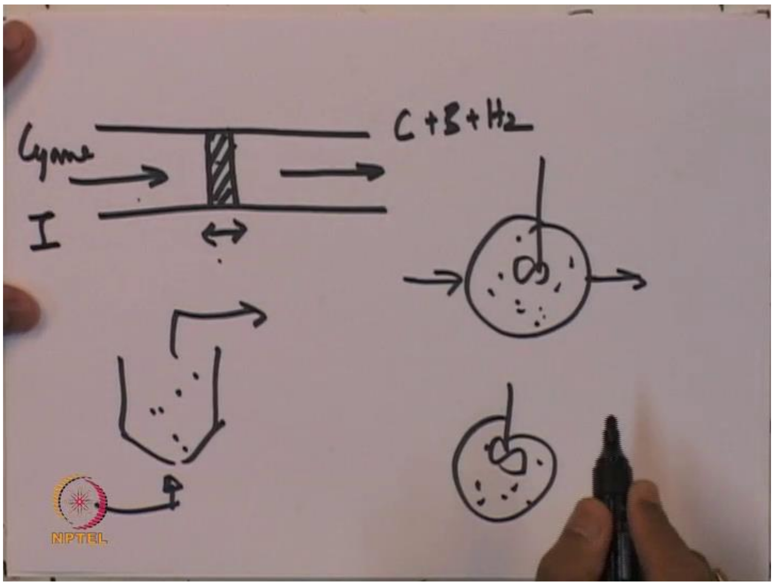
ro is equal to rd is equal to. So, desorption controlling r0 is equal to rd is equal to some k right Cc again the numerator look at this numerator is not changing CB into C Hydrogen divided by I will have very peculiar expression here, you have C Hydrogen plus k dash Cc plus k double dash Cc and C Hydrogen. Now, you can derive this equation on your own I am just writing a final form to equation, because I am going to make huge of this equation later to see whether this is the write equation based on the experimental data or not.

So, this is where desorption controls. So, I have 3 expressions when these 3 difference steps are controlling step. The first one is adsorption controls that is this occupation, then reaction controls for this particular reaction and when desorption controls this equation. These are 3 different expressions that I have got, now I want to know whether we which equation is valid is a real situation. So, how do I know this other said before I need to do an experiment laboratory.

Now, think of a situation you want to do experiment in laboratory for a solid catalyse reaction; you have Cyclohexane getting converting Benzene Nitrogen’s let us a vapour phase reaction and using any Hydrogenation catalyst. So, Nickel adsorption Alumina or whatever say Palladium adsorbent Alumina; Alumina is a support right the Porous support and reaction take place, right.

Now how I do the experiment in the laboratory? How do I get rate equation rate value for the rate the different type of reactor, which is use in laboratory for solid catalysis reactions. So, it is quite similar what we have already learn for simple reaction, normal reaction here we have a differential reactor.

(Refer Slide Time: 21:53)



So for example, you have a tube in which you have impact the catalyst and flow is taking place. Now this particular length is very small what is it mean? That means, there are no gradients along the length. So, it’s like a differential reactor though it tubular reactor in that catalyst volume that have I am using this very small. So, that concentration does not change drastically.

So, with that particular volume act like a Cs TR where the concentration is uniform; the it has an advantage, because it is going to get me the rate equation for the particular concentration. The concentration changes not much, so I can assume the concentration to be the feed concentration at which the reaction taking place. Anyway, that will be clear later, so this is a tubular reactor would difference or 1 can have a store reactor a continues reactor, 1 can have fluidise based reactor.

But of course, typically like such reactors are not so commonly in laboratory this is the most common reactive use in laboratory. 1 can have so it so your meaning with liquid phase; the reactant products are in the could phase in the catalyst is solid. In that case, again I will have a slurry reactor, similar reactor now this is a continues, but I may have batch reactor right. But, then I will have a concerned performance equation for the batch reactor and can evaluate a value of rate.

So, this is how can perform a experiment in laboratory for solid catalyst reaction not or in all this reactor I can use solid quite comfortably. In this case, in the fluidise based case that make sure that this particular florid should it good enough, for high enough the catalyst. So, all this reactor that the give you some performance based on the you can calculate the rate.

The fluidized bed and CS TR type of slurry reactors are integral reactors and by differentiating the conversion verses catalyst loading plot we can obtain the instantaneous rates and can calculate a reaction rate constant. Also it should be coated that, the differential reactor has a limitation as I said before that a conversion should be as small as possible.

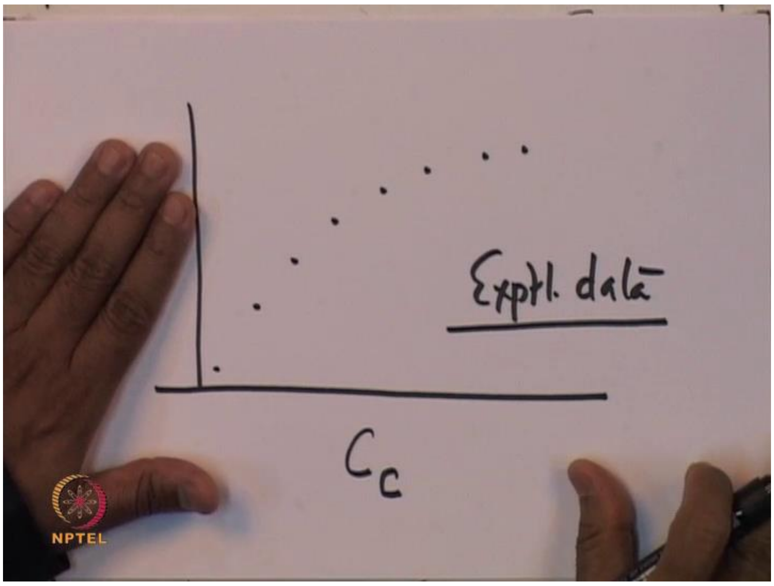
So, if we the conversion goes beyond a particular limit, then probably the differential reactor will not work like a differential reactor and then analysis will be incorrect. Now, let us get back 2 or more example of Cyclohexane, the Dehydrogenation to give Benzene and Hydrogen. So, in this case suppose I am using a tubular reactor here, Cyclohexane will go inside and a mixture of Cyclohexane plus Benzene plus Hydrogen will come out.

So, you may use some inert also here of course, which inert is used and all look at it, because in that we have some effect that may get adsorbed on the catalyst surface, if you look at it separately. But, then we can do this experiment here to returning the rate. So, let say I determine the rate, for this particular reactor by changing concentration of Cyclohexane in a field.

Now it’s not pure Cyclohexane, it you have the inert make an assumption that inert does not adsorb the surface. It is like Hydrogen; Hydrogen of course is not inert here it a product, but like Hydrogen there is another inert is a product. But like Hydrogen there is another inert say Argon or say Helium right all the Hydrogen for that matter which does not have any infinity for the catalyst. So, what I am doing is in this particular reactor I am passing Cyclohexane along with that I have some inert going inside.

So, it gives me an opportunity to play with the concentration of Cyclohexane. So, I can do or I can perform experiments at different concentration of Cyclohexane in the field I get a rate for every concentration all right.

(Refer Slide Time: 26:59)

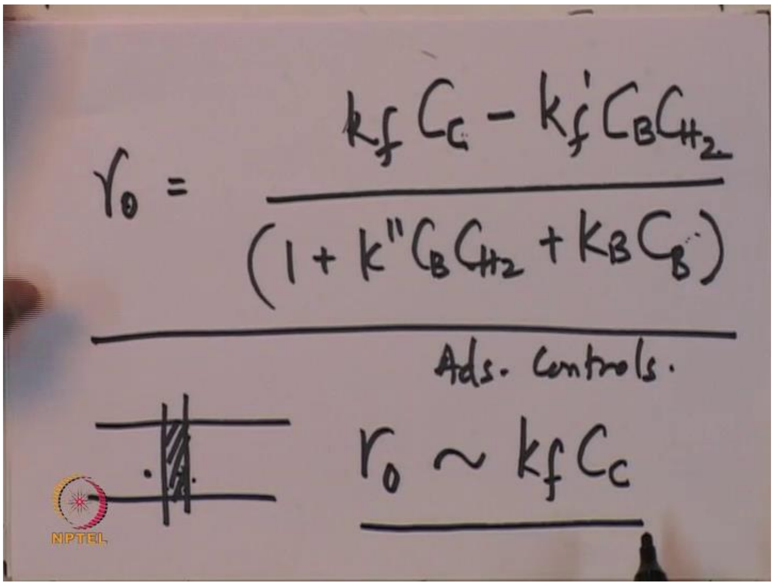


So, if I do this experiment what I get is at different partial pressure or different concentration of Cc what is the rate? What is the rate of the reaction? This is the rate that I have observed, this is the rate that that is overall there that we have derived a rate equation for. And this particular rate should fit very well in the rate equation that I am going to get. Now, Cc verses r overall or r observed let’s say I am getting a train like this I am getting a train like this. This is the experimental data.

Now I need to know whether any of these equations that I have derived falls in line with this this experimental data or not. So, what is that nature here? Initially it is big linear and then the slope is decreasing and it getting saturated, after some certain concentration of Cyclohexane in the field; which is sufficiently have there is no change in the rate it is almost becoming constant. So, that is general observation that I have.

So, this is the experimental data observed, I am going to get back to this let us observe our earlier rate equations that we have derive. Now, I have the equation where adsorption controls, what do I see here? If I change the concentration in the field. What is the rate? Now this is a finite value for this right whatever is a concentration that I am doing the experiment with, so there is some finite value here right. What is the field concentration Benzene? 0 reaction is taking place at field concentration remember what is said.

(Refer Slide Time: 29:04)



$$r_0 = \frac{k_f C_C - k_f' C_B C_{H_2}}{(1 + k'' C_B C_{H_2} + k_B C_B)}$$

Ads. controls.

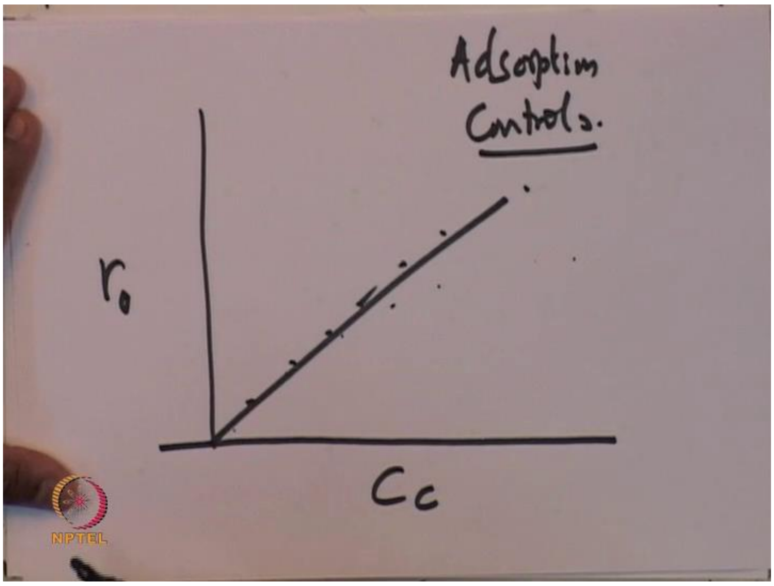
$$r_0 \sim k_f C_c$$

The concentration is not changing much here. So, whatever rate that I am calculating here is add a filed concentration. Suppose are concentration of Cyclohexane entering is 50 percent, the extend of reaction is not much it is going to come out which say 48 49 percent concentration of Cyclohexane. Some Benzene will be forms, some hydrogen will form, which will be very small depending upon the extend of reaction, but this extend is small.

So, that for all practical proposes, I can assume that the reaction takes place at a concentration corresponding to the field concentration; this a very important assumption and this valid. Provided this catalyst length that I am using is relatively small, so what happen here? Cc infinite value say 50 percent concentration unit of course, CB is negligible 0 CH2 0 CB 0 CH2 0 what does it mean? r0 is equal to kf Cc.

And what does it say, it says that the rate is directly proportional to the concentration of Cyclohexane right. So, what train I will get, I will get a train which is linear with respective Cyclohexane concentration the field.

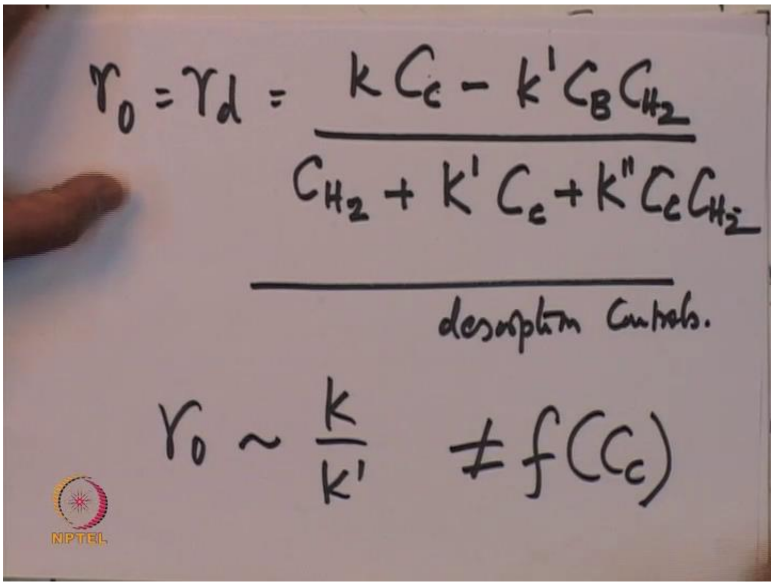
(Refer Slide Time: 30:48)



So, it is going to be like this, this Cc verses r overall when adsorption controls this is the train that would I get, is that the trained have got in the experiment no my trade was like this. So, what is it mean? It means that, the rate equation that I have got assuming that adsorption to be controlling is not valid here is not valid here.

So, let us look at desorption controlling now, let us look at the rate equation when we get, when we assume that desorption controls the overall rate. So, what is the rate equation that I have gone this is the desorption rate equation. What do I see here? Cc is finite, CB is 0, I do not have Benzene in the field, I do not have Hydrogen in the field; this is also 0, this is 0, this is 0, this is finite.

(Refer Slide Time: 32:03)



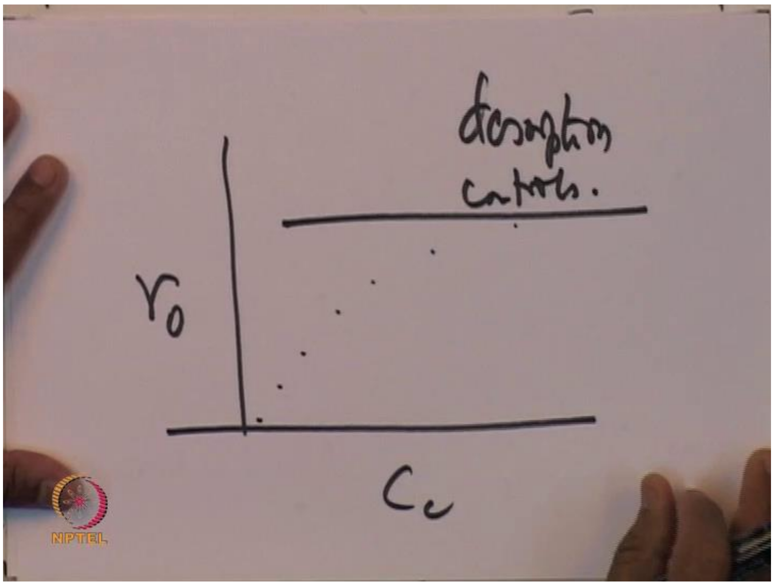
$$r_0 = r_d = \frac{k C_c - k' C_B C_{H_2}}{C_{H_2} + K' C_c + K'' C_c C_{H_2}}$$

desorption controls.

$$r_0 \sim \frac{k}{k'} \neq f(C_c)$$

So, r0 or r observer the overall is equal to K divided by K dash because c by Cc by Cc that that will get cancel right. So, rate is constant in desorption controls rate is independent of Cc. If the field is pure, Cyclo pure in the sense there are no product presents it will be, only Cyclohexane in some inner medium right. So, the change Cc and observe the rate and in desorption controls what is the train that I expect?

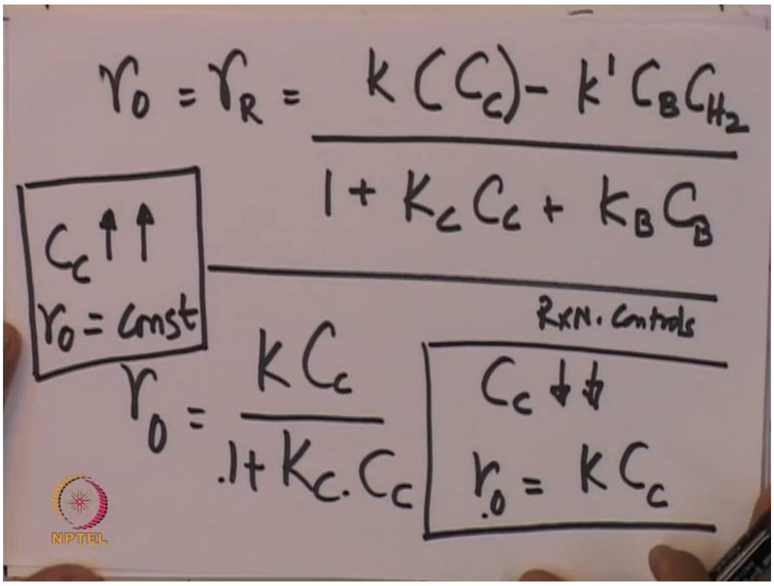
(Refer Slide Time: 32:56)



I expect that, so there is no change when desorption controls I hope this is clear. As the concentration changes the rate is unaffected, because of this or rather this it is a desorption of Benzene that is controlling. So, the rate does not depend on Cyclohexane concentration at all. So, is that my observation my fixed bed reactor or other that tubular reactor, a differential reactor that I am using; what is the observation there, I am seeing that the rate changes in this fashion. And what I should get is this not true or all does not fall in line.

So, what it mean is this, from the experimental data that I have got neither that adsorption controlling alone nor the desorption is controlling alone. So, let us look at a reaction now or let us look at a expression when the reaction controls the overall performance; reaction is a slowest step right. So, what is the expression that we have got the expression that we got is this; when the reaction control.

(Refer Slide Time: 34:54)



$$r_0 = r_R = \frac{k(C_c) - k' C_B C_{H_2}}{1 + K_c C_c + k_B C_B}$$

$C_c \uparrow\uparrow$

$r_0 = \text{Const}$

Rxn. Controls

$$r_0 = \frac{K C_c}{1 + K_c . C_c}$$

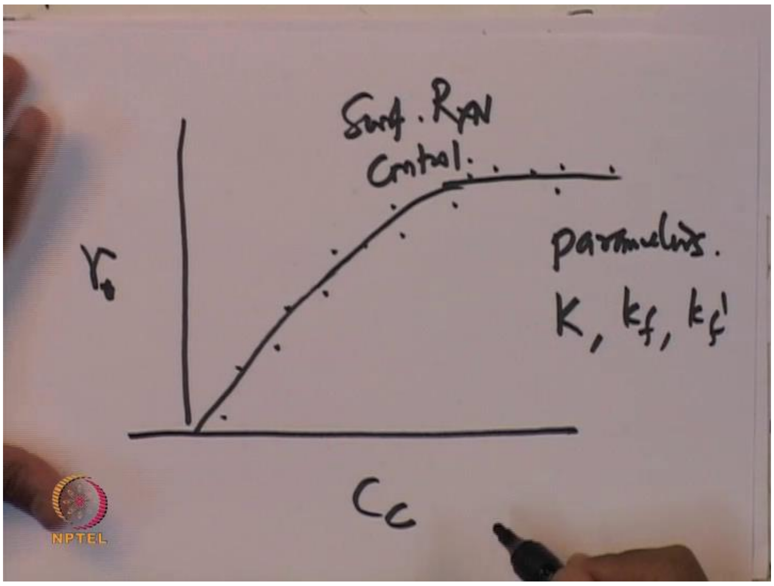
$C_c \downarrow\downarrow$

$r_0 = K C_c$

But then I get rate equation r overall is equal to K Cc divided by 1 plus Kc Cc. Now this is a very typical rate equation right. So, very small value of Cc when Cc is very small r0 is this is very small r0 is K into Cc right. For small values of Cc r0 is proportional to Cc is proportional to Cc and what happens if Cc is very large. If Cc is very large then this becomes very large compare to 1.

So, r0 for Cc to be very large r0 is constant this very typical rate equation that we have got, where in the nature would change depending on the concentration of Cyclohexane in the field. At very low concentrations the rate is proportional to Cc and a large concentration the rate remain is constant or it attains saturation. So, how it look like or the graph Cc verses rate it looks like this.

(Refer Slide Time: 36:33)



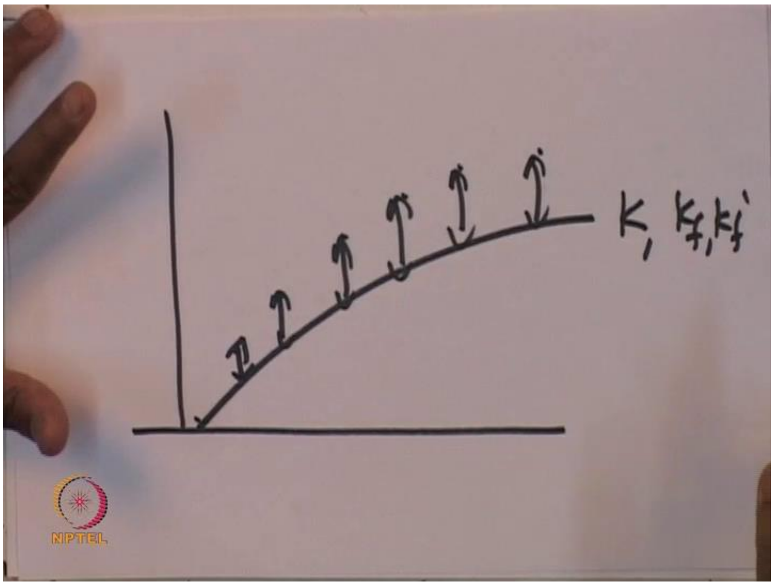
Cc verses rate overall or observed it almost concentration here, it is linear here and there will be some range; where it is neither linear or not nor constant right. This is when it is a reaction surface reaction controlling overall rate right. And remember that data experimental data, that I show you before falls in line with what 1 would get right by assuming surface reaction to be controlling right.

So, it is like you have initially linear and then going to saturation. So what it mean this is, the rate equation in this particular case for this experimental data is the rate equation when chemical reaction; surface chemical reaction controls overall rate at least the nature is quite similar. Now what do we do now later now nature is similar means, I will try and fit this particular model or this particular rate equation in the data that I have got and get the values of parameters.

Now which are these parameters? The parameters are adsorption constant, rate constants. So, I get a rate constants, I get a adsorption constants by fitting this data. So, if you have this particular equation, so this is some something that I obtained for certain values of parameters now which are these parameters, K the adsorption constants, kf k backward or k dash whatever all these are rate constants these 2 and these are adsorption constant. If the surface reaction controls the overall rate, that in the k by k dash is related to the overall chemical reaction equilibrium constant with the reaction and that can be determine independently.

So, the unknown parameters are only 3 those are KC KB and k that is the powered reaction rate constant. So, this will be determine in such a way that may data fix well in this particular equation right. So, once you do that if the data fixed well over a large range in the Cc, then you have got a right rate equation. And this data fitting is normally done by the many methods of rigration, a something going to least square method.

(Refer Slide Time: 39:38)



So, where what we do is you have the experimental and you have the curve certain values of parameters K, kf, kf dash right and for every point there is some difference with time minimise this difference. And there is a function called summation of this square of these errors. Why square? Because, sometime is quite possible that this difference is positive at 1 point, this difference is negative at certain point.

So, say if I just go on adding the differences they may compensate for each other and say that, find the overall total area is 0, but that is not correct, so we have to square it. So, that will magnitude waves are positive so that, I get a best fit fine. So, that is nothing, but parameter estimation or regression analysis which is called as least square method is the best method to other in commonly use method to estimate a parameter.

There are mathematical techniques; optimization techniques which are used to calculate this values parameters. Now, after doing all this does it mean that you have got a right rate equation work very well. Now there is 1 thing that we are not really look that. What is that? You have just look that, the effect of Cyclohexane concentration in the field here, not look that a effect of Benzene concentration, you're not look that a effect of Hydrogen concentration.

There are some constant associated to Benzene adsorptions right in the denominator. You would be able to determine them, only if you have Benzene present in the field. So, after doing all this you have to generate more data by doing some experiments with other Hydrogen filed, Benzene in the field, which certain proportion not negligible now or both of them in a field; doing all this you generate as much data is possible and see whether you rate equation fit or it falls in line with the experimental data and that is the complete excise.

Now, I have just shown you 3 different rate equation s here and say that 5 possibly the reaction controlling mechanism may work. But in real situation things are lightly to be more complicated where I need to make certain other assumption you get different type of rate equation; as I said before now I assuming the single site adsorption. They can be do a side of adsorption I am assuming Hydrogen to be present in bulk only, but the palladium may have affinity for Hydrogen and it has.

So, I can not this make at assumption. So, as I have to assume that there is another adsorptions steps that is Hydrogen. So, Hydrogen is firs present in adsorb striate and then there is a desorption not coefficient not just Benzene by Hydrogen as well. It will become more and more complicated, but there if you want a right rate equation you have to bear with these complications. And finally, you get aright equation then only you can use it for reactor design.

Because, ultimate aim is to proper reactor design for the given reaction of interest and that will be valid only range of concentration that I am studying, before we go ahead to the reactor design, let us look at this effect of temperature. Now I am not talked about, the temperature at all now let us look at a rate equation that we get when there is reaction control the overall rate of this is the reaction rate.

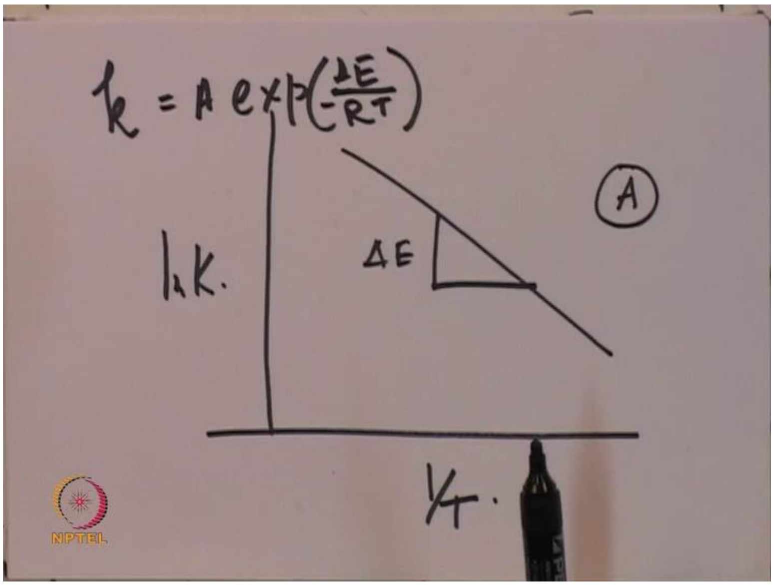
Now, in this rate expression I have several parameters this is 1 parameter, this is another parameter, this are adsorption related parameter. Now how will the temperature affect this parameters? Now, k is the rate constant k dash is the rate constant for the reversible reaction. The these 2 are lightly to be highly sensitive temperature of course, it will have a adsorption constant also, but it has the rate constant or this 2 will have the rate constant as well in them.

See I have got this by clubbing or other putting together many constant this the capacity CT also coming in picture. But in that if you remember you have forward rate constant and backward rate constant also in this. And those are the constants, which are highly sensitive to temperature that is why this, this constants are highly sensitive temperature. What about these constants? These are only based on adsorption, there is no rate constant here.

So, adsorption constant relative to or compare to rate constant these 2 are less sensitive to temperature; less sensitive to temperature by it is quite lightly that because of temperature or high temperature adsorption get effected. Now, you all know that if I increased to be temperature adsorption is less fevered and desorption fever. So, the adsorption constant will go down and you may make an assumption at very high temperature; the denominator which is related to adsorption this 2 terms are negligible.

What happen? If this 2 terms are negligible then you have an denominator just 1, so this based on to a normal rate equation; which is similar to homogeneous catalysis. So, in high temperature you may see such effects right. You can even change temperature in generate temp data different temperatures to get the hidden parameters, which are the hidden parameter activation in energy, frequency factor so on. Right now the parameter is that I was talking about was only like: forward rate constant, backward rate constant and adsorption constant.

(Refer Slide Time: 46:27)



But then if you generate data at different temperatures, you can get the activation energy also something that we already done at different temperatures you have 1 by T verses ln K or l n r0 that is equal to initial rate, you have a plot like this the slop gives you the activation energy and the interest gives you frequency factor, where k that is rate constant is nothing, but a into exponential minus E by delta E by RT right.

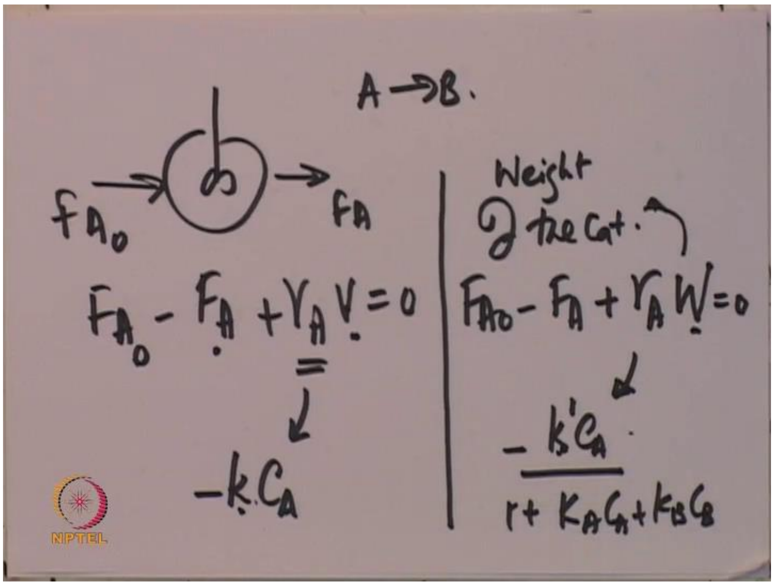
So, I can get activation and frequency factor for both the rate constant forward and backward. Now, both the example you have consider so far first Isomerisation and now Dehydrogenation both the example I have consider reaction to be reversible, but not necessary that is reaction has to be reversible; reaction can be reversible as well.

So, the same expression or the same methodology or procedure can be a apply to irreversible reactions and 1 can obtained the rate equation you can do that as a as a home work. Just take an example a going to b, but now it is not reversible it just irreversible reaction fine. So, you have the rate equation after we get a rate equation what do we do we need to design the reactor all right.

So, I have told you the procedure to get a rate equation, synthesis the rate expression for certain assumptions and then validate it again is the experimental data this is the entire procedure that I need to perform in laboratory before I design a chemical reactor. And remember we have not considered the external mass transfer effects, we are not consider the inter particle diffusion, that will come later any why.

Or right now, just assuming these are negligible and I have the rate equation. Now, how do I design a reactor? Now the procedure is not much different from what we have done before. What do I do?

(Refer Slide Time: 48:38)



Earlier I have a Cs TR I write a rate equation F A0 by minus FA plus r AV is equal to 0 you have F A0 FA here right. And then in rA I have minus k CA for irreversible first order reaction a going to b and by knowing F A0 for the required conversion I get a volume that is why reactor design. Or for a given volume I calculate the outlet concentration can gives me that conversion.

So, this is the excise that I have do now what is going to change for a Hydrogenous reactions. Now, I have a similar thing accept now will have F A0 minus FA plus rA and in most of the cases instead of v have W equal to 0. Now what is W? Here it is a volume, here it is the weight of the catalyst. Why? Because, the rate now is minus possibly k CA divided by 1 Plus KA CA plus KB CB something like this.

If the reaction is reversible will have a 1 more term here right. So, instead of this I have this; this is 1 difference and another difference is instead of volume I have W here. Why? Because, the rate constant here is per unit weight of the catalyst; the rate constant here is per unit volume of the reactor, here the rate constant is per unit weight of the catalyst.

So, this is the only difference otherwise the entire excise that I have done whatever problem is I have solved from homogeneous reactor. Similar procedure will be adopted for Hydrogenous reaction. Remember, volume is replace by the weight of the catalyst and the normal rate equation which is probably of the power law type is replaced by either Langmuir Hinshelwood, Eley Rideal whatever mechanism depending on whatever assumption I make slightly complicated rate equation but the methodology or procedure remain same.

Thank you.