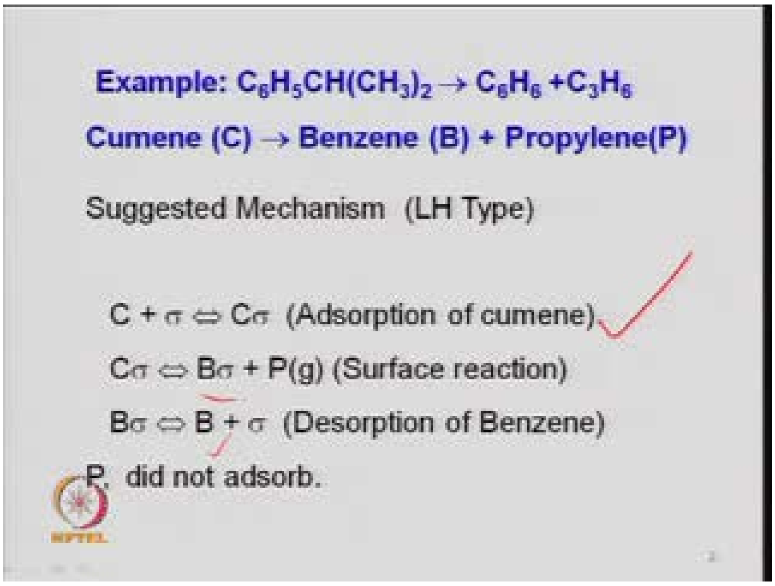
Heterogonous Catalysis and Catalytic Processes
Prof. K. K. Pant
Department of Chemical Engineering
Indian Institute of Technology, Delhi

Lecture - 25

(Refer Slide Time: 00:39)



Example: $C_6H_5CH(CH_3)_2 \rightarrow C_6H_6 + C_3H_6$

Cumene (C) → Benzene (B) + Propylene(P)

Suggested Mechanism (LH Type)

$C + \sigma \Leftrightarrow C\sigma$ (Adsorption of cumene)

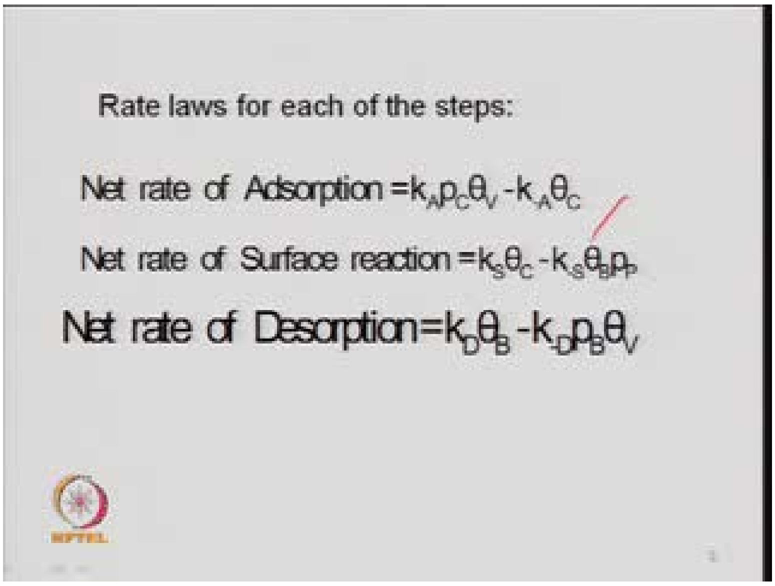
$C\sigma \Leftrightarrow B\sigma + P(g)$ (Surface reaction)

$B\sigma \Leftrightarrow B + \sigma$ (Desorption of Benzene)

P did not adsorb.

Good morning. So, the last lecture we were talking about Langmuir Insolate Kinetics and there are some mechanisms. So, we were just discussing an example problem which is Cumene converts to Benzene and Propylene. So, that is the reaction we were talking about last time. And, we had seen that the possibility of the different steps say Cumene adsorbs on the surface; that is the adsorption of Cumene. And, we have already done there are Cumene as a rate controlling step and determine the rate of reaction. Then 2nd 1 is the adsorb Cumene on the surface it transfers in to another adsorbed Benzene and the Propylene in the gas phase. So, Propylene does not adsorb; that is what we assume? and finally, this adsorb Benzene disrobes from the surface. And, the product Benzene comes in the gas phase.

(Refer slide Time: 01:22)



Rate laws for each of the steps:

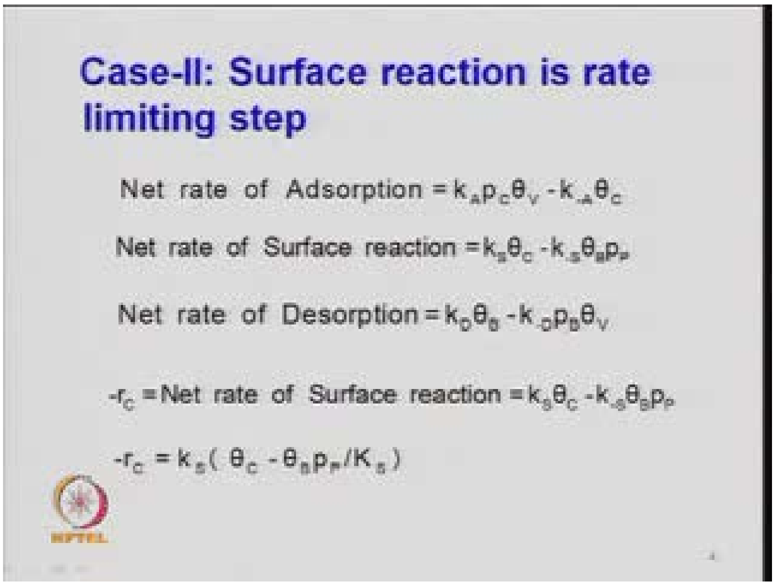
Net rate of Adsorption $= k_A p_C \theta_V - k_A \theta_C$

Net rate of Surface reaction $= k_S \theta_C - k_S \theta_B p_P$

Net rate of Desorption $= k_D \theta_B - k_D p_B \theta_V$

So, we discuss this rate equation; the rate of reaction all of you know that the rate of forward reaction minus rate of backward reaction that is net rate of adsorption. Similarly, net rate of surface reaction is forward reaction minus the backward reaction. If you just recall it this is your surface reaction and rate will be proportional to the concentration of the adsorb C. So, that is what written here in terms of the concentration; that is K s times theta C. So, theta C is the adsorb concentration of Cumene. And, then there was a reverse reaction which will depend on the Benzene the sigma and concentration of Propylene in the gas phase. So, the expression comes in the form of the adsorbed Benzene concentration and the partial pressure of Propylene which is in the gas phase.

(Refer Slide Time: 02:22)



Case-II: Surface reaction is rate limiting step

Net rate of Adsorption $= k_A p_C \theta_V - k_{-A} \theta_C$

Net rate of Surface reaction $= k_S \theta_C - k_{-S} \theta_B p_P$

Net rate of Desorption $= k_D \theta_B - k_{-D} p_B \theta_V$

$-r_C =$ Net rate of Surface reaction $= k_S \theta_C - k_{-S} \theta_B p_P$

$-r_C = k_S (\theta_C - \theta_B p_P / K_S)$

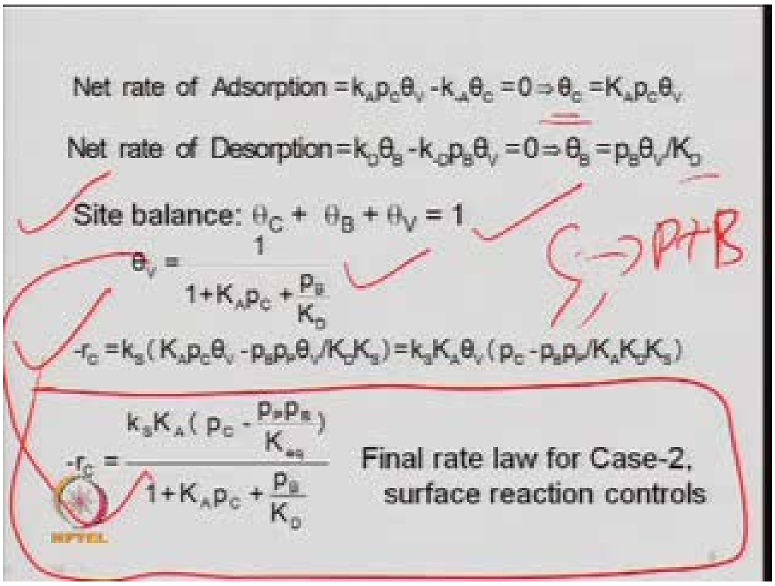
So, if the desorption is rate controlling then net rate of desorption that was the 3step then it will be written based on this which is again provided here from this equation. So, B sigma which is adsorbed on the surface of a catalyst desorption of the Benzene which is adsorbed on the surface of a catalyst.

(Refer Slide Time: 02:47)

So, either a step may be rate controlling b step or c. So, any step may be a rate controlling when you divides a mechanism right, you need to do some characterization to identify whether it is possible or not and then you can demystify. So, here in this rate postulation 1 step we assume that adsorption is rate controlling. And, the 2 case it is the surface reaction may be the rate determining step. So, in that way the net rate this is; the rate controlling step then your rate of reaction will be given by the 2 step of this reaction which is your RDS. Now, so this is your RDS Rate Determining Step or Rate Controlling Step. So, in that rate the R procumene will be written like this; rate of consumption Cumene or rate of reaction for Cumene. The composition that is given something like this so, theta C and theta B is the unknown of the reaction. So, you need to find out the unknown concentration which is adsorbed species concentration.

For that because this is; rate determining step it means this will take highest time or slowest step of the reaction. So, other 2 will be very fast or they are assumed to be at equilibrium. So, in 1 way you say net rate of adsorption of this is 0, and same thing net of rate of desorption is 0 or you say that they are very fast and at equilibrium. So, on1 can very easily calculate now from here a relationship between theta V and theta C. That is simply your K e adsorption equilibrium constant times the partial pressure of the Cumene from the 1 step. Same thing for the 3 which is rate of desorption, so from here also you can find out theta B divide by theta V and that is; again in the form of K minus D P B divide by K D. That is simply P B up on K D. So, from here and here so, whatever you have defined these can be substituted in this final rate.

(Refer Slide Time: 04:50)



Net rate of Adsorption $= k_A p_C \theta_V - k_{-A} \theta_C = 0 \Rightarrow \theta_C = K_A p_C \theta_V$

Net rate of Desorption $= k_D \theta_B - k_{-D} p_B \theta_V = 0 \Rightarrow \theta_B = p_B \theta_V / K_D$

Site balance: $\theta_C + \theta_B + \theta_V = 1$

$$\theta_V = \frac{1}{1 + K_A p_C + \frac{p_B}{K_D}}$$

$$-r_C = k_S (K_A p_C \theta_V - p_B p_P \theta_V / K_D K_S) = k_S K_A \theta_V (p_C - p_B p_P / K_A K_D K_S)$$

$$-r_C = \frac{k_S K_A \left(p_C - \frac{p_P p_B}{K_{eq}} \right)}{1 + K_A p_C + \frac{p_B}{K_D}}$$

Final rate law for Case-2, surface reaction controls

$S \rightarrow P + B$

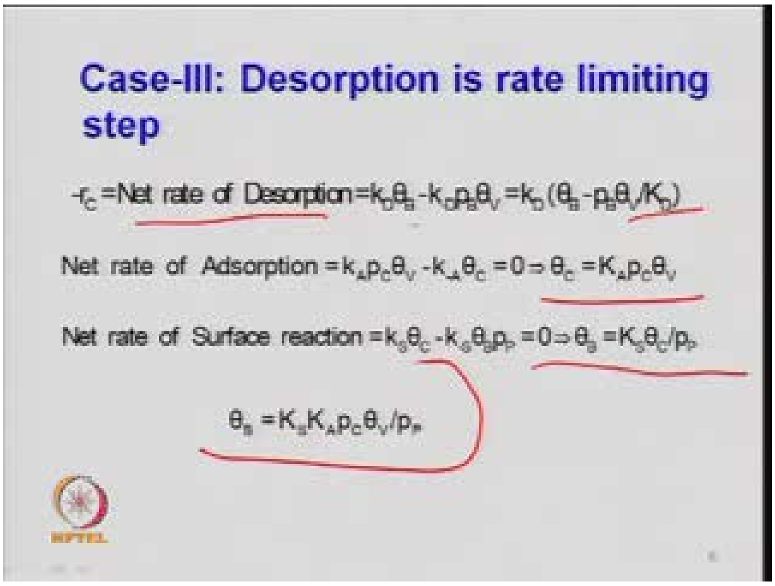
So, that is; what mentioned here that net rate of adsorption is 0 and you find theta C. So, theta C is K which is adsorption equilibrium constant for this reaction that is; rate of forward reaction is equal to rate of backward reaction. So, adsorption equilibrium constant, partial pressure of C times the concentration of the vacant side. Rate of desorption again because this is not a rate controlling step so again this is 0.So, 0 can calculate theta B which is partial pressure of Benzene times theta V divide by the equilibrium constant for the desorption of this reaction. So, now we can apply the site balance so, we have already done this so theta C plus theta B plus theta V is equal to 1. So, you can calculate theta V, from here because already theta C is calculated theta B is calculated. So, theta V which is the concentration of vacant side is depending on the partial pressure of the Cumene and partial pressure of the Benzene. So, 1 can see that if more concentration of these reactant species or the productive species is present in the reactor then, the there will be some drop in the concentration of the vacant side.

So, vacant side concentration is decreasing depending up on the partial pressure. So, substitute this value of theta V in your rate equation which is your surface reaction rate controlling right that we have already defined here so one can very easily find out the overall rate of reaction? So, this is the overall rate of reaction, net rate of reaction. So, minus K S which is already in this expression here; minus K S and substituted the value of theta C so, that expression is in the form of theta C. Now, converted in the form of theta V and the same thing for the 2 term of the equation. So, 1 can just take all these equilibrium constants say K S and K has been taken out theta V is again common so has been taken out so finally, in the bracket is some kind of the concentration difference. A difference which is the driving force for the reaction to happen right, or how for the reaction is away from equilibrium, when the concentration reached to the equilibrium composition there wont be any chemical reaction. And, this is the information which you get from Thermodynamics of this chemical reaction.

So, this is simply P C minus partial pressure of Benzene times partial pressure of Propylene divide by K A K D K S which is the adsorption equilibrium constant, desorption equilibrium constant and equilibrium constant for the surface reaction. So, this is the overall rate of reaction; and if this reaction is 0 suppose, then you say that the reaction is at equilibrium then this will be 0. And, if you write that then this term which is P C P B P P divide by P C. If I write that is adsorption equilibrium constant or sorry equilibrium constant, for the overall rate of reaction that is; what the k equilibrium? Because at equilibrium this driving force is 0 then the reaction raise to equilibrium this is 0. So, 1 can very easily calculate this K equilibrium for this reaction, because you know C is equal to pressure plus B. So, overall reaction is P plus B something like this: so, overall equilibrium constant is nothing but the partial pressure of P at equilibrium times partial pressure of B at equilibrium divide by the partial pressure of C at equilibrium and this is the term which is if you see here right.

So, that is; this term becomes your K equilibrium constant for the reaction. So, r c once you substitute the value of theta V also then this is K S times K A. And, in the bracket terms are P C minus P P P S divide by K equilibrium. Because theta V is a has already been calculated like this; so theta V is substituted here 1 up on 1 plus K A P C plus P B divided by K D. So, this equation is the overall rate of reaction, when surface reaction is rate controlling. And, I told you in most of the case these surface reaction controls the rate especially, in the Heterogeneous Catalytic Reaction.

(Refer Slide Time: 09:29)



Case-III: Desorption is rate limiting step

$-r_C$ = Net rate of Desorption $= k_D\theta_B - k_{-D}p_B\theta_V = k_D(\theta_B - p_B\theta_V/K_D)$

Net rate of Adsorption $= k_A p_C\theta_V - k_{-A}\theta_C = 0 \Rightarrow \theta_C = K_A p_C \theta_V$

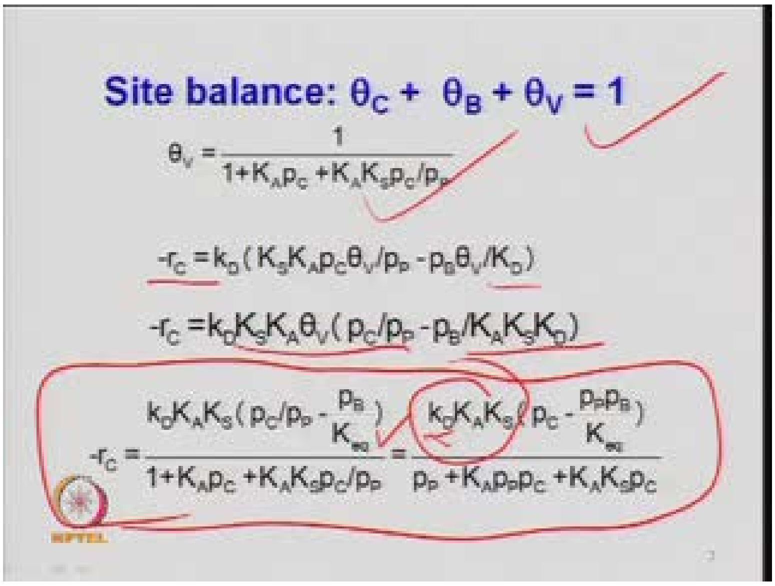
Net rate of Surface reaction $= k_S\theta_C - k_{-S}\theta_B p_P = 0 \Rightarrow \theta_B = K_S\theta_C/p_P$

$\theta_B = K_S K_A p_C \theta_V/p_P$

The 3 case may be the desorption is the rate controlling step so, I will quickly go to these steps because you know now the procedure. So, when desorption is rate controlling then net rate of desorption is equal to rate of forward reaction minus backward reaction. Rate of backward reaction; so, K D times theta B because Benzene is being disrobed, minus K minus D times partial pressure of Benzene times theta V. And, 1 can very easily write that expression, if you take K D out then this is; theta B minus P B theta V up on K D where K D is nothing but the rate constant for desorption, that is; K D is the forward reaction rate constant divide by the backward reaction rate constant. So, that is; what written here for the equilibrium constant for the desorption reaction.

So, net rate of adsorption we have already seen in the previous calculation. So, theta C is equal to this K A times K times P C times V. And, similarly, theta V is defined here and this is; again because this times the surface reaction is fast and at equilibrium in earlier case this was rate controlling so, net rate was determined based on this. But this time the 3rd step is the rate controlling this 1 net rate will be given by this. So, this will be fast and at equilibrium; so, 1 can very easily calculate form here, the theta B and this is your value of theta B.

(Refer Slide Time: 10:50)



Site balance: $\theta_C + \theta_B + \theta_V = 1$

$$\theta_V = \frac{1}{1+K_A p_C + K_A K_S p_C/p_P}$$

$$-r_C = k_D(K_S K_A p_C \theta_V/p_P - p_B \theta_V/K_D)$$

$$-r_C = k_D K_S K_A \theta_V (p_C/p_P - p_B/K_A K_S K_D)$$

$$-r_C = \frac{k_D K_A K_S (p_C/p_P - \frac{p_B}{K_{eq}})}{1+K_A p_C + K_A K_S p_C/p_P} = \frac{k_D K_A K_S (p_C - \frac{p_P p_B}{K_{eq}})}{p_P + K_A p_P p_C + K_A K_S p_C}$$

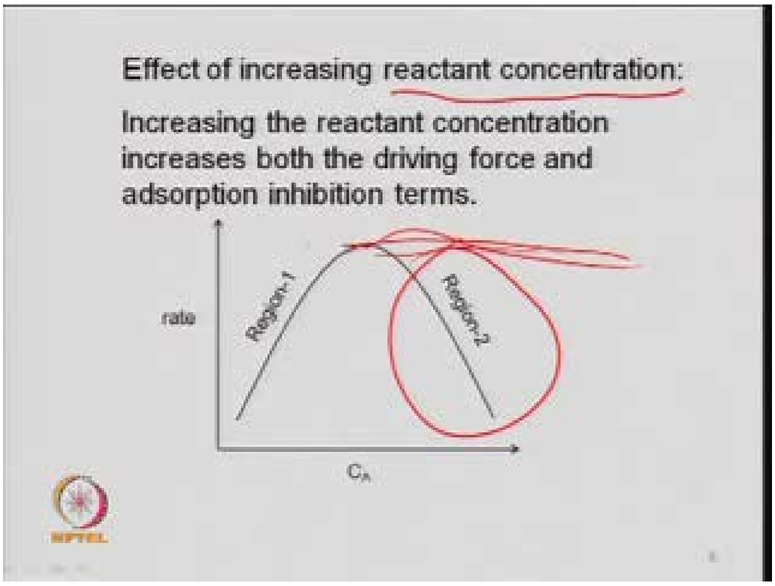
So, again site balance because you have to write a relationship among theta C theta B and theta V. So, which is the total fraction of the sites, which is some of this 1 sigma theta I, so, theta C plus theta B plus theta V that is equal to 1 right. So, 1 can calculate the concentration of the vacant site for this case also. So, vacant site concentration will change depending up on the rate determining step. If you have some inert in the reactant mixture then also the it will affect, if inert also adsorbs on the vacant site concentration then this will also appear in the denominator of the reaction. So, it means the presence of inert may affect the overall rate or overall kinetics of the reaction. So, 1 can very easily write now, our rate equation which is given in terms of the 3 step that is desorption K D times K S surface reaction equilibrium constant K A adsorption constant, P C and partial pressure, times theta V vacant site concentration divide by P P partial pressure of Propylene minus P B partial pressure of Benzene theta V concentration of the vacant site and divide by the adsorption desorption equilibrium constant.

So, minus r c can be written and theta V can be substituted here, which is given here in this rate and finally, this is the net rate of reaction when the desorption controls the rate. So, K D which is the kinetic constant for desorption, this is the rate constant. So, this is basically, a temperature dependent term in all cases when you have a small rate k that is deciding the rate of reaction as area function of temperature. The other terms are also depending on temperature but they are the heat of adsorption basically, how the heat of adsorption, heat of desorption changes with surface coverage. Because equilibrium constant is a function of temperature again. So, this is based on heat of adsorption term and this is based on the activation energy of the reaction that is; K D term temperature dependent C. So, this is K D times K A K S minus this is the driving force so, that is; temperature dependent term times the direct driving force which is P C minus P P P B up on K equilibrium which is written here in term this. Because this as I told when the reaction is at equilibrium overall reaction will be observed from the Thermodynamics that time this net rate is 0 right.

And, if you solve this just make it 0. And, you will have the same equation whatever we have discussed before that is; your partial pressure of the this P C up on P P minus P B divide by this is equal to 0. So, this will be your K equilibrium constant for the desorption reaction. So, 1 can very easily calculate that so that is; what written here directly P C up on P P minus P B up on k equilibrium. So, that is equilibrium constant for the desorption reaction. So, 1 can very do this but how the heat of reaction or delta h or effect of temperature on K equilibrium. 1 can very easily write it because this is a function of K A K S and K D. So, basically it will be delta h plus delta h s plus delta h d heat of adsorption of each terms, this is; from your because you know K is equal to delta minus delta h up on r t. So, that is; heat of adsorption for equilibrium constant. And, basically this is from the wont half equation right. Whereas, this k is from the Arrhenius equation K is equal to K 0, e to the power minus e up on r t. So, basically if I have 2 terms a k times the K means, the net heat effect if you take overall internal, overall activation energy it is something like e plus delta h right But you know that delta h is much low compared to e value. So, we neglect that and we just write in terms of e right.

So, depending up on the rate constant which is you that is what the kinetic term? Which I am talking here this is; a temperature dependent top here. And, this is the driving force that is the concentration dependent term. And, 3 is nothing but whatever the adsorption term which appears in the denominator of the reaction. And, that may hinder the overall rate of reaction.

(Refer Slide Time: 15:24)



Effect of increasing reactant concentration:

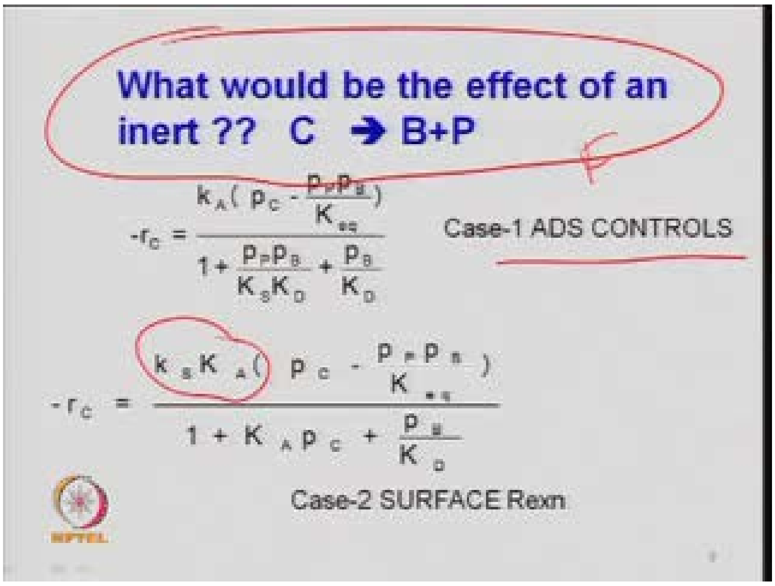
Increasing the reactant concentration increases both the driving force and adsorption inhibition terms.

So, it means now you have seen that, depending up on the term which is available in the denominator or that may hinder the rate of reaction. So, effect of increasing reactant concentration. So, that is the Cumene in this case. And, some time you can see the effect of product also. So, when you study experimentally, this thing then you can add some product concentration in the feed itself that is; say Propylene effect of partial pressure of Propylene say in this case effect of partial pressure of Benzene. So, in the feed along with feed you add some concentration of Propylene or Benzene and then again check the effect. Because the already is the Benzene is there now, it will adsorb on the surface. If it affects the reaction rate, if does not affect the rate partial pressure means, this will not whatever, the different concentration on Benzene that is; in the feed then overall rate will not change right.

So, 1 can postulate this mechanism and confirm them from the experimental result. Because based on this the experimental effect of each variable can be studied. And, that in this case the design of experiment how many experiments will be required to verify the mechanism? that becomes very important right. So, either you go with response surface methodology which is a kind of tool to optimize the number of parameters required or you do the design of experiment that is; factorial design where which says that, there are n number of experiment process variables then 2 to the power n will be the number of experiments required minimum number. So, 1 can decide the minimum range and maximum range of the variable experimental, variables effect of temperature effect of partial pressure concentration. So, all these can be studied by doing the design of experiment.

So, here you can see that increasing the reactant concentration, it increase the driving force and adsorption desorption term both term. So, what I am saying driving force is this term which is in the bracket P C minus P P P B divide by K equilibrium, for this 3 case where desorption is rate controlling. And, this denominator is representing the adsorption term. So, it means you will see that when you plot rate as a function of partial pressure or concentration of a then initially it increase and then finally, it decrease. So, you will have 2 regions in this case right.

(Refer Slide Time: 17:46)



What would be the effect of an inert ?? C ➔ B+P

$$-r_C = \frac{k_A\left(p_C - \frac{p_P p_B}{K_{eq}}\right)}{1 + \frac{p_P p_B}{K_S K_D} + \frac{p_B}{K_D}}$$

Case-1 ADS CONTROLS

$$-r_C = \frac{k_S K_A\left(p_C - \frac{p_P p_B}{K_{eq}}\right)}{1 + K_A p_C + \frac{p_B}{K_D}}$$

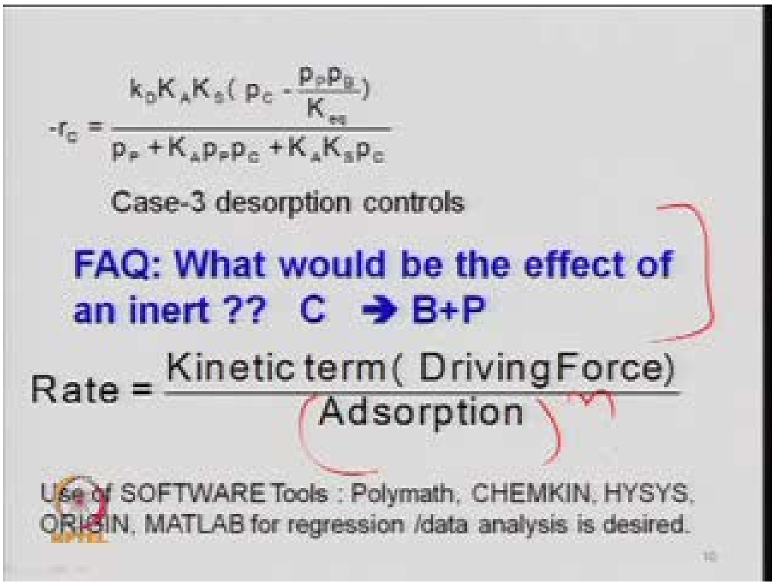
Case-2 SURFACE Rexn

So, that is; what because of these terms which is shown here in the earlier section, because of this term here partial pressure? Because if I just look at effect of partial pressure of each species. So, P C here so, increase the partial pressure of C. So, initially rate will increase depending up on the contribution of this P P and P C right. So, accordingly the rate will change because during the reaction if you have a kind of integral reactor or a commercial reactor then P P Propylene is also forming during the reaction. So, this is also you can see here, that it may hinder the rate of reaction so, what would be the effect of an inert? That is; a just I have left for thought. So, you just write suppose there is inert also. And, adsorbs on the surface then 1 can write the rate expression for that so, rate of adsorption of inert that is something like that, if the reaction is something like this; C is P plus B. And, then you have written the mechanism and suppose Nitrogen is added along with this feed right.

So, basically Nitrogen is not a reactant but, the presence of nitrogen the partial pressure of Nitrogen can be studied it may not adsorbed. So, if it adsorbed then the mechanism will be different Nitrogen plus star Nitrogen star and finally, desorbs. So,1 can very easily write down the step so, if it appears in the denominator of the rate equation or if you see that the effect of partial pressure of Nitrogen, hinders the rate of reaction then it means; the nitrogen is also adsorbing it has some effect at different partial pressure of nitrogen the net rate of reaction does not change it means the presence of inert has now roll right. So, this and it is not only for the inert. But some time for an element like poison precursor. The different Deactivation kinetic models have been developed by understanding this mechanism that is; if sulphur precursor is present in the feed stock it adsorbs, on the surface of the catalyst right. So, it will be a kind of C P poison precursor now, on this available sides will be less. So, when the sides are less your theta V is low and then finally, your rate which is proportional to the theta V also so, it will decrease. So, this is what the you have, I just written as a thought that look at that and a kind of f a quick and this is the question which is asked here.

So, basically when adsorption is rate controlling we have already seen minus r C. So, which is K A rate constant for the adsorption reaction times P C minus P P P B up on K equilibrium? So, this expression you have already seen divide by the denominator which is, the adsorption inception term and are reported in the form of partial pressure of Propylene Benzene and Benzene partial pressure right. So, this is first 1 and for surface reaction the rate is depend representing like this; something which is again here if you look at the driving force it remains here same. And, the denominator term is different and simultaneously, this term which is the kinetic term that also changes right. So, here the it is just activation energy of the first that is e a here, it is activation energy plus heat of adsorption. So, e a plus delta h a heat of adsorption that is the temperature dependent term.

(Refer Slide Time: 21:08)



$$-r_C = \frac{k_D K_A K_S \left(p_C - \frac{p_P p_B}{K_{eq}} \right)}{p_P + K_A p_P p_C + K_A K_S p_C}$$

Case-3 desorption controls

FAQ: What would be the effect of an inert ?? C ➔ B+P

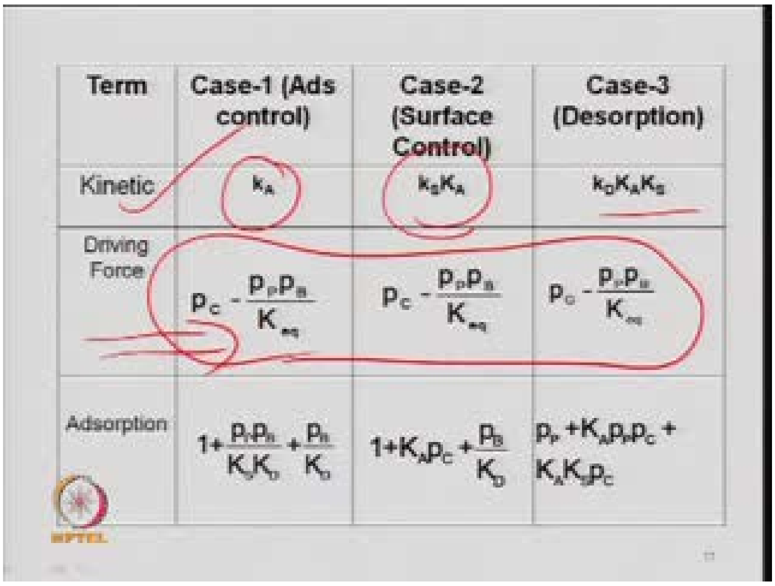
$$\text{Rate} = \frac{\text{Kinetic term(DrivingForce)}}{\left(\text{Adsorption}\right)^{n}}$$

Use of SOFTWARE Tools : Polymath, CHEMKIN, HYSYS, ORIGIN, MATLAB for regression /data analysis is desired.

And, if it is desorption then it is again the E D that is; desorption kinetic rate catalyst plus the delta h A and plus delta h S. So, 1 can postulate this kind of that is verify these models. So, model 1 model 2 model 3 and then, looks at the rate data and then, find redress the data. And, 1 can look at that which stuff is more suitably controlling the rate or guiding the mechanism. So, again 1 can see that effect of inert which I have already said last time. So, in general the rate is given by a kinetic term, times the Driving Force that is the difference of concentration and divide by the Adsorption term. And, sometime this may be written Adsorption term to the power N also, because in this case, if you see the denominator is the just the power is 1. But it can be 2 also it can be, 3 also, and when you see this kind of reaction rate, so, the power is not 1 rather it may be 2 or 3 also depending up on this drop because otherwise, if the power is 1 it will go just like a platu a constant line.

But when it decrease it means; the denominator has more role or the adsorption emotion term is dominating at higher concentration of the reactant species. So, that is important here in terms of that in a any Langmuir himself the type mechanism or any little type mechanism. The rate is given by a kinetic term, times the driving force divide by the adsorption term. And 1 can use the softwares like polymath is 1 software tool which is available for kinetics study. Chemkin, Hysys, origin Mat lab. So, they are used for data analysis or regressing the data, and that can be attached to some optimization tool also optimization package. And, then 1 can find out the optimal parameters for the reaction and which will be important for the designs. So, Alpine plus can also be used for that purpose right. When you scale up the reactors so, these kind of tools software tools or application tools can be used for the rate parameter stimulation or design of a kinetic reactor.

(Refer Slide Time: 23:26)



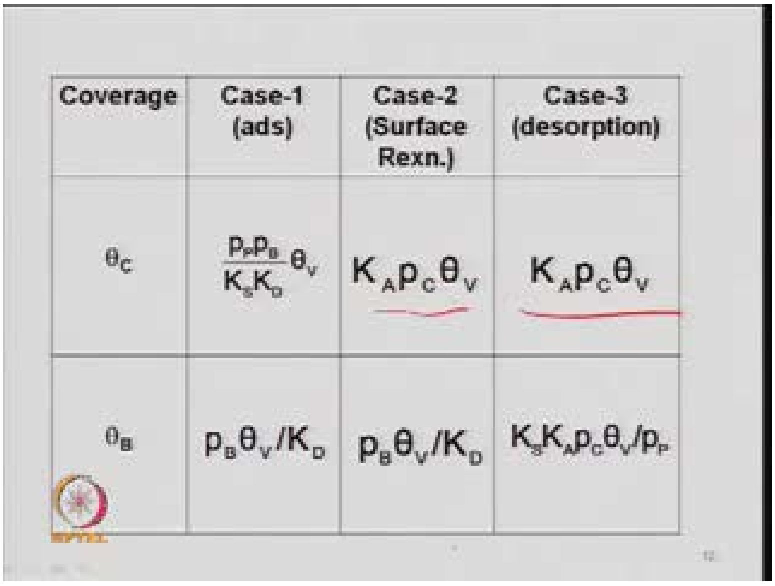
Term	Case-1 (Ads control)	Case-2 (Surface Control)	Case-3 (Desorption)
Kinetic	k_A	$k_S K_A$	$k_D K_A K_S$
Driving Force	$p_C - \frac{p_P p_B}{K_{eq}}$	$p_C - \frac{p_P p_B}{K_{eq}}$	$p_C - \frac{p_P p_B}{K_{eq}}$
Adsorption	$1 + \frac{p_P p_B}{K_S K_D} + \frac{p_B}{K_D}$	$1 + K_A p_C + \frac{p_B}{K_D}$	$p_P + K_A p_P p_C +$ $K_A K_S p_C$

So, we have already seen the data now, so kinetic terms which are K A K S K A as I told the temperature dependence. The kinetic means, the term which depends on the temperature rate. So, the temperature dependency so, based on arrow Arrhenius equation or the active how the heat of reaction? Or how the equilibrium constant changes with the temperature? That is basically, in terms of delta h g top adsorption right. So, K S K and for desorption K D times K A K S for this reaction driving force that is; depending on the difference of the constituents. So, P C minus P P P B up on K equilibrium P C minus P P P B up on K equilibrium, and this is again same.

So, when the reaction is at equilibrium net rate of reaction is 0. So, this is; what the definition of the thermo, this you get from the Thermodynamics. So, effect of temperature on these product distribution that can be change. If you change the temperature the Thermodynamic results will change. And, 1 can just find out the optimum conditions depending up on the Thermodynamics of the reaction and the kinetics of the reaction. So, that 1 can see that 1 important Thermodynamics is that, gives you the idea whether a reaction is possible or not, as I discussed in the beginning right. And, simultaneously, the maximum extent of the reaction is also governed by the Thermodynamics of the reaction. So, equilibrium conversions suppose 60% at a given temperature it cannot be change, by changing the catalyst. So, catalyst cannot do that job, catalyst can only enhance these terms that is; kinetics towards that. So, the activation energy of the reaction may be lowered in the presence of catalyst. For change in the catalyst you can do the adsorption better even at a lower temperature but the maximum limit cannot be changed which is governed by this term right. So, at equilibrium this term is 0. Rate forward reaction is equal to rate of backward reaction.

Adsorption term again which is kind of inception term and will appear in the denominator. So, that can also for this reaction the difference you can see, for different cases the parameters are different or adsorption value. So, for 1 can postulate the mechanism developed the rate equation for different condition or set of the rate determining step. And, then do the model that is analysis that is model discrimination and parameter analysis or estimation.

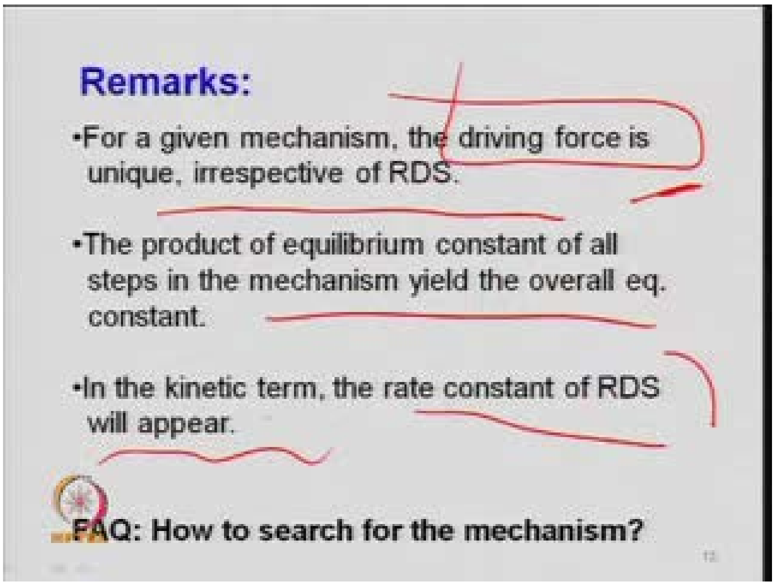
(Refer Time Slide: 26:03)



Coverage	Case-1 (ads)	Case-2 (Surface Rexn.)	Case-3 (desorption)
θ_C	$\frac{p_P p_B}{K_S K_D} \theta_V$	$K_A p_C \theta_V$	$K_A p_C \theta_V$
θ_B	$p_B \theta_V / K_D$	$p_B \theta_V / K_D$	$K_S K_A p_C \theta_V / p_P$

Same thing for coverage theta C that is; the fraction of the surface which is covered by Cumene. 1 can calculate in which is depending on the partial pressure of the Propylene, Benzene and the concentration of the vacant site divide by K S K D. Surface reaction case it is this and for desorption case it is this. So, this is just analysis for1 typical set of data which is for Cumene reaction we have given and that say for, different reaction to reaction these will change correct. And, 1 has to identify same thing for Benzene also, 1 can see that for adsorption step, for surface reaction and for desorption right. So, 1 has to define this depending up on the reaction and rate controlling step that how the coverage change for a given reactant species or a productive species?

(Refer Slide Time: 26:53)



Remarks:

- For a given mechanism, the driving force is unique, irrespective of RDS.
- The product of equilibrium constant of all steps in the mechanism yield the overall eq. constant.
- In the kinetic term, the rate constant of RDS will appear.

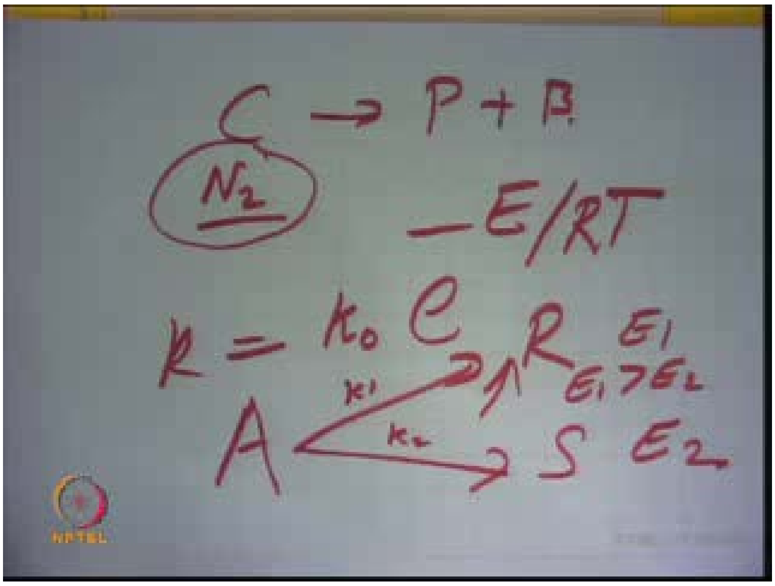
FAQ: How to search for the mechanism?

So, what we have inferred from this, the analysis whatever the mechanism revising a mechanism which is basically, to design a reactor or evaluate the rate data and finally, decide a rate of reaction. So, the comments which can be made now, that for a given mechanism the driving force is very important it is a unique, right. You have seen that this is; the driving force the other terms whatever the RDS the terms are changing here in the nominator, denominator in terms of the kinetics and the adsorption. But this does not change, the driving force is the unique for a given reaction and that is what I said is govern by the thermodynamics. So, thermodynamics plays a very important role whether a reaction is possible or not. So, this is irrespective of RDS the driving force does not change right.

The second is the product of equilibrium constant; of all step in the mechanism yield the overall equilibrium constant. So, as I said that overall equilibrium constant is what you will decide from this. Now, you have just written here; the equilibrium constant something like whatever the rate expression this term; at equilibrium this rate is 0. And, then you decide the overall equilibrium constant right. So, overall equilibrium constant will depend on the adsorption, desorption and surface reaction equilibrium rate constant right. And, that what we have seen; when you calculate the overall equilibrium constant you set this term 0. Because that is the meaning of equilibrium right; and that is what the meaning here is that the equilibrium constant product of equilibrium constant of all step in the mechanism yield the overall equilibrium constant. So, whatever the equilibrium constant for a usual steps that is to check; and that will give you the overall equilibrium constant.

So, adsorption, desorption, surface reaction and that will give you the idea about the equilibrium constant; that we have seen form the mechanism. Kinetic term if you look at the rate constant of rate determining step will appear right. So, the kinetic term this one; so which is the rate which one is the rate determining rate controlling step right its that will come here. So, here you see the rate constant for a adsorption step has come, here the rate constant for surface reaction is come here, the rate constant for desorption is come. So, it means this step if this is rate controlling as I how already said that the kinetics is something which is giving you rate constant is equal to some pre exponential factor times e to the power minus e up on R T.

(Refer Slide Time: 29:48)

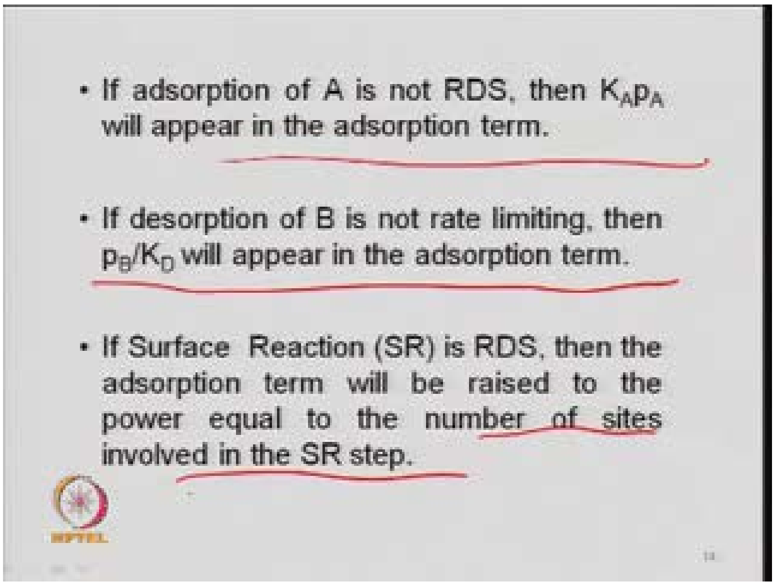


And, when I am writing this step suppose if you must have learned this is for multiple reaction goes like this r plus s right; then this may have a rate constant k 1; this may have a rate constant k 2. And, the temperature dependency will decide if I say that activation energy for this as E 1 and activation energy for this reaction E 2 and E 1 is greater than 2 right. So, the if E 1 is greater than E 2 suppose; then if you increase the temperature then reaction will shift towards this side right.

Because high temperature favors the reaction of higher activation energy right. So, that is important. So, same case is been done here when I say the step is a rate controlling. Rate controlling means that is the slowest step of the reaction. So, slowest step means it reaches either high temperature right to activate a reaction or activation energy is high. So, the reaction is low activation energy when it be done at a lower.

So, that is what the meaning here. So, the rate controlling step whatever the step rate control a kinetics of that will appear here. Because the second step rate constant is very high compared to the other this is the slowest step k a; when a this step is rate controlling say adsorption is rate controlling. It means it is a rate constant order is 0.001 suppose right; where as its rate constant is order may be 10 and its rate constant order may be 100 right. So, slowest rate constant is this; so this is a rate governing step right. Because rate is controlled by the slowest step the reaction; whenever its k is low it means that the rate will be low and that will be rate control.

(Refer Slide Time: 31:13)



- If adsorption of A is not RDS, then $K_A p_A$ will appear in the adsorption term.
- If desorption of B is not rate limiting, then p_B/K_D will appear in the adsorption term.
- If Surface Reaction (SR) is RDS, then the adsorption term will be raised to the power equal to the number of sites involved in the SR step.

So, this is the postulation; what we have discussed here K A P A will not appear in the adsorption term if A is not a rate determine step; that I think let me just go here if I in the kinetic term that the rate constant of RDS will appear. So, that we have seen. So, again how to search a mechanism that you have to do with different case to case, select different reactions right. And, just for practice you can try defined the mechanism and then determine the overall rate. And, that will give you more and more understanding about this mechanism and determining the rate equation for different rate controlling step. So, some comments again here if adsorption of A is not determining not RDS rate determining step then K A P A will appear in the adsorption term; that is what we have seen that the step which is not the rate determining term; that adsorption of A is not RDS. So, it means this K A P A will appear in the adsorption term which is in the denominator right.

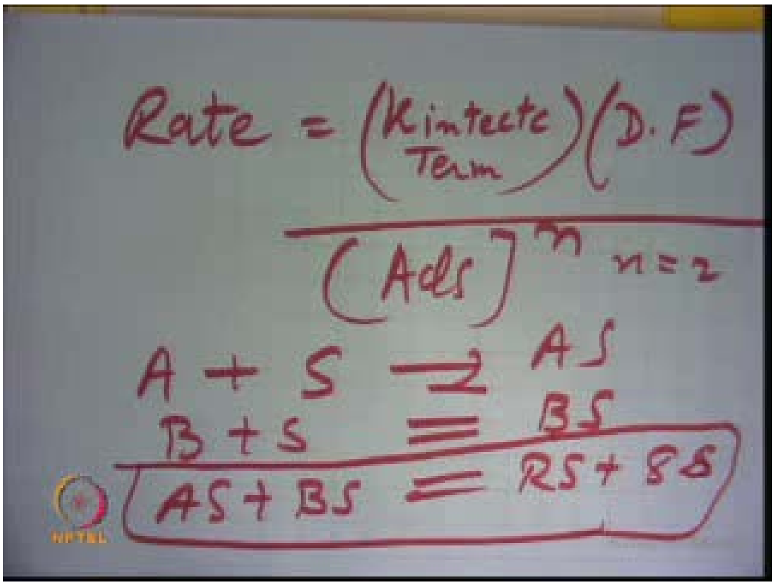
And, that we have already seen here that the denominator term here. So, adsorption terms this adsorption control. So, this appear this K P has not come here because a adsorption of a is rate controlling. Here, surface reaction has not come in the denominator K s here; this term has appeared in the denominator which is desorption. So, what does it mean that the step which is rate controlling will not appear; in the its term will not appear in the denominator.

So, that is at RDS step will sorry then K A P A if this is not rate determine; then it will appear in the denominator. If it is not R D it R D S then it will not appear in the denominator right; that is what the interpretation which I made. And, if desorption of B is not rate limiting right. If B is not rate controlling step then P B up on K D will appear in the adsorption term. So, the that is what the some postulation which we have defined here right; the term which are appearing in the denominator. So, that is the second case surface reaction right; is the rate controlling it means desorption of B is not rate controlling right. So, that term has arrived here.

So, this is again the observation which has been made from this that B is not the rate limiting desorption of B. Then, P B up on K D appear in the adsorption term; denominator of the adsorption; that is a reaction a surface reaction is rate determining. Then, adsorption term will be raised to the power equal to number of sites involved in the surface reaction step; and this is what I was talking here to the power n. So, what are the number of reactant species; which are involved right which involved in the surface reaction rate controlling their number will appear here. So, in that case only 1 reactant here. Suppose 2 reactants suppose if i write A S plus B as gives you r r plus s. So, 2 sites are involved now right and rate will be the concentration of this A and B right A S plus B S. So, these will go square term here.

So, that is the meaning of this term that in kinetic term the surface reaction is RDS rate determining step. Then, adsorption term will be raised to the power equal to the number of sites involved in the surface reaction step. So, A plus B; if I write it dual mechanism then also dual site mechanism, then also the power will come to like that.

(Refer Slide Time: 34:52)



$$\text{Rate} = \frac{(\text{Kintectc Term})(\text{D.F})}{(\text{Ads})^{n}} \quad n = 2$$

$$A + S \rightleftharpoons AS$$

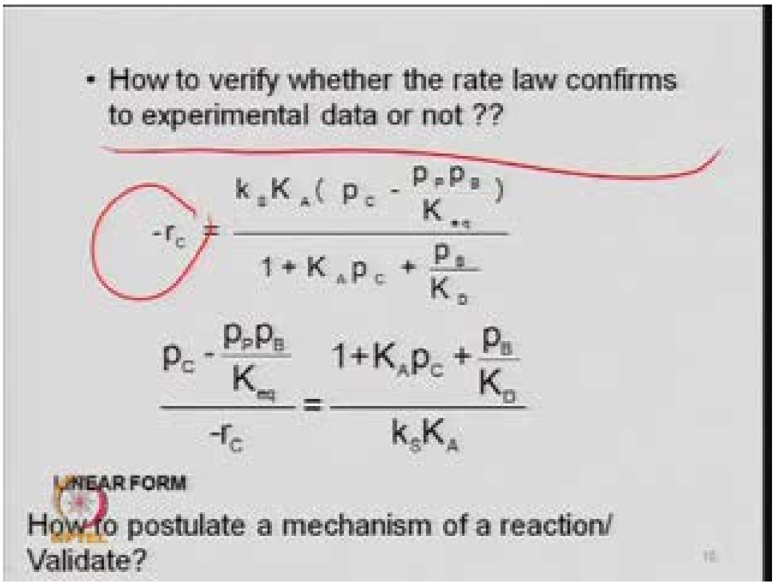
$$B + S \rightleftharpoons BS$$

$$\boxed{AS + BS \rightleftharpoons RS + SS}$$

So, basically if this adsorption that is rate is equal to kinetic term times the driving force; which we have already discussed divide by adsorption term to the power n. So, that is the value of this suppose the surface session it controls. So, depending up on that if you write that A plus S gives you A S and B plus S gives you B S. And, then A S plus B S gives you some product species which is adsorbed R S plus S S something like this right. Then, this if this is the rate controlling this is your surface reaction step; then you will have a denominator n is equal to 2. So, this is the meaning of this step right.

So, there the rate drop will be faster that is when the this adsorption this step is rate controlling based adsorption desorption surface reaction. Then, you will have a faster drop at higher concentration, higher pressure of these 2 species which is shown here in the region 2. Because this shows that the drop is much faster and this simply says that it is a kind of a tool site or tool species are reacting. And, that step is the rate controlling or forming the product.

(Refer Slide Time: 36:20)



- How to verify whether the rate law confirms to experimental data or not ??

$$-r_C = \frac{k_S K_A \left(p_C - \frac{p_P p_B}{K_{eq}} \right)}{1 + K_A p_C + \frac{p_B}{K_D}}$$

$$\frac{p_C - \frac{p_P p_B}{K_{eq}}}{-r_C} = \frac{1+K_A p_C + \frac{p_B}{K_D}}{k_S K_A}$$

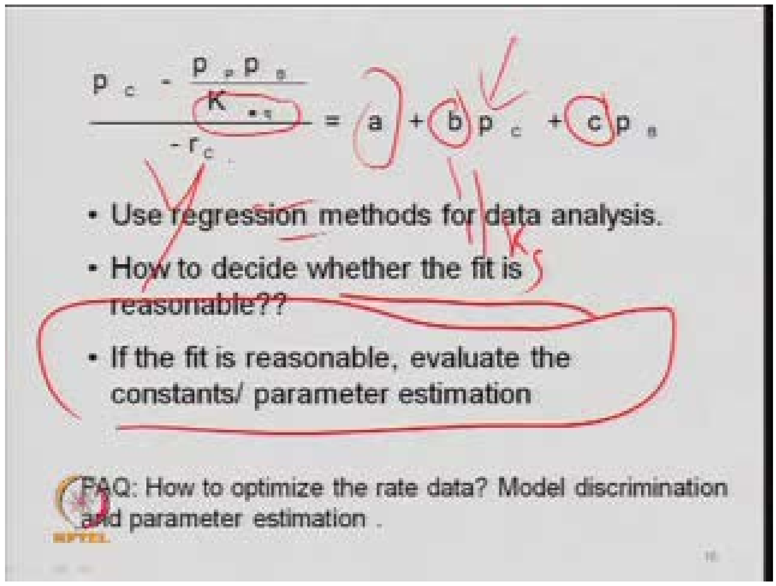
LINEAR FORM

How to postulate a mechanism of a reaction/ Validate?

So, this is what we have postulated from this here; that the term will appear in the denominator and its power will be raised by that number. So how to verify whether the rate law confirm the experimental data or not right. As I said you need to do that the design of experiment first; identify the number of variables. And, to understand what should be the range of these experimental conditions right find out some optimum conditions right up to these experiments can be carried out further. So, design of experiment or factorial method will help you in that way. So, rate of reaction I said that it is given by something like this. So, from experimental data you have read certain analysis; effect of partial pressure of each component, temperature effect, space time effect right and then you measured this rate right.

Now, this rate is to be verified from your experimental data because this is simulated data, theoretical data analysis. Now, you have just linearised this is one method of this linear regression what you call right linear or non-linear if this method when you just R is equal to K P to the power n. So, you can analyze the data non by non-linear regression method also just take all these combined R A is equal to K P to the power n right. But if I take R A log of this R A is equal to log of k plus n log p. So, that is a linear regression method right. So, in that case it is expected that you are getting a line you is equal to a 0 plus a 1 x 1 plus a 2 x 2 and so on. So, on right so you have lineraize the equation. So, same thing something like here. So, this if you rewrite this equation that can be P C minus P P P B divide by K equilibrium and divide by this r c right. And, that site you have the term which is your one plus K P C plus P B this divide by this.

(Refer Slide Time: 38:21)



$$\frac{p_C - \frac{p_A p_B}{K_{eq}}}{-r_C} = a + b\,p_C + c\,p_B$$

y

K_S

- Use regression methods for data analysis.
- How to decide whether the fit is reasonable??
- If the fit is reasonable, evaluate the constants/ parameter estimation

FAQ: How to optimize the rate data? Model discrimination and parameter estimation .

So, now this is a kind of equation which is in the linear form of this right and that is shown here just like this y left hand side is 0; y now which is here. And, that is equal to some constant which is because of this term 1 up on K A. Now, I have spitted it like this 1 upon K A plus K A PC upon K S KA. So, cancels K A K A and third one is P B upon K S K A K D. So, it is something like equation in the linear form right. Because what is your list square method? You are just calculating the some error function that is your objective function which you have defined right. And, you are minimizing the error between experimental and the theoretical value right. So, and then you are just taking sigma for all number of data right and try to minimize the error. And, where you get the minimum error or among all the set of data which you are taken using that; and you can analyze the data and you can report the value of the parameter.

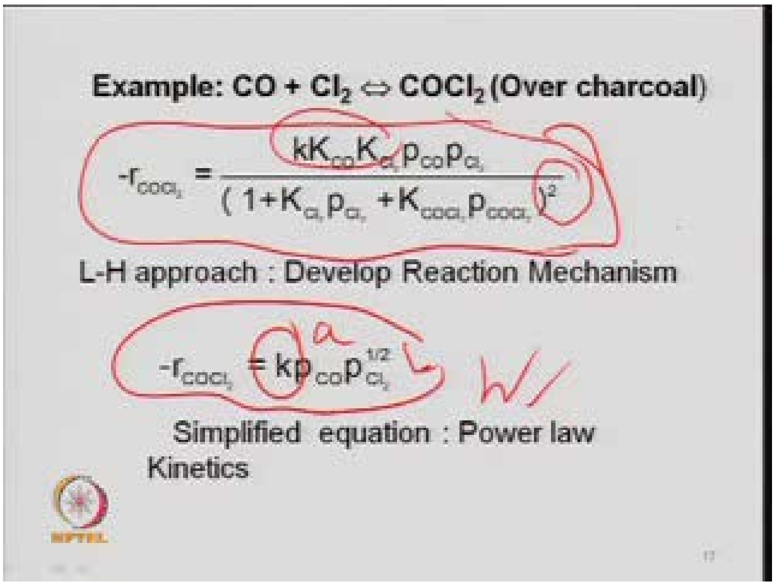
So, this is what has been done in the linear regression method. So, this is what you a kind of you and this is you are a plus b P c plus P b. So, how to do the experiment now? You have to change the partial pressure of c right keeping this constant; same thing at different partial pressure c you will have data in terms of rate right. And, same thing second set you change the partial pressure of b and then keep this constant; and then again measure the rate. So, you can rate can be measured experimentally, observed experimentally and these are known partial pressure. And, all the stuff and this is your thermodynamic equilibrium constant. So, that you can find from the or calculate from the thermodynamics of the reaction right. So, every term is known in the form of you is equal to this these are the parameters a b c; these are the parameters of the reaction. And, what are these parameters; all of you know now because 1 upon K S k is your a right; one parameter.

Similarly, K upon K S A is the second parameter. So, it is basically 1 upon K S is your so your if you do this. So, your b is simply 1 upon K S right here. So, and then third one is your one upon K D K S K A right. So, 3 that is the total parameter if you look at these are K A K S K D; right and this can be determine experimentally by selecting the parameter conditions. So, that has been here and once you do that; then you use the regression method as I said use the any software tool right or one you can do analytically also depending up on the number of data available. So, but now a days the software tools are available; so matlab like as I said origin. So, one can do this these kind of regression; and thermodynamic analysis can also be done using this hysis software tools which are available right.

So, now a day not difficult. So, one can regress the data and how to analyze this right how to decide the feet whether it is reasonable or not that you have to define some confidence limit right or say you decide some 95 percent confidence of that? What about data if all the data fit to that 95 percent confidence. So, that is correct; if it comes to 90 percent you have to generate further data or develop a some change in the mechanism; which can postulate more to these experimental set of data. So, if the fit is reasonable then evaluate the constants and the parameters of that is reaction parameter. So, this is how the kinetics is done or kinetic data for a catalytic or even non catalytic reaction is studied. So, you know the differential method of analysis; you know integral method of analysis for calculation rate of rates.

So, the similar approach is being used once you have the mechanism. And, these kind of data then r a can be calculated from those differential method or integral method of analysis which I will talk little later very briefly. So, again how to optimize rate data? So, one need to understand about that right; how to analyze a model. And, discriminate that right model discrimination we have this decided say adsorption rate controlling, desorption rate controlling, surface reaction and even in the steps of the reaction it may be changing right. So, you can have 1, 2, 3, 4, 5, 6 and so may be and number of models right. But ultimately you have to use that that is discriminate the model where the error which is the most suitable or most theoretically fitting to your experimental data. And, also verifying from the thermodynamics or the kinetics of the reaction and then you decide the parameter of that reaction.

(Refer Slide Time: 43:06)



Example: $CO + Cl_2 \Leftrightarrow COCl_2$ (Over charcoal)

$$-r_{COCl_2} = \frac{kK_{CO}K_{Cl_2}p_{CO}p_{Cl_2}}{(1+K_{Cl_2}p_{Cl_2}+K_{COCl_2}p_{COCl_2})^2}$$

L-H approach : Develop Reaction Mechanism

$$-r_{COCl_2} = kp_{CO}p_{Cl_2}^{1/2}$$

Simplified equation : Power law Kinetics

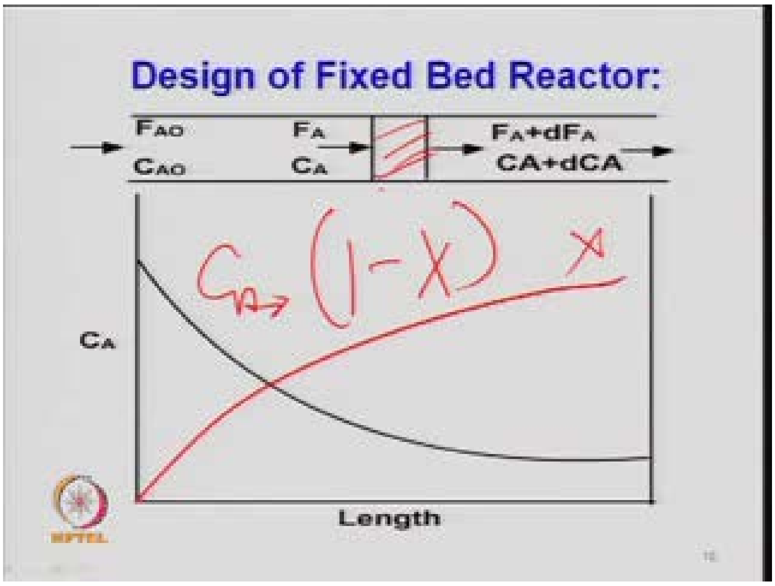
So, just as an example I have just left it here to for your understanding one can do that. So, the suppose the rate of reaction this is for the C O C l 2 right fortune gas which is formed by right which carbon monoxide and chlorine and carbonyl chloride is formed right. And, the rate of reaction which has been postulated and verified also is something like this type of. So, here you can see that this a square term here in the denominator. So, as I said that if first one can start with surface reaction as the rate controlling. So, here you have to say c o is adsorbing and then chlorine is adsorbing on the surface. And, then these two adsorbed species are reacting and forming this adsorbed species right. And, this adsorbed species finally desorbs. So, this can be one mechanism right; so adsorption of this then adsorption of this and then these two adsorbed species are reacting and transforming into one adsorbing species and one vacant site. And, then this vacant this C O C l 2 star finally desorbs to C O C l 2 and star right. So, adsorption, desorption, surface reaction and as I said most of the heterogeneous reaction if adsorption is not controlling. Then, possibility is that this is controlled by the surface reaction.

So, surface reaction one can also confirm here because this is what the square right. So, C O C l 2 star plus C O star plus C l 2 star is giving a C O C l 2star plus this star right. So, that may be a kind of surface reaction which may be rate controlling right. So, one can very easily write the rate equations and then finally check whether it is matching or not right. So, this is just for exercise and sometimes you write this simple power law model also. Because understanding a mechanism needs lot of surface characterization as I talked micro kinetic model right. And, then you have to look at surface characterization I r spectra, proton in a NMR spectra just to look at whether this star is species adsorbed during the reaction or not whether it is possible or not TPR is one right, TPD is another. So, TPR, TPD can be done.

So, by these information so this C O is taken on some catalyst this charcoal and you will feel that C O is adsorbing on that right. So, that confirms that your C O will adsorbed over charcoal under these conditions of temperature right and same thing for chlorine. So, one can very easily check by doing the TPD whether this is happening or not experimentally whatever you have postulated right. So, one can look at that. And, sometimes if you do not need these kind details to understand the what is going on in the reaction. Then, a simple problem order can be used right although not very correct in the heterogeneous catalytic point of view. But just one can co relate because this value of k will be different then this will now. So, this is some kind of overall rate constant which is a combination which can be a combination of this like.

And, here again we have written in terms of the partial pressure of chlorine and partial pressure of carbon monoxide. So, it just a someone can write it simply P a to the power a n P c l 2 to the power b. And find out a, b and k right y by linear regression or non-linear. But this is a just a this is true only for homogenous reaction kinetics not for heterogeneous reaction kinetics. So, actual mechanism cannot be understood from this one right. But is the data are not available, the soft ware tools are not available, time is limited then one can use this also. And, then one can find out the total mass of the catalyst required right for a given in this reaction.

(Refer Slide Time: 46:47)

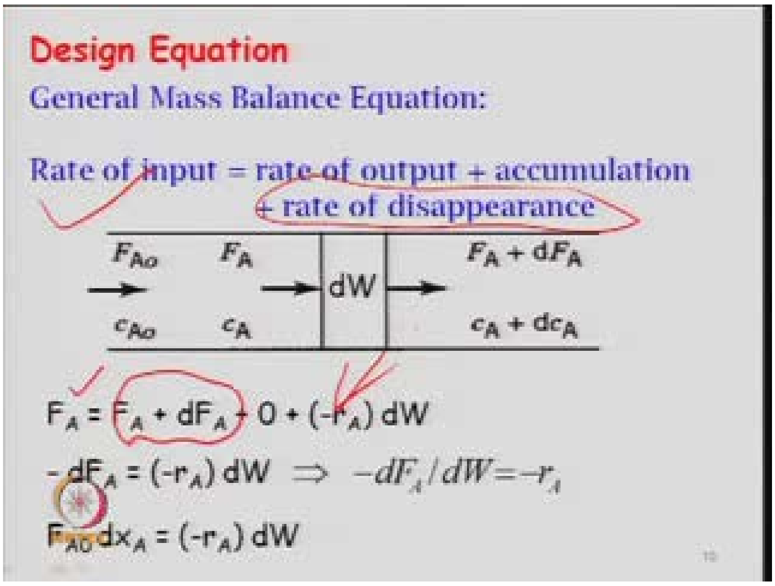

Design of Fixed Bed Reactor:

So, designing of a fixed bed reactor if you what whatever the that kinetic data you have provide obtained right or exponential data you generated. And, then you evaluated the rate parameter. So, one can use that. So, because the minus r a is known rate of reaction is now defined. And, then one can look at the sizing the reactor or the mass of catalyst required for a given conversion. So, that is what the meaning of design of a fixed bed reactor now right I am talking right.

So, I have already talked this part that you have a differential basically here when you look at the log scale delta. So, generally preferred one is the differential reactor. And, I told you that the theoretically if you look at the conversion should be less than 10 percent that is the definition of this persinator. So, we should have a small diameter reactor with small particle size and maintain the plug flow condition in side that. So, that is the neglect the HCL and the radial dispersion. So, by selecting this reactor size, particle size right and high velocity of the gas that is F A one can control this. So, once you have that information right or you have just selected a rector and the experimental condition. And, you know that when the conversion is taking place; then C A will decrease down the length right C A is the concentration of the reactant species right.

Which is basically if there is constant volume in the system? Then, it is C A naught 1 minus x A just for a constant volume you know that C A is equal to C A naught 1 minus x right; where x is the fractional conversion. So, it means if I write the data in terms of conversion it will go like this. So, this is your conversion as a function of length of the reactor.

(Refer Slide Time: 48:26)



Design Equation

General Mass Balance Equation:

Rate of input = rate of output + accumulation + rate of disappearance

$$F_A = F_A + dF_A + 0 + (-r_A)\,dW$$

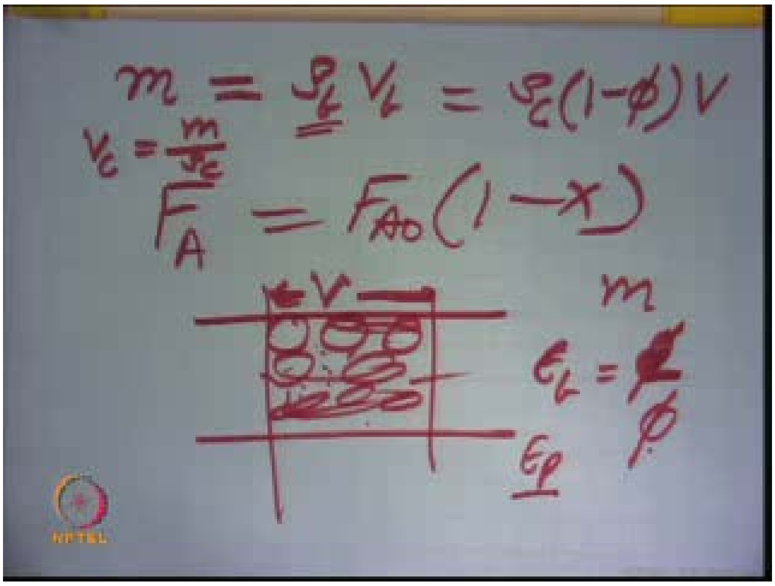
$$-dF_A = (-r_A)\,dW \Rightarrow -dF_A/dW = -r_A$$

$$F_{A0}\,dx_A = (-r_A)\,dW$$

A metal valence part I have discussed earlier also just quickly I will go here. And, all of you must be knowing now that the for a differential section; your material balance equation is something like that rate of input is equal to rate of output plus the disappearance. Because of chemical reaction and plus the accumulation in the reactor right. So, for a differential section input minus output minus disappearance. Because of chemical reaction is equal to rate of accumulation that is what the definition or any reactor design or any system right you are writing a metal balance. Input at any section as I said before earlier also F A at this section F A and output is F A plus d F A here this is your output right rate of output accumulation we are assuming a steady state. Because the time you have to check when the conditions are not changing with time. And, that is the steady state condition; the variation in property with respect to time is 0. So, that is 0 here; and the rate of disappearance what I have written here that will depend on suppose rate equation minus r A is the disappearance. And, this is defined based on per unit mass of the catalyst rate of reaction can be defined in either many ways.

So, in the heterogeneous reaction generally the moles reacted per unit time per gram of catalyst or mass which is reacted per unit time per gram of catalyst. So, either of the units can be used or definitions can be used then minus r A here it is per unit mass. So, multiplied by the mass of catalyst. So, this is the total moles which are disappeared in this zone. So, one can write down expression because this cancels so minus d F A is equal to minus r A times d W from this equation. And, equation will come minus F A by d W is equal to minus r A; if you integrate this equation. Because F A is changing on the length right d W is changing down the length.

(Refer Slide Time: 50:53)



So, your equation in general is F A naught because F A you knows the moles F S is equals to F A naught 1 minus x; that is input F A naught minus F A naught x A which is the moles reacted right. So, at any point this is the moles present. So, F A is the moles which are present at any point here say z is equal to 0 or z is equal to z plus delta z whatever right. So, this had been written now in the form of F A naught 1 minus x A. So, equation gives you F A naught d x A right and that is equal to minus r A times d W. So, this is the differential form of reaction and minus r A dash sometimes we write here; which is the representing that rate has been defined per unit mass of the catalyst. In homogenous you define rate per unit volume of the reactor right; here it is per unit mass of the catalyst right. And, based on that one can define because mass of catalyst is related to the volume of the reactor. And, times the why this T of the of the bed, right. So, catalyst bed density sometimes we call it right.

So, volume of catalyst multiplied by the bed density right and bed density will be catalyst density into 1 minus the white fraction of the bed. So, one can very easily define this density of the catalyst that is as I discussed earlier. And, based on the bed volume right when you are calculating mass of the catalyst which is given in a bed. So, volume will increase because there are white between the particles. Now, that is bed white fraction I am talking right. So, 1 minus epsilon b; if epsilon b is the bed fraction white fraction of the bed. So, 1 minus epsilon b is the solid fraction the right that is the catalyst which is present. So, and if I define my density which is based on the mass of the catalyst divide by the volume of bed this is the bulk density of the catalyst. So, this term should be very clear to you because some time different terms may be used here. So, when this catalyst has been placed in the bed like this. So, there is a mass of the catalyst which is m suppose this mass right and the volume of this is the volume of the bed v b; because it includes the whites here gaps. So, actual this volume of the bed is nothing but the volume of the catalyst plus the whites; that is which we are defining epsilon b basically the white fraction of the bed.

So, white fraction of the bed you can define in terms of the volume of the bed white fraction will be nothing. But the if I say the white fraction of the catalyst epsilon b which is the bed white fraction. And, epsilon p is the pellet porosity these are different term right. So, here if I am defining. So, if I say that1 minus epsilon b or sometime I write it phi also some time also phi, also which is the bed white fraction. So, sometime I will write it like this also in some cases right. So, either you write epsilon b which is now pellet porosity based on whole bed fraction white fraction of the bed right; when I say bed porosity so basically it is based on the white fractions of the bed. So, that is mass of the catalyst if you define based on this; that is will define based on the density of the catalyst which is based on the bed right times the volume of the bed.

So, density of the catalyst based on the bed means that will be equal to density of the catalyst times the fraction of the bed like this, correct. So, basically this phi is the white bed fraction 1 minus phi is the solid fraction. So, because you this mass of catalyst when you are saying the white should bed white should be avoided. But when you size a reactor because the catalyst will be placed in the reactor. So, the actual side of the rector will be larger compare to the volume of the catalyst. So, volume of catalyst how do you do? What is the volume of catalyst if I write just V c; that is mass of catalyst divide by density of the catalyst right; this is the one the density of the catalyst density. So, that is important. So, it means when the epsilon p is the pellet porosity, epsilon b is the porosity based on the bed white side. So, I will continue it next time, I stop here today.