Chemical Reaction Engineering II
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Lecture - 4
Heterogeneous data analysis for reactor design – I

Friends, I am Ganesh Vishwanathan from department of chemical engineering Indian Institute of Technology Bombay. I am going to give several lectures in the second course of chemical reaction engineering. And today I am going to start with heterogeneous reactor analysis. So, we will start with looking at heterogene reactor data and the reactor design.

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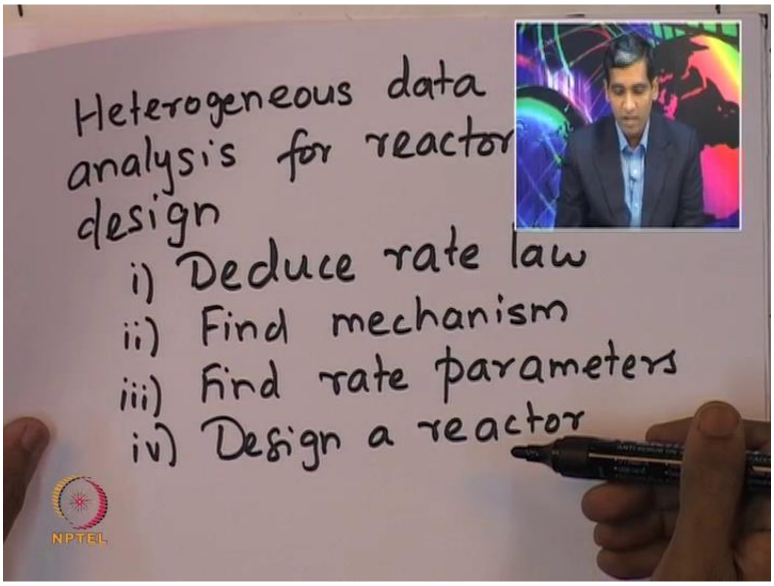

Heterogeneous data analysis for reactor design
i) Deduce rate law
ii) Find mechanism
iii) Find rate parameters
iv) Design a reactor

So, we will look at the heterogeneous analysis for reactor design. So, the general algorithm for designing and a actor a is as follows. So, the first step is to deduce a rate law; the second step is to find the mechanism behind the reaction and the third is to find the rate parameters and the fourth step is to design a reactor using all the information that has been found from previous 3 steps. So, that is the, that is what we are going to start today. So, today we are going to look at the rate law and we are going to look at the mechanism and how to estimate rate parameters. Then we will go march forward to the design of the reactor.

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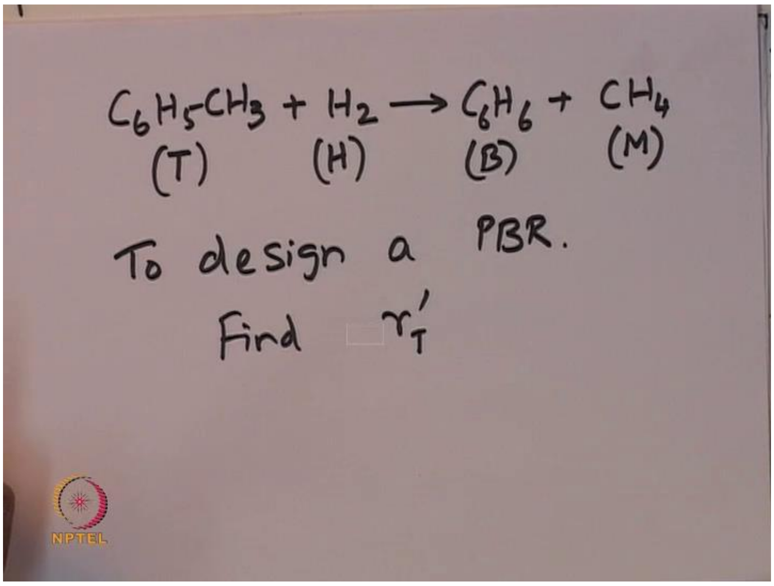

$$C_6H_5\text{-}CH_3 + H_2 \longrightarrow C_6H_6 + CH_4$$

(T) (H) (B) (M)

To design a PBR.

Find r_T'

So, as an example let us take the hydro demethylation of toluene, whose reaction essentially follows this scheme c 6 h 5 c h 3, which hereafter I will call as T. T the stands for toluene and plus hydrogen which will hereafter be called as h leads to benzene which is which will be henceforth called as b and methane which will be henceforth called as m. So, the objective is to design a packed bed reactor which will be henceforth referred to as PBR and in order to do this we need to find a rate law.

That is we need to find the rate of generation of toluene per unit gram of or per weight of the catalyst that is used in the packed bed reactor. So, in order to achieve this objective, let us start with the with the experimental data.

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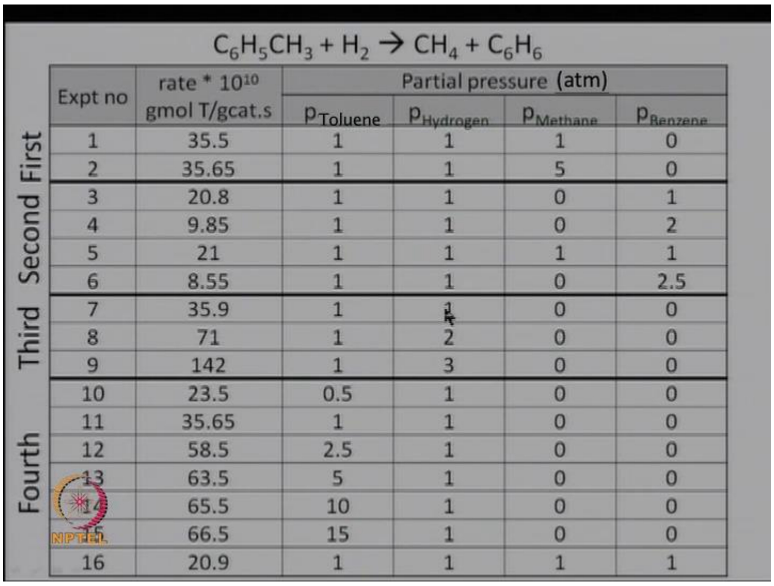

$C_6H_5CH_3 + H_2 \rightarrow CH_4 + C_6H_6$

	Expt no	rate * 10^{10} gmol T/gcat.s	Partial pressure (atm)			
			$p_{Toluene}$	$p_{Hydrogen}$	$p_{Methane}$	$p_{Benzene}$
First	1	35.5	1	1	1	0
	2	35.65	1	1	5	0
Second	3	20.8	1	1	0	1
	4	9.85	1	1	0	2
	5	21	1	1	1	1
	6	8.55	1	1	0	2.5
Third	7	35.9	1	1	0	0
	8	71	1	2	0	0
	9	142	1	3	0	0
Fourth	10	23.5	0.5	1	0	0
	11	35.65	1	1	0	0
	12	58.5	2.5	1	0	0
	13	63.5	5	1	0	0
	14	65.5	10	1	0	0
	15	66.5	15	1	0	0
	16	20.9	1	1	1	1

So, there has been experiments that I have been performed under different conditions and different partial pressures of these different species: toluene, hydrogen, methane and benzene. And different combinations various experiments have been performed and the rate in terms of gram mole of toluene per gram catalyst per unit time have been measured. So, there is 16 experiments and you could actually classified them in 4 different sets. The first 1 and the second 1 by changing the partial pressure of methane;, and then the second 1 by changing the partial pressure of benzene and then the third set by varying the partial pressure of hydrogen; the fourth set by varying the partial pressures of toluene.

Now, remember that partial pressure is a reflection of the mole fraction of each of the species. So, we can now deduce a rate law by looking at this experimental data and so as a first step let us try to see hollow the rate law depends on.

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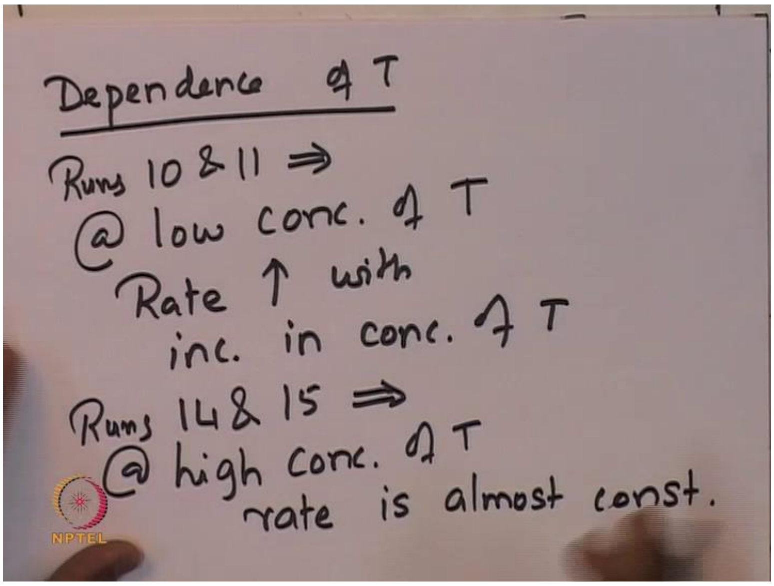

Dependence of T

Runs 10 & 11 ⇒
@ low conc. of T
Rate ↑ with
inc. in conc. of T

Runs 14 & 15 ⇒
@ high conc. of T
rate is almost const.

So, dependence on let us say methane. So, start with let us look at the dependence of methane a concentration of methane on the rate of the reaction. So, if you look at the data here. So, if you look at the first 2 datasets, we will see that as the partial pressure of methane is increased by 5 times 1 can observe clearly from the data that the rate is hardly changing which means that the methane has little or almost no effect on the rate of the reaction.

So, clearly we can observed that the methane m is weakly or weekly adsorbed or goes directly into the gas stream into the gas phase. So, that is an important reduction. So, which means that methane is hardly contributing to the rate of the reaction methane does not affect the rate of the reaction. So, that is an important reduction that1 can observe from the experimental data. So, next let us look at what is the dependence of benzene on the reaction train, if you look at the second set that is runs 3 4 5 and 6.

You can see that there is a significant effect of benzene on the reaction rate particularly, if the partial pressure of benzene is increased then there is a decrease in the reaction rate overall reaction rate. So, which suggests that the concentration of the benzene has to appear in the denominator of the reaction rate, so which means that … So, if look at the dependence if a look at the dependence. So, runs 3 and 4 they suggest that the rate decreases with increased in the benzene concentration or the partial pressure.

So, this suggests that the reaction rate must somehow be proportional to the partial pressure of benzene which appears in the denominator of the rate law. This is because the rate now decreases with increase in the concentration of the benzene; that is the partial pressure of benzene. So, therefore, the rate of generation of toluene which is r T prime which now is given by1 by is should be approximately proportional to1 by1 plus k KB into p b plus other components, where KB is basically the corresponding equilibrium constant.

So, next if we look at the if you look at the dataset again and you want to know, what is the dependence, of toluene on the reaction rate. So, let us look at the dataset 11 and 12 and 10 and 11 excuse me and a it suggests that 10, 11 and 12 suggests that as the toluene partial pressure is increased. There is an increase in the overall reaction rate. Which means that at lower concentration of toluene there is an increase in the reaction rate; however, if we go to a much higher concentration of toluene.

for example, look at the run 13, 14 and 15 that a significant increase in the concentration of toluene does not have a any effect or marginal that has only marginal effect on the reaction rate. Therefore, this suggests that the dependence of toluene must appear both in the numerator and the denominator of the reaction rate. So, let us summarize this here. So, dependence of t … So, runs 10 and 11 it suggests that at low concentrations of toluene the rate increases with increased in concentration of t.

And similarly, runs 14 and 15 it suggests that at high concentrations of T the rate remains constant is almost constant. So, that is the reduction that we can get from the experimental data on the dependence of toluene, concentration of toluene on the reaction rate. So, the only other component which is left is basically the hydrogen. And so let us look at the experimental data again. So, the partial pressure of hydrogen, if it is increased by2 fold 1, 2 and 3.

It appears that there is a a linear increase in the reaction rate which means that, when the partial pressure goes from1 to 2 the reaction it is almost double. And from 2 to 3 it is almost double that. So, this suggests that the reaction rate perhaps depends linearly on the concentration of hydrogen.

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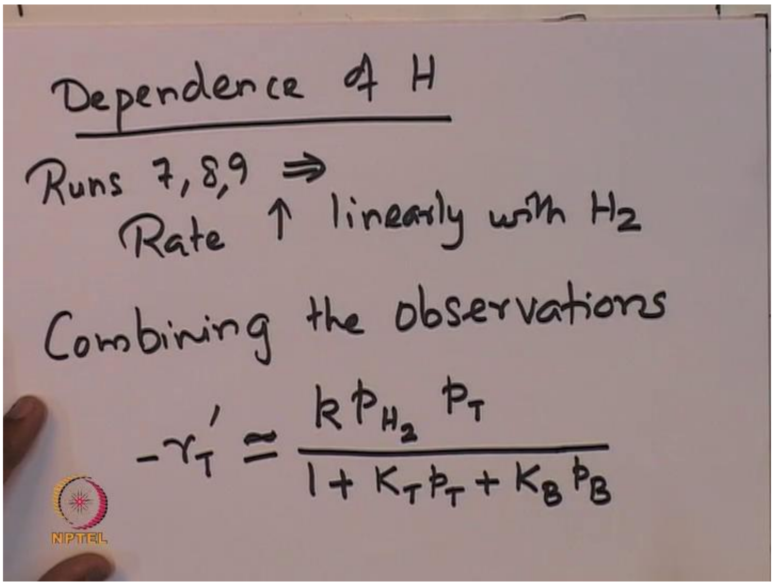

Dependence of H

Runs 7, 8, 9 ⇒
Rate ↑ linearly with H_2

Combining the observations

$$-r_T' \simeq \frac{k\, p_{H_2}\, p_T}{1 + K_T p_T + K_B p_B}$$

So, if we look at the dependence of hydrogen on the reaction to rate. So, run 7 and 8 and 9 suggests that the rate increases linearly with the concentration of hydrogen. So, this means that the hydrogen is perhaps either not adsorbed on the surface or it is immediately goes into the it is not adsorbed on the surface or the surface coverage of hydrogen on the catalyst site is insignificant. So, therefore, now we can combine all of these different reaction a different observations from experimental data.

So, combining the observations 1 can deduce that the reaction rate perhaps must have a form which looks like this. So, the it has to depend linearly on the concentration or partial pressures of hydrogen. And it has to depend it it has to increase with the concentration of toluene when the concentrations lowered; however, it has to remain constant when the concentration of toluene is larger. So, therefore, it has to appear both in the numerator and the denominator. And similarly, the benzene has a reverse effect benzene as the concentration of benzene increases the rate decreases and therefore, it has to appear in the denominator.

So, now he can convert this proportionality in to an equivalence by putting a rate constant in front. So, if I stare at equation you can see that the rate now is directly proportional to the a partial pressure of hydrogen. And it appears both in the numerator and the denominator of the reaction date for with respect to the partial pressure of toluene. And then it appears in the partial pressure of benzene appears in the denominator of the rate expression.

So, this actually provides a method by which you1 could actually deduce to what is the possible reaction rate law based on the experimental observations. This data is only an example and in general, data may not be available in such a form and it may not always be possible to deduce rate law by inspection.

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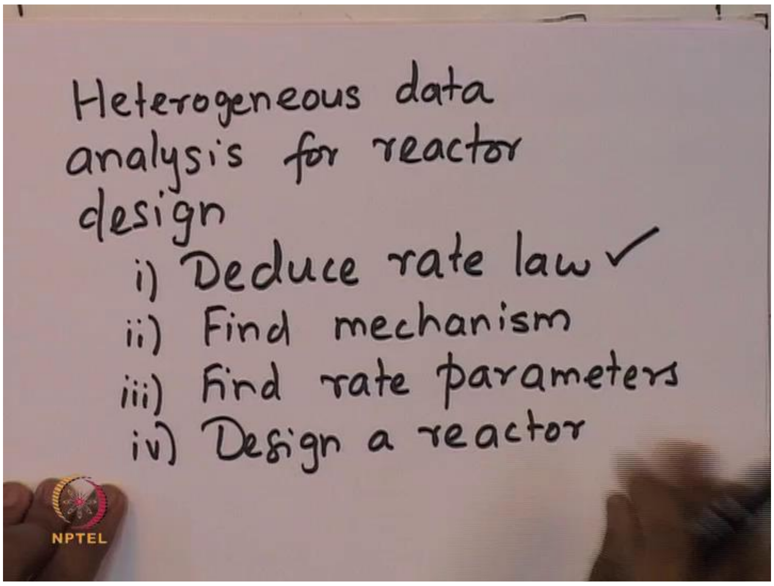

Heterogeneous data analysis for reactor design

i) Deduce rate law ✓
ii) Find mechanism
iii) Find rate parameters
iv) Design a reactor

So, the next step towards finding the rate law, if we go back to the steps which is involved. So, we have now found the rate law. So, we need to next go ahead and find the mechanism that governs this particular set of heterogeneous reaction. So, the next step is towards finding a mechanism.

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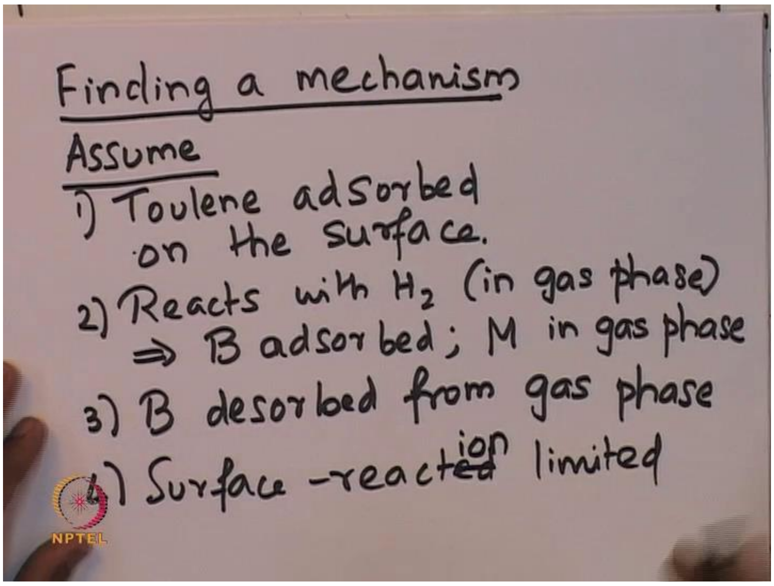

Finding a mechanism

Assume

1) Toulene adsorbed on the surface.
2) Reacts with H_2 (in gas phase) ⇒ B adsorbed; M in gas phase
3) B desorbed from gas phase
4) Surface -react~~ed~~ion limited

The next step is finding a mechanism. So, now, we have to make certain assumptions here. So, if we assume that the toluene is adsorbed on the surface. So, remember that from the experimental data we observed that at low concentrations of toluene the reaction rate actually increases with the partial pressure of toluene. However, at high concentrations or high partial pressures of toluene the reaction rate almost remains constant which suggests that, the toluene must actually be adsorbed onto the surface

So, based on that observation we will make an assumption that the toluene actually is adsorbed on the surface of the catalyst at which the reaction is occurring. Then the second important assumption we will make is that, the toluene which is adsorbed on the surface it reacts with the hydrogen which is percent. And when, it reacts with the hydrogen which is present, because the partial pressure of hydrogen affects linearly the reaction rate.

We will assume that, the reaction rate reaction actually occurs between the toluene which is adsorbed on the surface and the hydrogen which is present in the gas phase. Now after the reaction is completed the products which are formed are basically benzene and methane. Now, we observed that the methane hardly has any effect on the reaction rate which perhaps suggests that the methane must actually directly or immediately go in to the gas phase. And benzene must it affects as the as the partial pressure of the benzene increases we can see that there is a deduction and the reaction rate which suggest that, the benzene actually has to stay adsorbed on the surface and then later get released into the gas phase as a product.

So, this can be captured on this statement here. So, the reaction the toluene which is reacts with hydrogen in gas phase in gas phase. And it leads to the production of benzene which is which reminds adsorbed on the surface and methane it goes into the gas phase. Then as a third assumption after the benzene gets absorbed on the surface the product has to come out of the reactor.

So, therefore, the benzene actually gets desorbed from the surface and then it goes into the gas face, and then leaves that the actor. So, this can be stated as benzene is desorbed from gas phase. And then … So, you must have learnt in the previous lectures that there has to be a rate limiting step. So, we will assume that the heterogeneous reaction is actually a surface reaction limited step. And this is in fact, not a bad assumption because 75 percent of the heterogeneous reactions are actually limited by the surface reaction. So, therefore, is let us assume that it is a surface the reaction limited.

So, let us take each of these steps1 by1 and then try to capture write a simple rate law for each of the steps. And so there are key steps which we have actually deducted from the experimental data and the form of the rate law.

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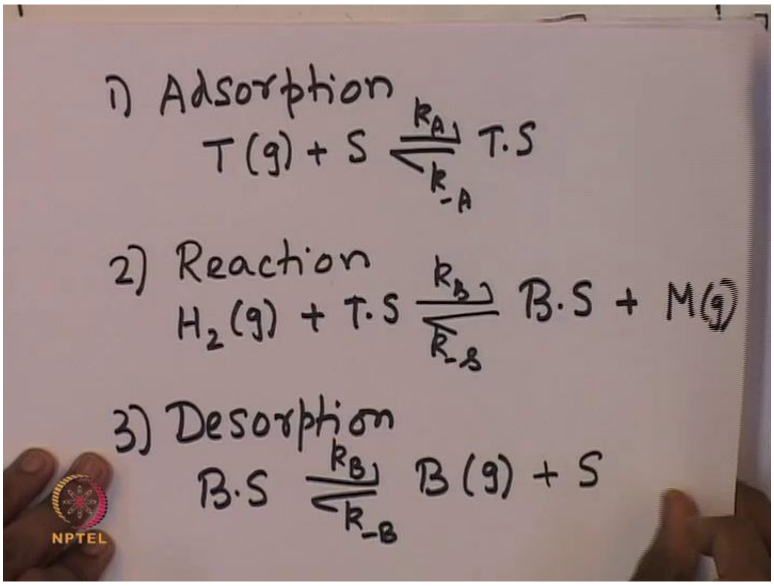

1) Adsorption

$$T(g) + S \underset{k_{-A}}{\overset{k_A}{\rightleftharpoons}} T \cdot S$$

2) Reaction

$$H_2(g) + T \cdot S \underset{k_{-S}}{\overset{k_S}{\rightleftharpoons}} B \cdot S + M(g)$$

3) Desorption

$$B \cdot S \underset{k_{-B}}{\overset{k_B}{\rightleftharpoons}} B(g) + S$$

So, the first 1 is the adsorption. So, this is the toluene which gets adsorbed onto the catalyst surface. And so this can be captured by the following reaction this can be depicted by the following reaction. So, it is the toluene in the gas phase which actually goes and occupies a vacant site s, s represents the catalyst site at which the toluene gets adsorbed. And that leads to the formation of this complex which is basically the toluene and the site. Just basically means that the toluene is now attached or resides on the location of the catalyst site.

So, we can now also represent saying that there is a specific constant which corresponds to the formation of or adsorption of the toluene on the catalyst site and also it is a it is an equilibrium process. And so therefore, there can also be a simultaneous desorption. So, if KA corresponds to the specific constant which captures the adsorption of toluene onto the site and k minus a corresponds to say desorption of the toluene from the catalyst site into the gas stream.

Then the second step yes the reaction. So, the hydrogen which is present in the gas phase that now reacts with toluene, which is residing on the catalyst site to give the to give the products; where this will be benzene which is adsorbed which continuous to be absorbed on the surface trust methane which goes into the gas phase. So, this is the second step where hydrogen in the gas phase reacts with the toluene which is now adsorbed onto the surface of the catalyst site.

That leads to the product formation where the benzene which is 1 of the product it remains adsorbed on the catalyst site and then methane is formed along with it which immediately goes into the gas phase. And the reaction rate corresponding to that can actually be the you here we it is depicted as k s n k minus s for forward and the backward reaction.

The third step is the desorption of benzene, where by the benzene which is absolved onto the surface of the catalyst is now desorbed into the gas phase where benzene goes into the gas phase and leaves the and the catalyst site is empty. And so this reaction they a specific constants can be represented as kB n k minus B. So, these are the 3 steps that we have identified based on the experimental data and also based on the some of these observations that we got from the experimental data.

So, now, what we're going to do is we are going to take each of these step each of these individual steps and then try to find out what is the reaction rate law. And then we are going to we have identified what is we have assumed what is the limiting step in each of these 3, which one of these 3 is a limiting step and then based on that, we are now going to find out a rate law for this particular heterogeneous reaction.

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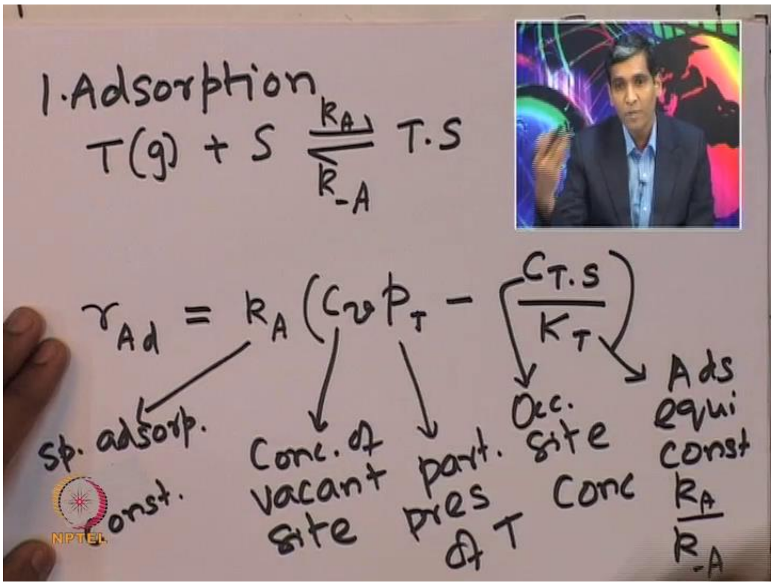

1. Adsorption

$$T(g) + S \underset{k_{-A}}{\overset{k_A}{\rightleftharpoons}} T.S$$

$$r_{Ad} = k_A \left(C_v p_T - \frac{C_{T.S}}{K_T} \right)$$

So, let us now go into the first step of adsorption. So, let us look into the little go little bit deeper into the adsorption process. So, toluene in the gas phase it get adsorbed onto the vacant site s on the catalyst and leading to the t s which is the site which has adsorbed the toluene and k A and k minus A are the corresponding a specific constants. As toluene adsorbs to the catalyst site and the catalyst and the adsorbed species reacts with hydrogen in gas phase we assume a single site mechanism.

So, the rate of adsorption can now be writ 10 as k A multiplied by the concentration of the vacant site Cv multiplied by the partial pressure of toluene. That is basically captures the rate at which the forward reaction is going to happen in order for toluene from the gas phase to get adsorbed on the catalyst site. Minus the concentration of the or the number of concentration of the sites in which the toluene is already adsorbed divided by the corresponding adsorption equilibrium constant.

So, k A is the specific constant adsorption rate, adsorption constant, and Cv stands for concentration of the vacant site, vacant site on the catalyst and pT is the partial pressure of toluene and then CTS is the occupied site concentration CTS and K T is the adsorption equilibrium constant and that is typically given by k A divided by k minus A. So, that sort of captures the rate at which the toluene in the gas phase is gets adsorbed onto the catalyst site. So, let us take a look at the let us go into the details of the next step that, we outlined that is the surface reaction part.

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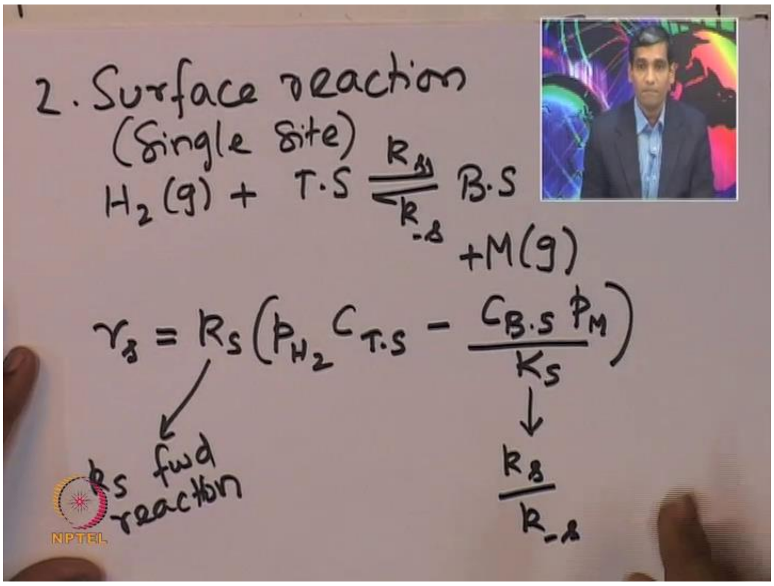

2. Surface reaction
(Single site)

$$H_2(g) + T\cdot S \underset{k_{-s}}{\overset{k_s}{\rightleftharpoons}} B\cdot S + M(g)$$

$$r_s = k_s\left(p_{H_2} C_{T\cdot S} - \frac{C_{B\cdot S}\, p_M}{K_s}\right)$$

k_s fwd reaction

$$\frac{k_s}{k_{-s}}$$

So, let us look at the surface reaction. So, let us look at the surface reaction. So, let us assume that it is a single site reaction where only toluene molecule which is adsorbed onto 1 site is what is involved in the reaction in the catalytic reaction. And so we have hydrogen which is in the gas face plus the toluene which is now adsorbed onto the surface; reacts with each other and then it leads to the formation of benzene and the methane in the gas phase.

So, now we can now capture the rate at which this particular reaction occurs. So, the surface reaction rate is now given by k s multiplied by partial pressure of hydrogen into the concentration of the sites in which the toluene is this actually adsorbed. Minus the concentration of the number of sites concentration of the sites in which the benzene is adsorbed which is a product multiplied by the partial pressure of methane divided by k s. So, the first term here corresponds to the rate of the forward reaction and the second term here corresponds to the rate of the reverse reaction.

So, here k s is basically the specific constant for forward reaction forward reaction and p H2 corresponds to the partial pressure of hydrogen in the gas phase and CTS corresponds to the concentration toluene number of sites in which the toluene is adsorbed. And CBS corresponds to the concentration on the number of sites in which benzene is adsorbed; the product benzene is adsorbed. And PM corresponds to the partial pressure of methane in the gas phase and k s is basically the corresponding equilibrium constant which is given by k s divided by k minus s.

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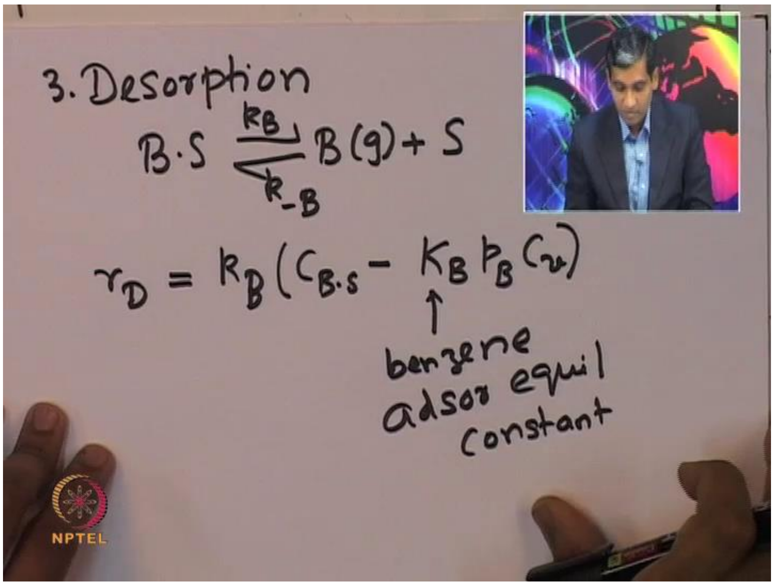

3. Desorption

$$B\cdot S \underset{k_{-B}}{\overset{k_B}{\rightleftharpoons}} B(g) + S$$

$$r_D = k_B\left(C_{B\cdot S} - \underset{\uparrow}{K_B}\, p_B C_v\right)$$

benzene
adsor equil
constant

So, next we look at what look at the desorption process. So, that is the 3rd step which is the desorption process. Now, here the benzene which is absolved onto the surface gets dissolved to give benzene in the gas phase and an empty site or a vacant site. So, if the corresponding specific constants desorption constants or k B and k minus B …

Then the rate can be return as rate of desorption is given by k B into CB.S minus KB into PB into Cv. Where the KB corresponds to the benzene adsorption equilibrium constant and Cv corresponds to the concentration of the vacant site. Remember that the reverse reaction is basically where the benzene in the gas phase can actually go and adsorb onto the vacant catalyst site.

Therefore, KB PB into Cv tells you what is the rate at which the free benzene which is available in the gas phase gets adsorbed onto the catalyst surface. So, next we have assumed that, the surface reaction is the limiting reaction. So, therefore, all the other reaction rates really do not contribute. So, the key reaction which key rate which contributes to the overall reaction rate of this heterogeneous reaction is basically the surface reaction.

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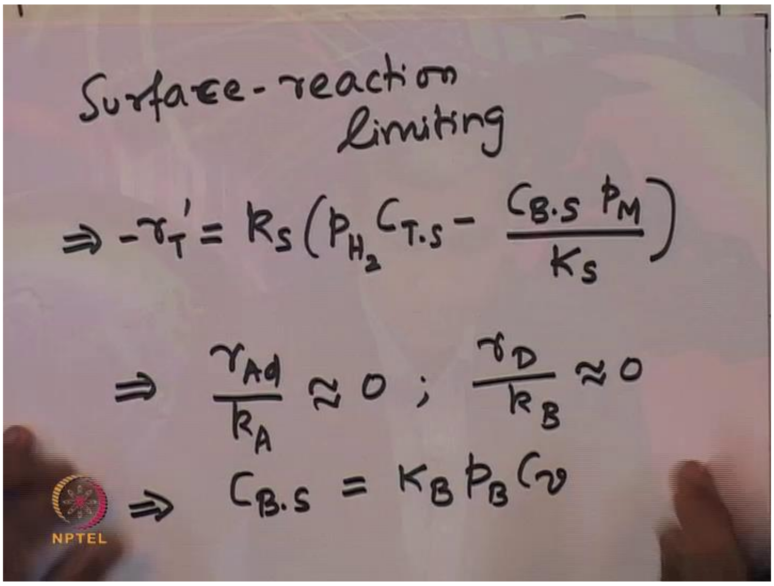

Surface-reaction limiting

$$\Rightarrow -r_T' = k_S\left(p_{H_2} C_{T.S} - \frac{C_{B.S}\, p_M}{K_S}\right)$$

$$\Rightarrow \frac{r_{Ad}}{k_A} \approx 0 \; ; \; \frac{r_D}{k_B} \approx 0$$

$$\Rightarrow C_{B.S} = K_B\, p_B\, C_v$$

So, we said that it is a surface reaction limiting. So, therefore, the rate of generation of toluene should actually be equal to the rate of the surface reaction; the rate at which the surface reaction is occurring because it is the limiting step.

So, that’ll be given by k S into p H2 partial pressure of hydrogen multiplied by the concentration of the sites in which the toluene is absorbed minus the concentration of benzene that is adsorbed to the catalyst surface and then multiplied by the partial pressure of methane divided by the corresponding equilibrium constant. Now, this also means that the other reaction rates actually have to be 0.

So, that also means that the r absorption divided by the corresponding k A is approximately equal to 0 and also or desorption divided by the corresponding constant is also approximately 0. Now, from this we can actually deduce that the concentration of the benzene which is adsorbed to the vacant sites is actually equal to KB PB into Cv.

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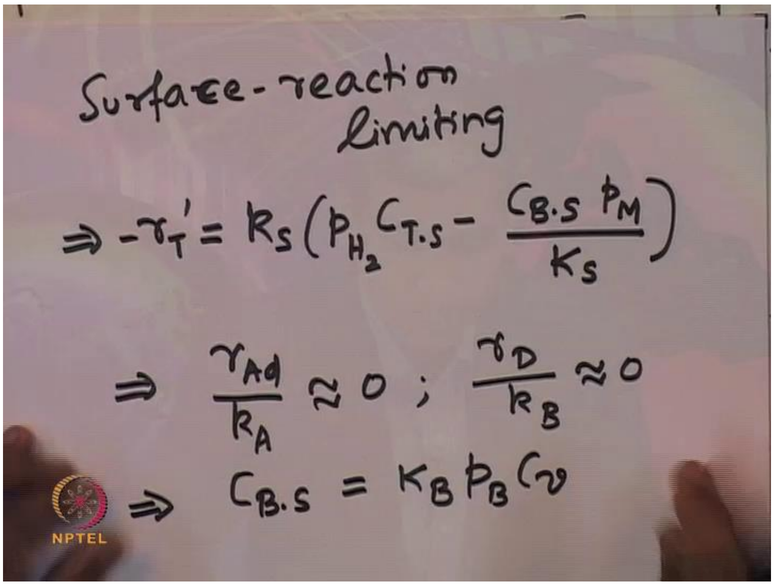

Surface-reaction limiting

$$\Rightarrow -r_T' = k_S\left(p_{H_2} C_{T.S} - \frac{C_{B.S}\, p_M}{K_S}\right)$$

$$\Rightarrow \frac{r_{Ad}}{k_A} \approx 0 \; ; \; \frac{r_D}{k_B} \approx 0$$

$$\Rightarrow C_{B.S} = K_B\, p_B\, C_v$$

Similarly, the concentration of the vacant sites I mean concentration of the sites on which toluene is adsorbed is actually given by KT PT and Cv. So, this is actually obtained by setting r adsorption divided by k A equal to 0. It is obtained by setting up this this particular equivalence by setting up r adsorption divided by k A to be approximately 0.

Now, in addition to this the total number of sites in a given catalyst is approximately constant. So, we can now depict that by saying if Ct is the total number of sites in the catalyst that should be equal to the total number of vacant sites plus the sites on which toluene is adsorbed plus the sites on which the benzene is absorbed. So, these are the 2 possible ones that and be principally be adsorbed onto the surface, because we assume that hydrogen is primarily in the gas phase and so is meeting.

So, therefore, see total should be equal to vacant sites plus the concentration of the sites in which the toluene is adsorbed plus the concentration of the sites on which benzene is adsorbed. So, by using this in this conservation property and also the expressions for the concentration of toluene adsorbed onto the catalyst site. And the concentration of benzene adsorbed onto the catalyst site, we can find that the concentration of the vacant site is given by Ct divided but 1 plus KB partial pressure of benzene plus KT into partial pressure of toluene.

So, if we know what is the rate limiting step and if adsorption desorption processes in this particular case are not the rate limiting step. Then we will be able to estimate the an amount or concentration o the vacant site in terms of the observable quantities. That is the partial pressure of benzene, partial pressure of toluene or the measurable quantities. So, now so once we know the concentration of the vacant site we can now go back and try to estimate what is the overall rate at which the heterogeneous reaction is occurring.

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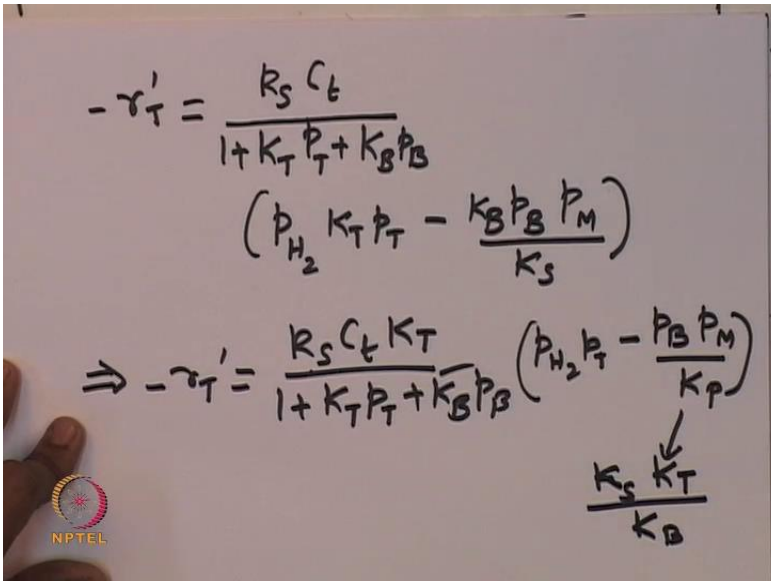

$$-r_T' = \frac{k_S C_t}{1+K_T P_T+K_B P_B}\left(P_{H_2} K_T P_T - \frac{K_B P_B P_M}{K_S}\right)$$

$$\Rightarrow -r_T' = \frac{k_S C_t K_T}{1+K_T P_T+K_B P_B}\left(P_{H_2} P_T - \frac{P_B P_M}{K_P}\right)$$

$$K_P \rightarrow \frac{K_S K_T}{K_B}$$

So, because surface reaction is the limiting reaction, so the reaction rate is now given by k S in C total divided but 1 plus KT P partial pressure of toluene plus KB PB multiplied by partial pressure of hydrogen KT PT minus KB PB into PM and divided by KS. So, this can be obtained simply by plugging in the expression for the vacant site catalyst concentration into the expression for the reaction rate. And we can obtain this particular expression.

So, from here we can rewrite this as minus rT prime equal to k S Ct. So, pull out KT from the expression divided by 1 plus KT PT plus KB into PB; that multiplied by partial pressure of H2 partial pressure of toluene minus partial pressure on benzene partial pressure of methane divided by another constant KP. So, this KP is nothing, but the equilibrium constant of the surface reaction multiplied by the corresponding constants for the adsorption of toluene and the adsorption of benzene.

Note that, KP can be determined from the thermodynamic data of the overall reaction. Now, suppose if we neglect the reverse reaction, if we suppose we say that the total amount of the reaction primarily goes in the forward direction.

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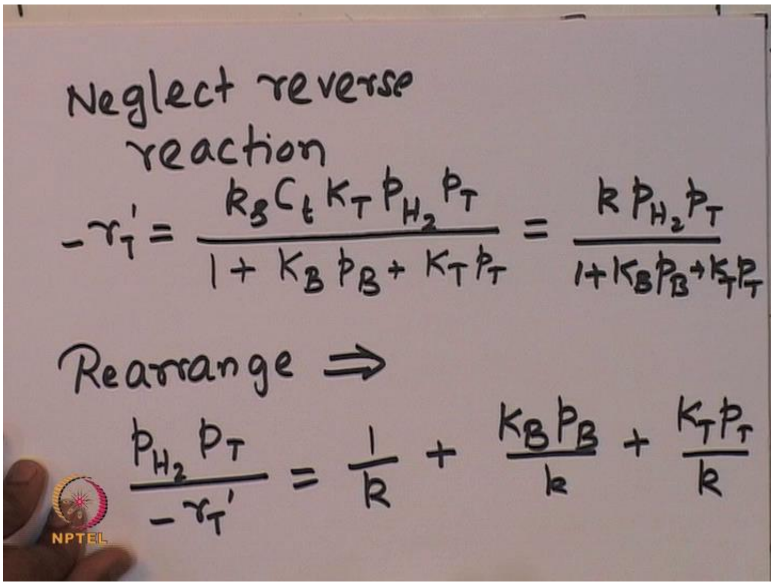

Neglect reverse reaction

$$-r_T' = \frac{k_S C_t K_T p_{H_2} p_T}{1 + K_B p_B + K_T p_T} = \frac{k p_{H_2} p_T}{1 + K_B p_B + K_T p_T}$$

Rearrange ⇒

$$\frac{p_{H_2} p_T}{-r_T'} = \frac{1}{k} + \frac{K_B p_B}{k} + \frac{K_T p_T}{k}$$

So, if we neglect the reverse reaction then we will see that the rate can actually be given by ks which is the corresponding rate constant for the surface reaction multiplied by Ct which is the total number of catalyst sites which is available in the catalyst. And KT which is actually the corresponding constant desorption constant for toluene and partial pressure of hydrogen partial pressure of toluene divided by1 plus KB PB plus KT into PT.

So, by clubbing in the 3 the ks Ct and KT into 1 constant, so you can write this as k into partial pressure of H2 partial pressure of toluene divided by1 plus KB PB plus KT into PT. So, that can be written as this expression here. And so now, we can actually rearrange this expression and we can rewrite this as… Rearrange the expression as partial pressure of hydrogen, partial pressure of toluene divided by the corresponding rate should be equal 1 by k plus KB PB divided by k plus KT PT divided by k.

The final form of the rate expression is actually a linear equation. So, the with this we have actually found the second step. So, remember that there are 4 steps here first we deduce the rate law and then we find the mechanism. So, what we have done is we have found the mechanism and after we found the mechanism we now need to go ahead and estimate the rate parameters.

So, in order to estimate the rate parameters, it is useful to write in this in the form of this rearranged expression. And you can see that the there are 3 constants which are present:

1 is k, the other 1 is KB, another 1 this KT. So, now, these 3 constants need to be estimated and we will have to use the experimental data in order to estimate these constants. So, when we write the expression in this form here, then we will be able to use the experimental data and we will be able to perform certain regression analysis in order to estimate these parameters.

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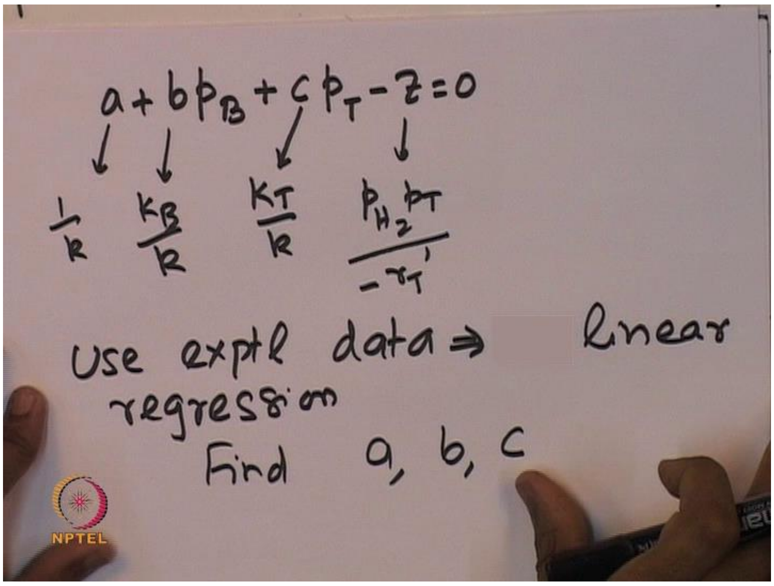

$$a + b p_B + c p_T - z = 0$$

$$a \downarrow \frac{1}{k} \qquad b \downarrow \frac{K_B}{k} \qquad c \downarrow \frac{K_T}{k} \qquad z \downarrow \frac{p_{H_2} p_T}{-r_T'}$$

Use exptl data ⇒ linear regression

Find a, b, c

So, the rearranged equation can actually be written as a plus b into partial pressure of benzene plus C into partial pressure of toluene minus z equal to 0, where z is given by partial pressure of H2 partial pressure of toluene divided by the rate which is measured experimentally. And a is given by 1 by k and b is given by KB by k and C is given by KT by k.

So, once we have experimental data which is presented in the in the experiments that have been measured. So, as can be seen from these experimental data. So, the partial pressure can be measured the partial pressure of toluene, hydrogen, methane, benzene have all been measured and different reaction rates have been measured under these conditions. So, using this data 1 can perform a regression analysis and using the regression analysis 1 can find these constants a b and c.

So, use experimental data and 1 can perform a linear regression analysis I am using a linear regression analysis. So, we can now find these constants a b and c. So, once we know these 3 constants then we will be able to estimate what is the value of k, we will be able to estimate the value of KB and we will be able to estimate the value of KT. And then we can find out by using the experimenter date which was presented the there the constants have been formed.

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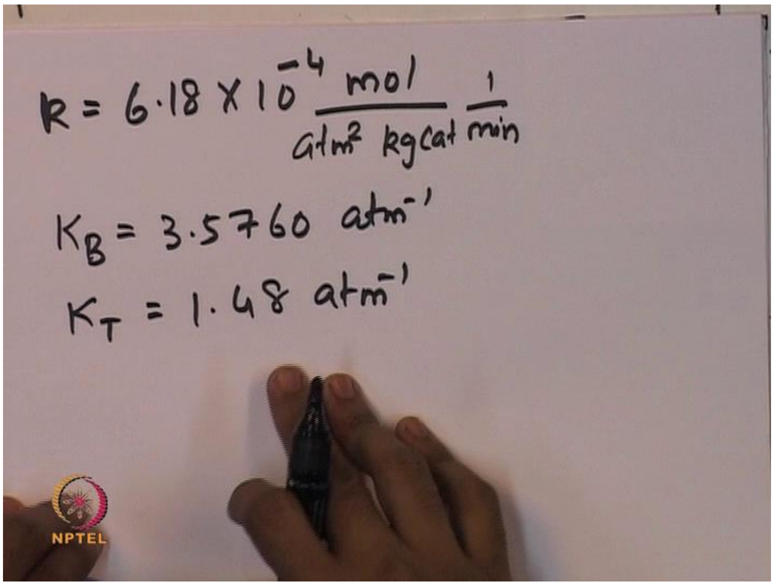

$$k = 6.18 \times 10^{-4} \frac{mol}{atm^2\ kgcat} \frac{1}{min}$$

$$K_B = 3.5760\ atm^{-1}$$

$$K_T = 1.48\ atm^{-1}$$

From the data k will be equal to for the data that is shown to you that k will be equal to 6.18 into 10 power minus 4 moles per atmosphere square multiplied by kilogram catalyst per minute. And KB which is the corresponding equilibrium adsorption desorption constant for benzene is comes out to be 3.5760 atmosphere minus 1 and KT turns out to be about1.48 atmosphere minus 1.

So, these are the constants that are being estimated from the experimental data, using the rate law mechanism that we have just found out and by performing a linear regression analysis on the experimental data. Now, what do we do with this data? So, what we can do is we can we can estimate some other we can deduce some other information in addition to these.

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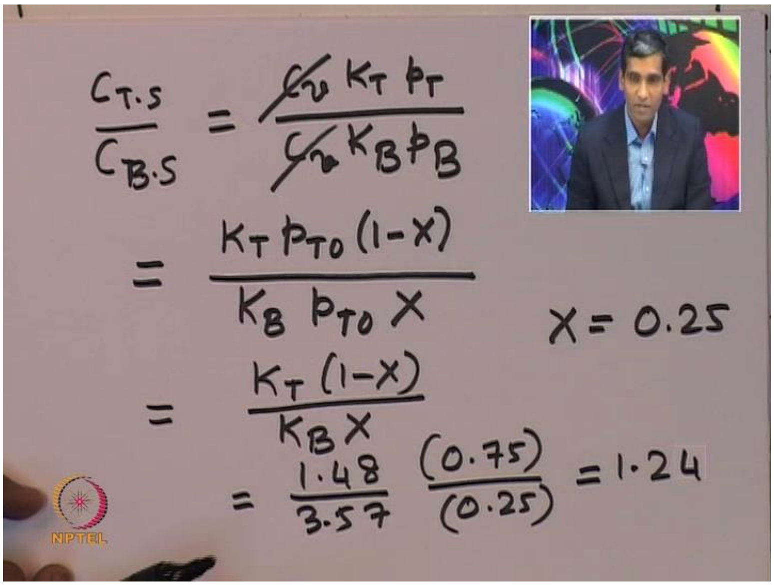

$$\frac{C_{T\cdot S}}{C_{B\cdot S}} = \frac{\cancel{C_v} K_T p_T}{\cancel{C_v} K_B p_B}$$

$$= \frac{K_T p_{T0}(1-x)}{K_B p_{T0} x} \qquad x = 0.25$$

$$= \frac{K_T(1-x)}{K_B x}$$

$$= \frac{1.48}{3.57}\,\frac{(0.75)}{(0.25)} = 1.24$$

For example we can find out what is the ratio of the ratio of the sites on which the toluene is adsorbed to the sites on which benzene is adsorbed. So, how do we do this? Because, we have assumed that the surface reaction is a limiting step. So, the concentration of the adsorbed sites on which the toluene is adsorbed is given by Cv multiplied by the corresponding equilibrium constant; adsorption desorption constant k toluene multiply by the corresponding partial pressure.

So, using that expression we can rewrite this as by substituting those expressions we can rewrite this as Cv me KT into PT divided by Cv KB into PB. So, that is given by … So, therefore, canceling the vacant sites will see that this is equal to KT into … If the total partial pressure at the inlet of the reactor is given by PT naught, then PT is given by PT naught multiplied by 1 minus x, where stands for the conversion of that particular reaction divided by KB which is the corresponding adsorption desorption constant multiplied by PT naught into x.

This is equal to KT into 1 minus x divided by KB into x. Suppose, if the conversion x is about 0.25 that is it is a 25 percent conversion, then we can plug in these numbers and we will see that this is equally to 1.48 divided by 3.57 multiplied by 0.75 divided by 0.25. So, this is approximately equal to 1.24. So, what this suggests is that the number of sites on which the toluene is adsorbed is actually about 25 percent more than the number of sites on which benzene is adsorbed for the given set of experimental conditions.

So, that is an important piece of information that1 can actually deduce. So, if 1 needs to have a 25 percent conversion of x to be 0.25 then the 25 percent of these sites has to be greater than the number of sites on which the toluene adsorbed, has to be greater than 25 percent greater than that of the number of sites on which the benzene is absorbed. So, the so let us get back to the algorithm of designing a reactor. So, we looked at rate law we looked at the mechanism and by using the regression analysis we found out what is the rate parameter is that is the parameter that is involved in the rate law. So, the next step is actually to design a reactor.

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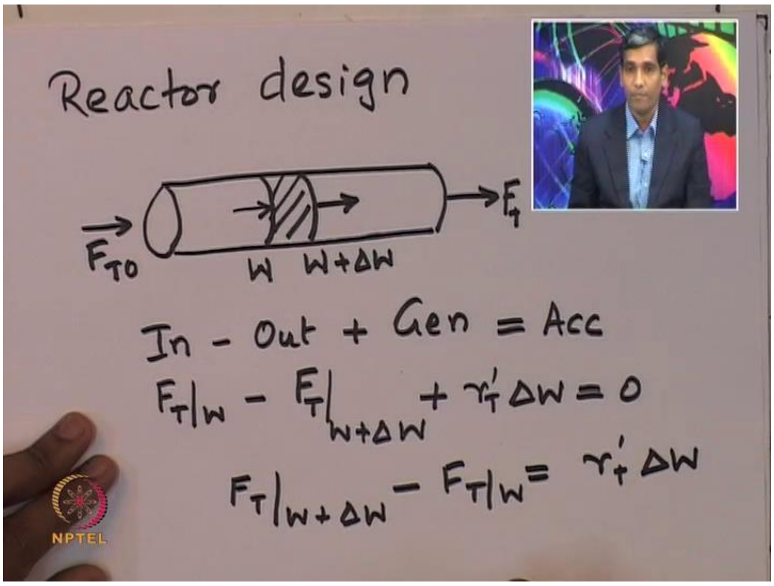

Reactor design

In - Out + Gen = Acc

$$F_T|_W - F_T|_{W+\Delta W} + r_T' \Delta W = 0$$

$$F_T|_{W+\Delta W} - F_T|_W = r_T' \Delta W$$

So, let us consider a tubular reactor filled with catalyst. So, we get into the reactors design. So, let us consider a tube which is filled with catalyst. And if FT naught is the molar flow rate at which toluene is actually entering this particular reactor. And let us assume that, FT is the molar flow rate at which the toluene leaves the reactor.

Now, if I take a small element and if the total weight of catalyst which is packed till that location is w and the weight of catalyst packed at the other end of the element is w plus delta w. Then we can write a simple mass balance in order to account for what is happening inside the reactor. So, the mass balance is what enters the element minus what leaves this element plus whatever is generated in this particular element in this element should be equal to the amount of material that is being accumulated in that element.

So, what enters that element it is the FT that is the molar flow rate of T at W, where the weight of the catalyst up to that point is W minus the molar flow rate FT of toluene at W plus delta W. Plus if the reaction rate is minus rT, then rT prime multiplied by delta w equal to 0. So, that is the rate law. So, where rT prime is the generation of the rate at which the toluene is being generated and delta w is basically the amount of catalyst which is packed in that particular element. So, we can simply rewrite this as FT W plus delta W minus FT W equal to rT prime into delta W.

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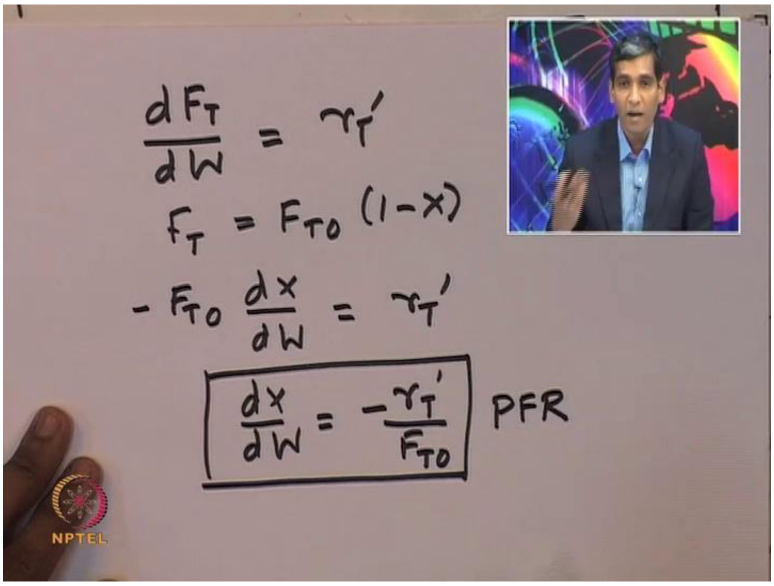

$$\frac{dF_T}{dW} = r_T'$$

$$F_T = F_{T0}(1-x)$$

$$-F_{T0}\frac{dx}{dW} = r_T'$$

$$\boxed{\frac{dx}{dW} = -\frac{r_T'}{F_{T0}}}$$ PFR

This can be rewritten as dFT divided by dW equal to rT prime. Now, FT can be written in terms of the conversion that is equal to FT naught into 1 minus x. So, substituting the expression for the relationship between the molar flow rate of toluene and conversion we can rewrite this as minus f t naught into dX by dW equal to rT prime.

So, therefore, dX by dW equal to minus rT prime divided by FT naught. So, that is the performance equation by assuming that it is a plug flow reactor, by assuming that the reactants are a plug flow reactor. Now, moment we find moment we write the model equation for the reactor we need to now plug in the rate law.

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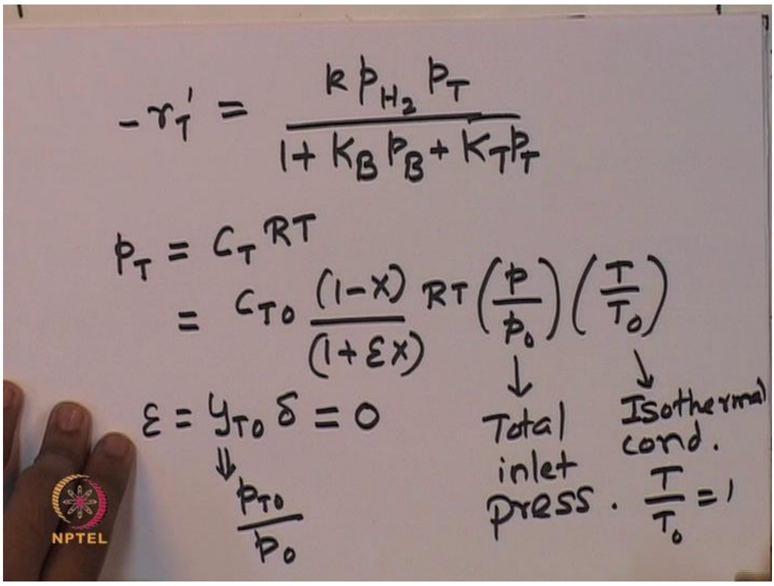

$$-r_T' = \frac{k\, p_{H_2}\, p_T}{1 + K_B p_B + K_T p_T}$$

$$p_T = C_T RT$$

$$= C_{T0} \frac{(1-X)}{(1+\varepsilon X)} RT \left(\frac{p}{p_0}\right)\left(\frac{T}{T_0}\right)$$

$\downarrow$ Total inlet press.

$\downarrow$ Isothermal cond. $\frac{T}{T_0} = 1$

$$\varepsilon = y_{T0}\,\delta = 0$$

$\Downarrow$ $\frac{p_{T0}}{p_0}$

.

So, we know that the rate law is given by K into the partial pressure of hydrogen partial pressure toluene divided by 1 plus KB into partial pressure of benzene plus KT into partial pressure of toluene. So, we can now plug in this rate law into the model equation and then we will be able to estimate what is the how the conversion changes how much toluene is actually being consumed inside the reactor. Now, in order to do that we need to now express the partial pressures of toluene in terms of the a conversion. So, we can do that.

So, partial pressure of toluene is given by the concentration of toluene multiplied by R into T using an ideal gas law. And from stoichiometric relationship this can actually be expressed as CT naught into 1 minus X divided by 1 plus epsilon X into rT multiplied by P divided p naught into T divided by T naught. Where, P naught is the total inlet pressure and epsilon is basically given by YT naught into delta where YT naught is the partial pressure of toluene at the inlet divided by the total pressure at the inlet. And delta is the change in the number of moles.

So, because this particular in this particular reaction the number of moles is actually 0 so therefore, this epsilon is equal to 0, which accounts for the change in the volume. And if we assume that it is isothermal if the I we assume that you the reaction is conducted at isothermal conditions isothermal conditions, then T by T naught is equal to 1.

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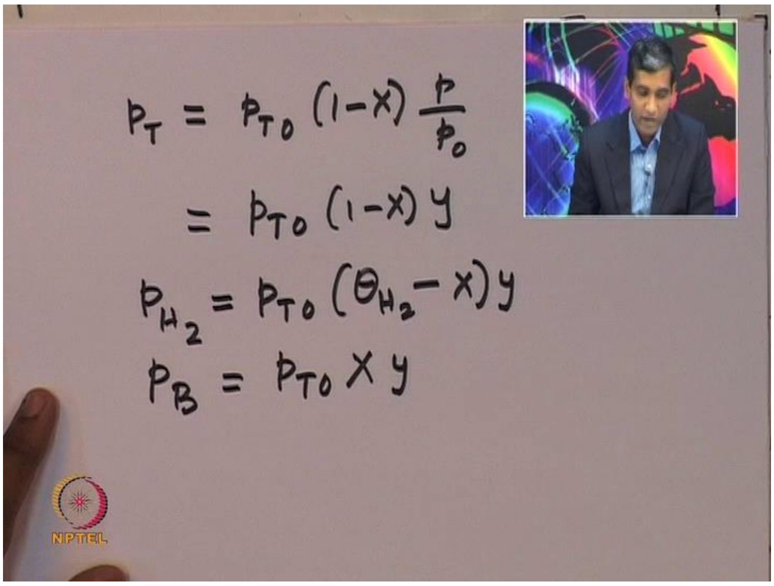

$$p_T = p_{T0}(1-X)\frac{p}{p_0}$$

$$= p_{T0}(1-X)\,y$$

$$p_{H_2} = p_{T0}(\theta_{H_2} - X)\,y$$

$$p_B = p_{T0}\,X\,y$$

So, now, using these assumptions we can now rewrite the we can now express the pressure, partial pressures of toluene in terms of the conversion as PT naught multiplied by 1 minus x into T by P naught. Now, P is essentially the pressure at that particular location.

So, if I call that as y, then you can write this as PT naught into 1 minus X into X which is the ratio of the pressure at that location divided by the total inlet pressure. Now, similarly we can write the partial pressure of hydrogen as PT naught multiplied by theta H2 minus X into Y. And partial pressure to benzene can be written as PT naught into X, where theta H2 is the ratio of the concentration ratio of the amount of hydrogen which is present in the feed with respect to the amount of toluene; which is percent in the feed.

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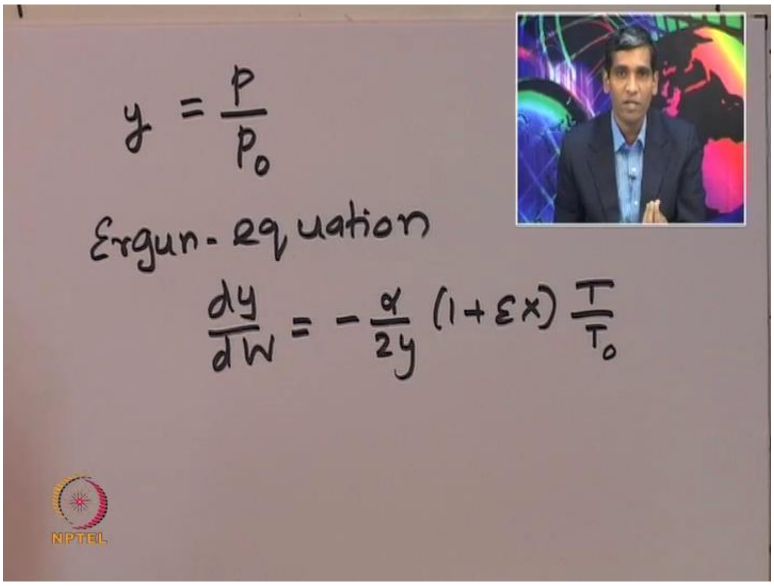

$$y = \frac{P}{P_0}$$

Ergun-equation

$$\frac{dy}{dW} = -\frac{\alpha}{2y}(1+\varepsilon x)\frac{T}{T_0}$$

So, in order to find the conversion profile as a function of the catalyst weight need to estimate this quantity y which is the ratio of the local pressure with respect to the total pressure at the inlet. So, how do we find this? We can actually use the Ergun equation we can use the Ergun equation in order to find this ratio find this quantity y. So, the Ergun equation can actually be written as dy by dW equal to minus alpha by 2y into 1 plus epsilon X into T by T naught.

So, so what we have seen. So, far in today’s in this lecture is essentially how to use the experimental data. In order to find out what is the deduce the rate law which corresponds to the particular heterogeneous reaction. And, then using that rate law and to find using the observations from the experiment to understand and deduce a mechanism by which that particular heterogeneous reaction perhaps occurs. And what is the rate limiting step in that particular series of in that particular heterogeneous reaction.

Once we find this rate limiting step, then we can actually using the rate law we can write the rate expressions for each of these steps. And by identifying the rate limiting step we can find out what is the rate of reaction in terms of the observable or measurable quantities. And from that we will be able to use that rate law expression find the rate law expression that we have derived in terms of the measurable quantities and use the actual measurements and the reaction rate and plug it in and using a regression analysis we can find out the rate constants and the other constants which is involved in the reaction rate law.

Thank you.