Chemical Reaction Engineering - II

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Module - 2
Lecture - 9
Heterogeneous Data Analysis for Reactor Design I

Today I am going to start with heterogeneous reactor analysis. So, we will start with looking at heterogeneous reactor data and the reactor design.

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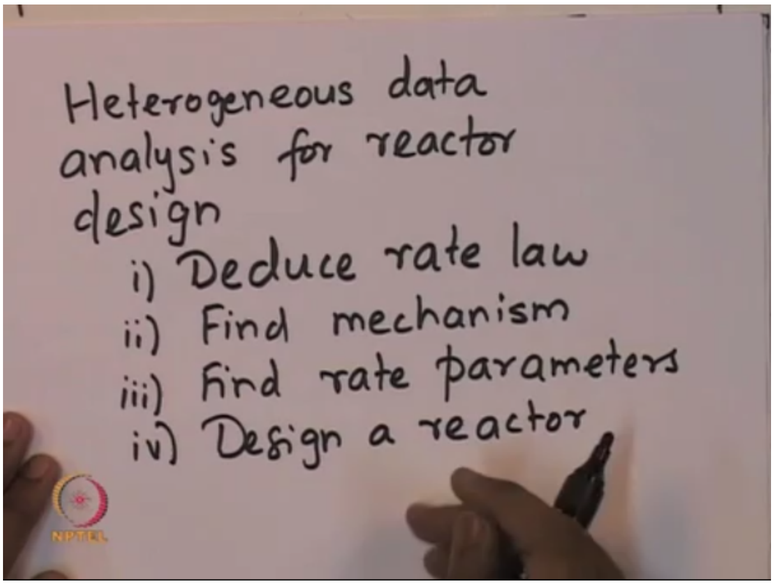

Heterogeneous data analysis for reactor design

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 a reactor is as follows. So, the first step is to deduce a rate law, deduce 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 the previous 3 steps.

So, that is the, that is what we 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. And then we will go, march forward to the design of the reactor. So, as an example, let us take the hydro demethylation of toluene whose reaction essentially follows this scheme.

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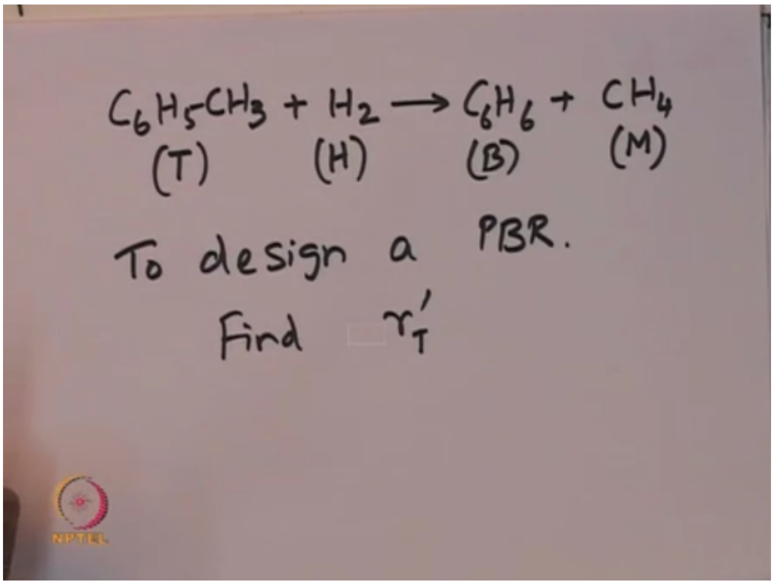

$$C_6H_5\text{-}CH_3 + H_2 \longrightarrow C_6H_6 + CH_4$$

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

To design a PBR.

Find r_T'

C 6 H 5 C H 3 which hereafter I will call as T; T stands for toluene. And + hydrogen which will hereafter be called as H. Leads to benzene 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, upper weight of the catalyst that is used in the packed-bed reactor. So, in order to achieve this objective, let us start with the experimental data.

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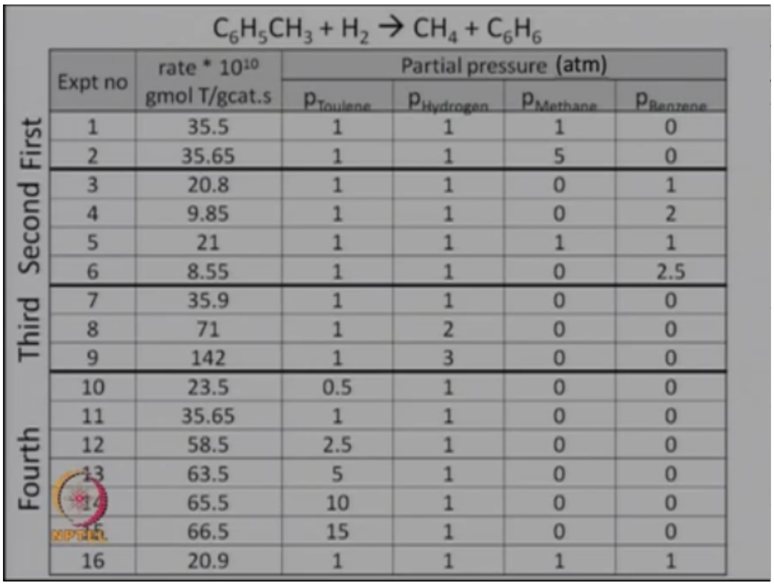

$C_6H_5CH_3 + H_2 \rightarrow CH_4 + C_6H_6$

	Expt no	rate * 10^{10} gmol T/gcat.s	Partial pressure (atm)			
			$p_{Toulene}$	$p_{Hydrogen}$	$p_{Methane}$	$p_{Benzene}$
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 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 classify them into 4 different sets.

The first one and the second one by changing the partial pressure of methane. And then the second one by changing the partial pressure of benzene. And then, the third set by varying the partial pressure of hydrogen. And 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 these 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 how the rate law depends on;

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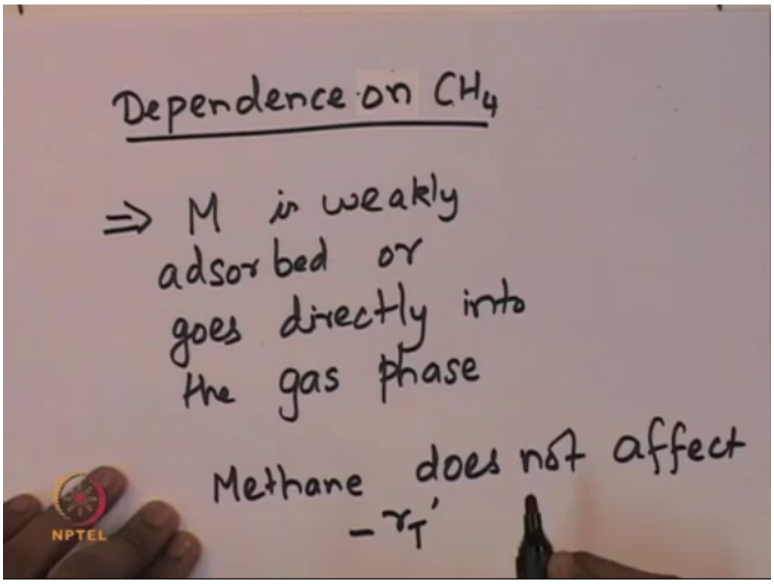

Dependence on CH_4

⇒ M is weakly adsorbed or goes directly into the gas phase

Methane does not affect $-r_T'$

So, dependence on let us say methane. So, start with, let us look at the dependence of methane. The concentration of methane on the rate of the reaction. So, if we look at the data here. So, if we look at the first 2 data sets. We will see that, as the partial pressure of methane is increased by 5 times, one 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 observe that the methane M is weakly or weakly adsorbed or goes directly into the gas stream, into the gas phase. So, that is an important deduction. 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 deduction that one can observe from the experimental data. So, next let us look at what is the dependence of benzene on the reaction rate.

If we look at the second set, that is runs 3, 4, 5 and 6. And 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 I look at the dependence;

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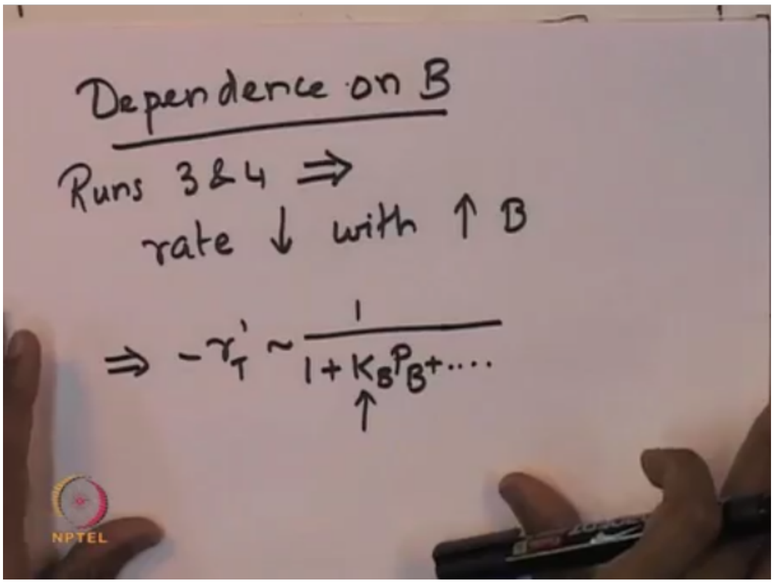

Dependence on B

Runs 3&4 ⇒

rate ↓ with ↑ B

$$\Rightarrow -r'_T \sim \frac{1}{1+\underset{\uparrow}{K_B P_B}+\cdots}$$

So, runs 3 and 4, they suggest that the rate decreases with increase 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 by 1 by, it should be approximately be proportional to 1 by 1 + K B into P B + other components, where K B is basically the corresponding equilibrium constant. So, next if we look at the data set again and we want to know what is the dependence of toluene on the reaction rate. So, let us look at the data set 11 and 12; 10 and 11 excuse me.

And it suggests that 10, 11 and 12 suggest 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, 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 summarise this here.

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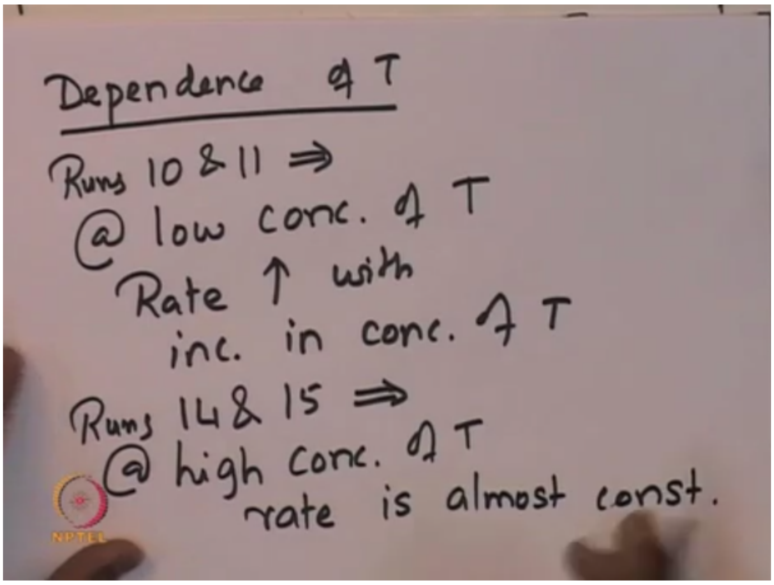

Dependence of T

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 of T. So, runs 10 and 11, it suggests that at low concentrations, at low concentration of toluene the rate increases with increase in concentration of T. And similarly, runs 14 and 15 suggests that, at high concentrations of T 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 by 2 fold 1, 2 and 3, it appears that there is a linear increase in the reaction rate. Which means that when the partial pressure goes from 1 to 2 the reaction rate is almost double. And from 2 to 3 it is almost double of that. So, this suggests that the reaction rate perhaps depends linearly on the concentration of hydrogen.

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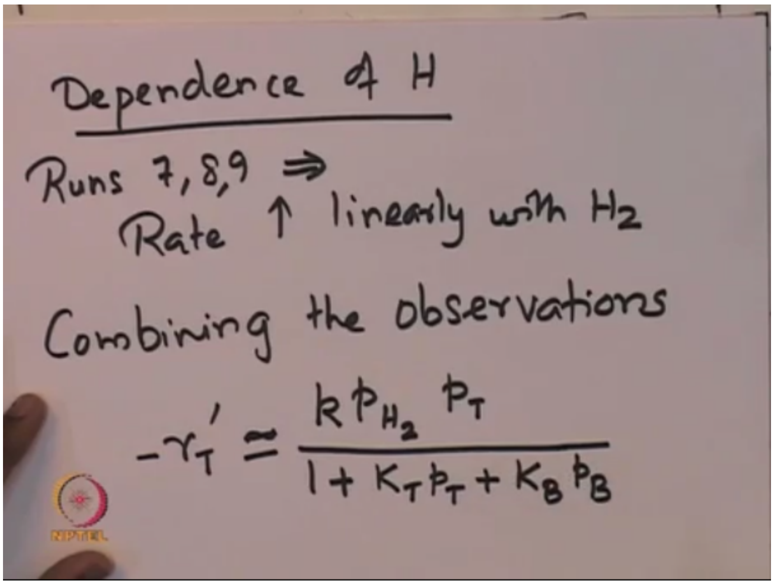

Dependence of H

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 rate. So, runs 7 and 8 and 9 suggest that the rate increases linearly with the concentration of hydrogen. So, this suggests, 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, different observations from experimental data. So, combining the observations. One 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 has to increase with the concentration of toluene when the concentration is lower.

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 we can convert this proportionality into an equivalents by putting a rate constant in front.

So, if I stare at this equation, you can see that the rate now is directly proportional to the partial pressure of hydrogen. And it appears both in the numerator and the denominator of the reaction rate for, with respect to the partial pressure of toluene. And then, it appears in the, the partial pressure of benzene appears in the denominator of the rate expression. So, this actually provides a method by which you, one could actually deduce 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. So, the next step towards finding the rate law. If we go back to the set of different steps which is involved. So, we have 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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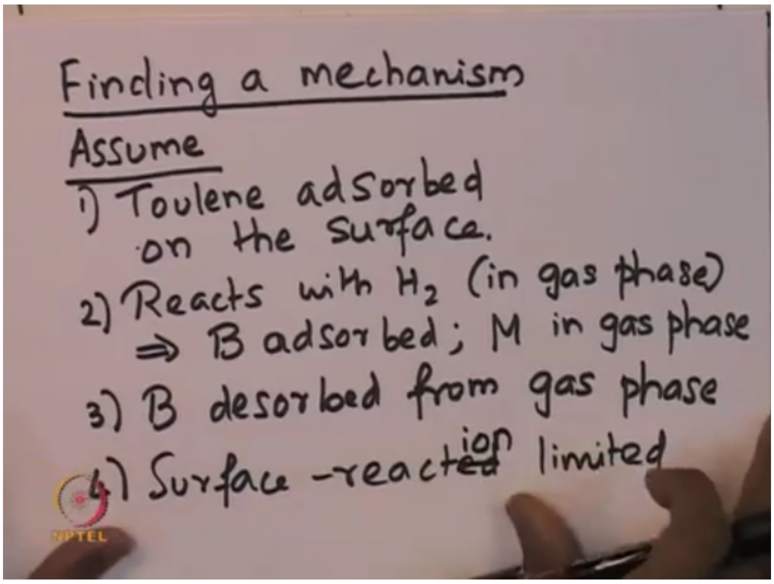

Finding a mechanism

Assume

1) Toulene adsorbed on the surface.
2) Reacts with H_2 (in gas phase) $\Rightarrow$ B adsorbed; M in gas phase
3) B desorbed from gas phase
4) Surface -reac~~ted~~ion limited

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 observe that at low concentrations of toluene, the reaction rate actually increases with the partial pressure of toluene. However, at high concentrations or high partial pressure of toluene the reaction rate almost remains constant.

Which suggests that the toluene must actually be adsorbed onto the surface. And 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 make is that the toluene is adsorbed on the surface. It reacts with the hydrogen which is present.

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 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 into the gas phase. And benzene must, it affects, as the partial pressure of the benzene increases, we can see that there is a deduction in the reaction rate. Which suggests 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 in this statement here. So, the reaction, the toluene which is adsorbed reacts with hydrogen in gas phase. And it leads to the production of benzene which is, which remains adsorbed on the surface and methane which goes into the gas phase. Then, as a third assumption, after the benzene gets adsorbed 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 phase and then leaves the reactor. So, this can be stated as benzene is disorbed 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% of the heterogeneous reactions are actually limited by the surface reaction. So, therefore these, let us assume that it is a surface reaction limited. So, let us take each of these steps one by one. And then try to capture, write a simple rate law for each of these steps. And so, there are 3 key steps which we have actually deducted from the experimental data and the form of the rate law. So, the first one is the adsorption.

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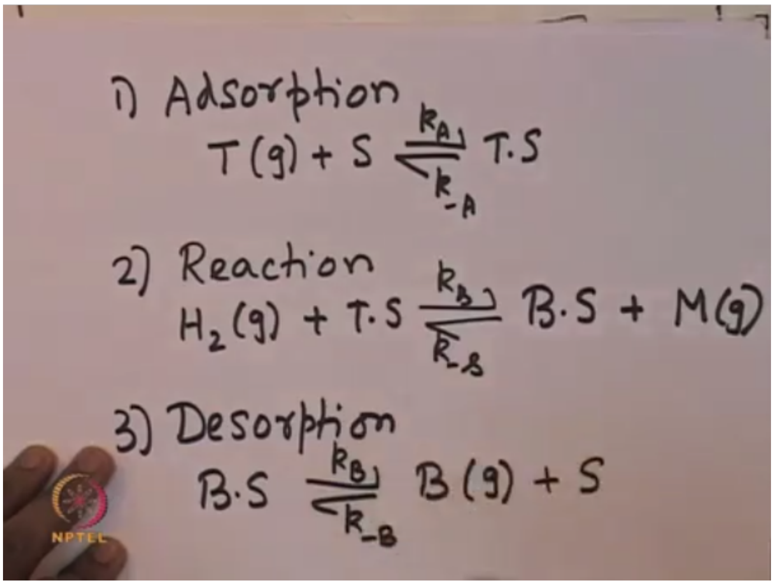

1) Adsorption

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

2) Reaction

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

3) Desorption

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

So, the first one 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.

Which is, 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 toluene on the catalyst site. And also, it is an equilibrium process. And so, therefore there can also be a simultaneous desorption. So, if k A corresponds to a specific constant which captures the adsorption of toluene onto the site and k – A corresponds to the desorption of the toluene from the catalyst site into the gas stream.

And then, the second step is 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 products. Where this will be benzene which is adsorbed which continues to be adsorbed on the surface + 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 this catalyst site.

And that leads to the product formation where the benzene which is one 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, hear it is depicted as k s and k – s for forward and the backward reaction. And the third step is the desorption of benzene.

Where the benzene which is adsorbed 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, there is specific constants that can be represented as k B and k – 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 are going to do is, we are going to take each of these steps, 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 the, 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 going, now going to find out a rate law for this particular heterogeneous reaction. So, let us now go into the first step of adsorption. So, let us look into the, let us go little bit deeper into the adsorption process.

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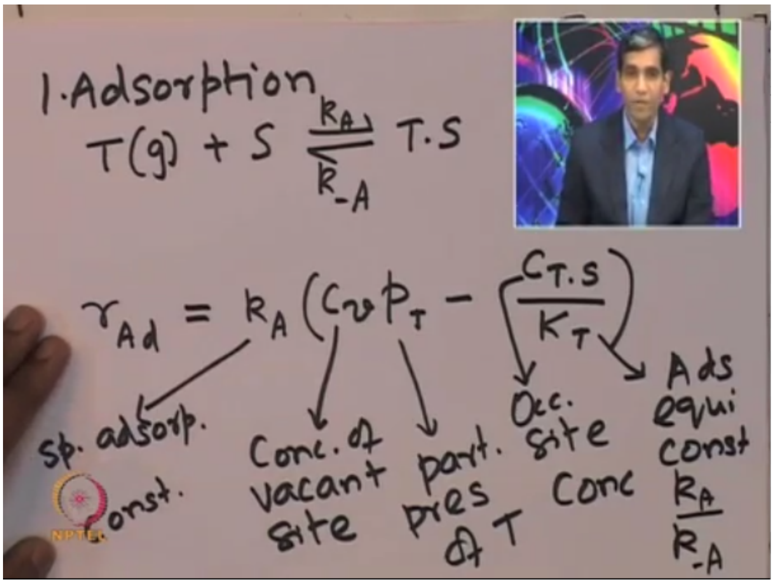

1. Adsorption

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

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

So, toluene in the gas phase, it gets adsorbed onto the vacant site S on the catalyst. And leading to the T S which is the site which is adsorbed with toluene. And k A and k – A are the corresponding 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 written as k A multiplied by the concentration of the vacant site C v 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 onto the catalyst site – 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 C v stands for concentration of the vacant site on the catalyst.

And P T is the partial pressure of toluene. And then, C T S is the occupied site concentration. And K T is the adsorption equilibrium constant. And that is typically given by k A divided by k – 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. So, let us look at the surface reaction.

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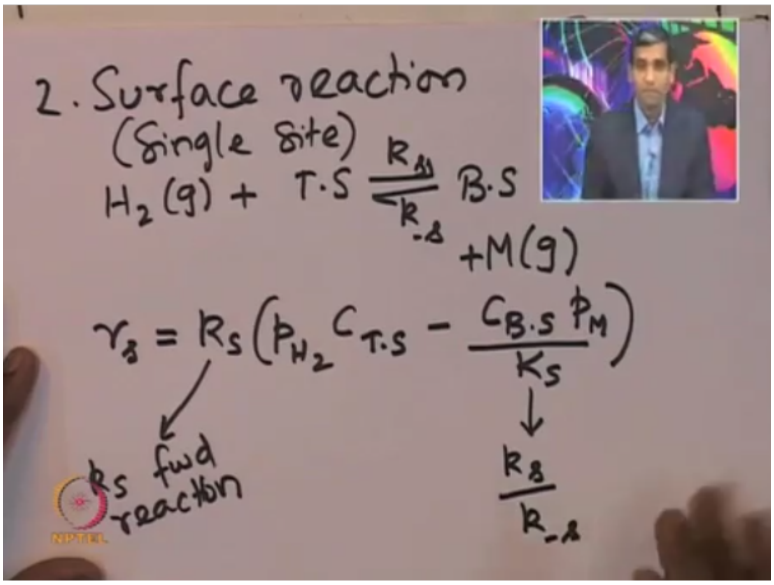

2. Surface reaction
(Single site)

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

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

k_s fwd reaction

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

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 phase + 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 in now given by k S, multiplied by partial pressure of hydrogen, into the concentration of the sites in which the toluene is actually adsorbed – the concentration of the number of sites, concentration of the sites in which the benzine 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.

And P H 2 corresponds to the partial pressure of hydrogen in the gas phase. And C T S corresponds to the concentration of toluene, number of sites in which the toluene is adsorbed. And C B S corresponds to the concentration of the number of sites in which benzene is adsorbed, the product benzene is adsorbed. And P M 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 – s. So, next we will look at what, look at the desorption process.

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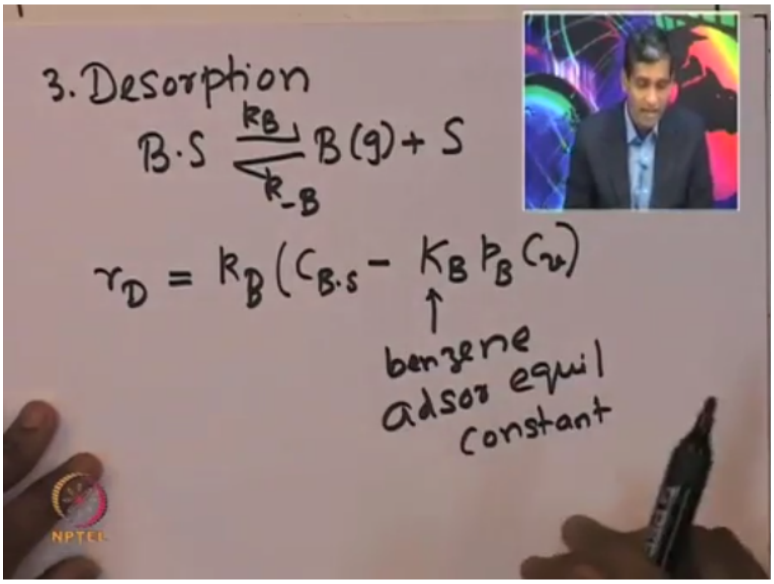

3. Desorption

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

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

benzene
adsor equil
constant

So, that is the third step which is the desorption process. Now here, the benzene which is adsorbed onto the surface gets desorbed to give benzene in the gas phase and an empty site or a vacant site. And so, if the corresponding specific constants, desorption constants are k B and k – B. Then the rate can be written as, rate of desorption is given by k B into C B dot S – K B into P B into C v.

Where the K B corresponds to the benzene adsorption equilibrium constant, and C v corresponds to the concentration of the vacant site. Remember that the reverse reaction is basically where the benzine in the gas phase can actually go and adsorb onto the vacant catalyst site. And therefore, K B P B into C v tells you what is the rate at which the free benzene which is available in the gas phase gets adsorbed onto the catalyst surface.