Chemical Reaction Engineering - II
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Module - 2
Lecture - 10
Heterogeneous Data Analysis for Reactor Design II

Rate at which the heterogeneous reaction is occurring. So, because surface reaction is the limiting reaction, so the reaction rate is now given by K S into C totaled divided by 1 + K T P partial pressure of toluene + K B P B multiplied by partial pressure of hydrogen K T P T – K B P B into P M divided by K S.

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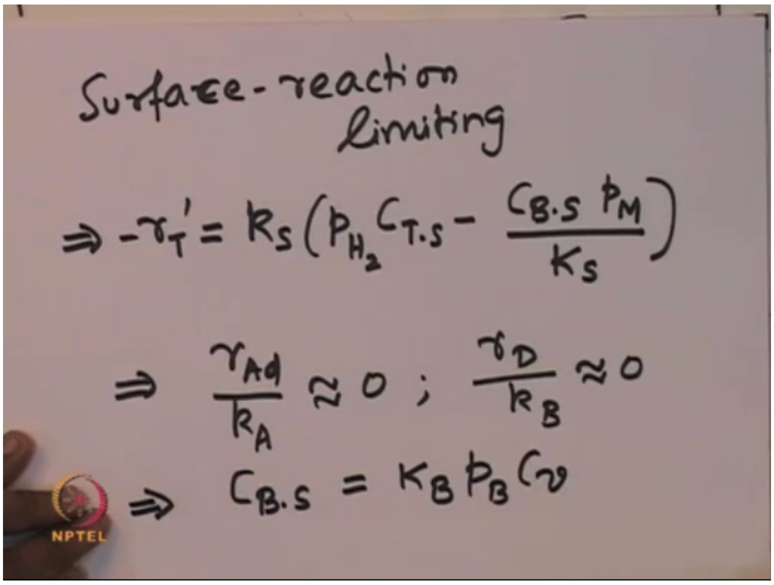

Surface-reaction limiting

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

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

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

So, 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 – r T prime = k S C T, so pull out K T from the expression, divided by 1 + K T P T + K B into P B. That multiplied by partial pressure of H 2 partial pressure of toluene – partial pressure of benzene, partial pressure of methane divided by another constant K P.

So, this K P is nothing but the equilibrium constant of the surface reaction multiplied by the; now, from this we can actually deduce that the concentration of the benzene which is adsorbed to the vacant sites is actually = K B P B into C v.

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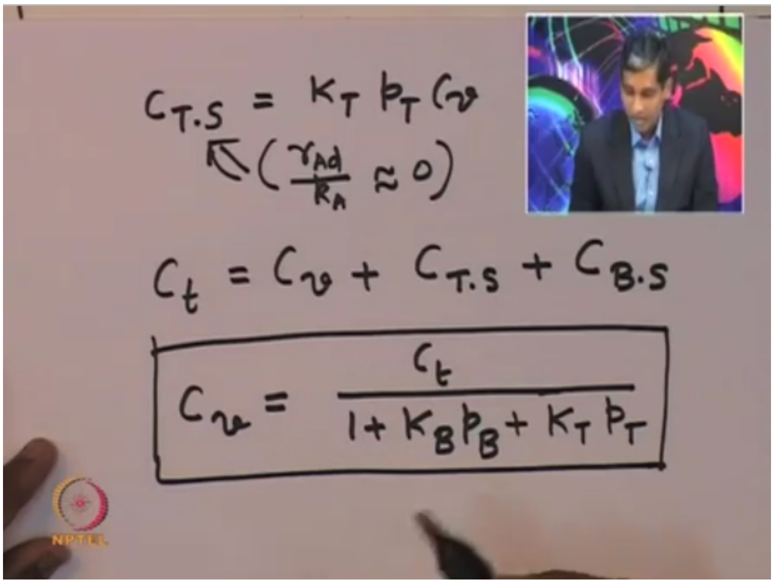

$$C_{T.S} = K_T p_T C_v$$

$$\nwarrow \left(\frac{r_{Ad}}{k_A} \approx 0\right)$$

$$C_t = C_v + C_{T.S} + C_{B.S}$$

$$\boxed{C_v = \frac{C_t}{1+K_B p_B + K_T p_T}}$$

Similarly, the concentration of the vacant sites, I mean concentration of the sites on which toluene is adsorbed is actually given by K T P T and C v. So, this is actually obtained by setting r adsorption divided by k A = 0. This is obtained by setting up this particular equivalents, 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 C t is the total number of sites in the catalyst that should be = the total number of vacant sites + the sites on which toluene is adsorbed + the sites on which the benzene is adsorbed. So, these are the 2 possible ones that can in principle be adsorbed onto the surface because we assume that hydrogen is primarily in the gas phase and so is methane.

So, therefore, C total should be = vacant sites + the concentration of the sites in which the toluene is adsorbed + 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 C t divided by 1 + K B partial pressure of benzene + K T 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 amount or concentration of 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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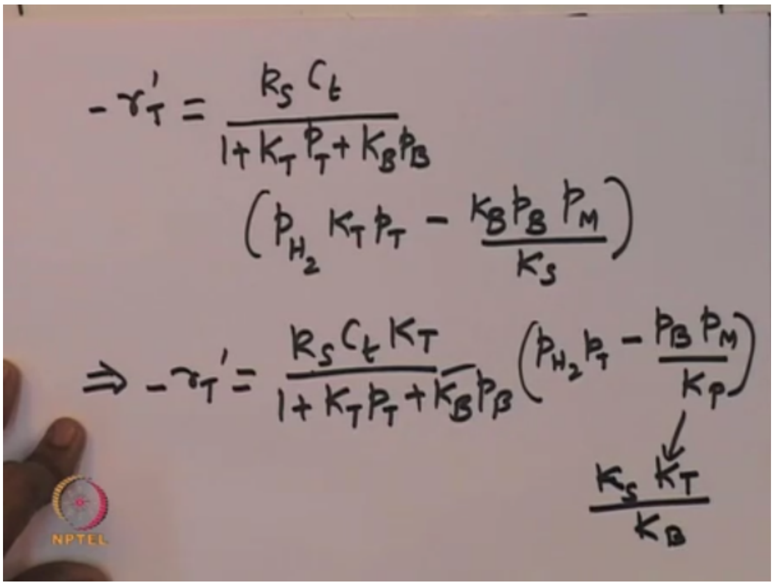

$$-r_T' = \frac{k_S C_t}{1+K_T p_T+K_B p_B}\left(p_{H_2} K_T p_T - \frac{K_B p_B p_M}{K_S}\right)$$

$$\Rightarrow -r_T' = \frac{k_S C_t K_T}{1+K_T p_T+K_B p_B}\left(p_{H_2} p_T - \frac{p_B p_M}{K_P}\right)$$

$$\downarrow$$

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

So, because surface reaction is the limiting reaction. So, the reaction rate is now given by K S into C totaled divided by 1 + K T P partial pressure of toluene + K B P B multiplied by partial pressure of hydrogen K T P T – K B P B into P M divided by K S. 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 – r T prime = k S C t, so pull out K T from the expression, divided by 1 + K T P T + K B into P B. That multiplied by partial pressure of H 2 partial pressure of toluene – partial pressure of benzene, partial pressure of methane divided by another constant K P. So, this K P 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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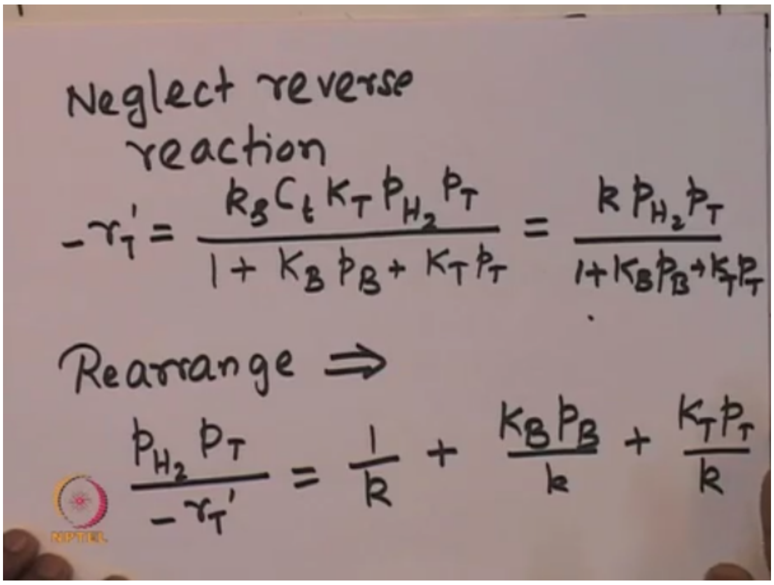

Neglect reverse reaction

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

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, neglect reverse reaction, then we will see that the rate can actually be given by k s which is the corresponding rate constant for the surface reaction multiplied by C t which is the total number of catalyst sites which is available in the catalyst. And K T which is actually the corresponding constant, adsorption constant for toluene and partial pressure of hydrogen partial pressure of toluene divided by 1 + K B P B + K T into P T.

So, by clubbing in the 3, the k s C t and K T into one constant, we can write this as k into partial pressure of H 2 partial pressure of toluene divided by 1 + K B P B + K T 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 = 1 by k + K B P B divided by k + K T P T divided by k.

The final form of the rate expression is actually a linear equation. So the, so 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, it is useful to write in the form of this rearranged expression. And you can see that the, there are 3 constants which are present. One is k, the other one is K B, another one is K T. 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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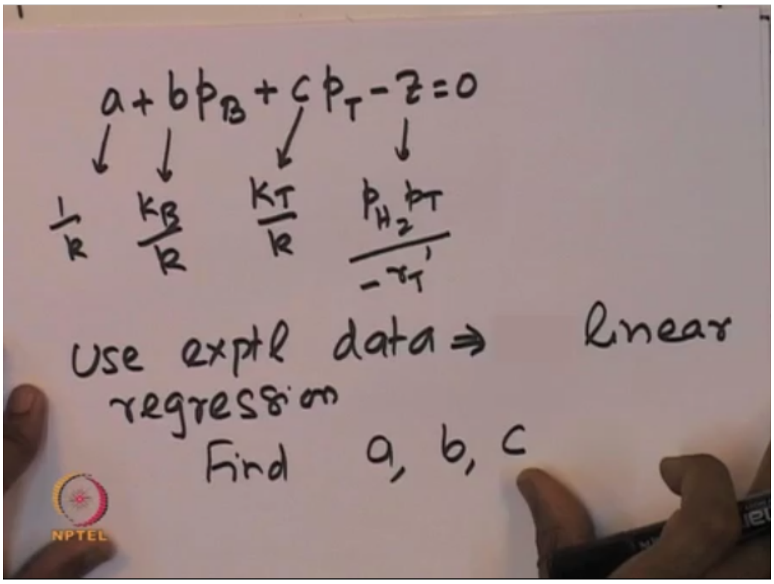

$$a + b\,p_B + c\,p_T - Z = 0$$

$$\begin{array}{cccc}\downarrow & \downarrow & \downarrow & \downarrow \\ \frac{1}{k} & \frac{K_B}{k} & \frac{K_T}{k} & \frac{p_{H_2}\,p_T}{-r_T'}\end{array}$$

Use exptl data ⇒ linear regression

Find a, b, c

So, the rearranged equation can actually be written as a + b into partial pressure of benzene + C into partial pressure of toluene – Z equal to 0 where Z is given by partial pressure of H 2, 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 K B by k and C is given by K T by k. So, once we have experimental data which is presented 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, one can perform a regression analysis. And using the regression analysis one can find these constants a, b and c. So, use experimental data.

And one can perform a linear regression analysis. And using the linear regression analysis, 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 K B and we will be able to estimate the value of K T. And then, we can find out by using the experimental data which was presented the constants have been found.

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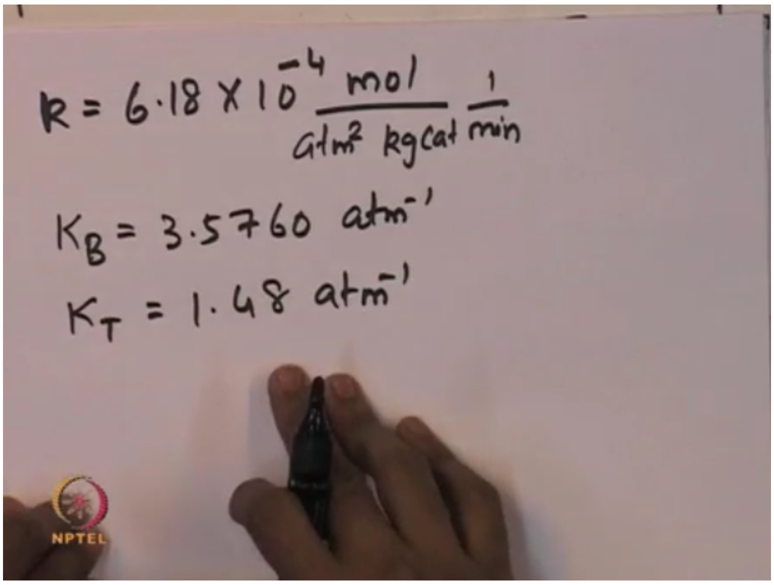

$$k = 6.18 \times 10^{-4} \frac{mol}{atm^2 \; kgcat} \frac{1}{min}$$

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

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

And from the data k will be =, for the data that is shown to you, the k will be = 6.18 into 10 power – 4 moles per atmosphere square multiplied by kilogram catalyst per minute. And K B which is the corresponding equilibrium adsorption desorption constant for benzene is comes out to be 3.5760 atmosphere – 1. And K T turns out to be about 1.48 atmosphere – 1.

So, these are the constants that have been 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 estimate some other information, we can deduce some other information in addition to these.

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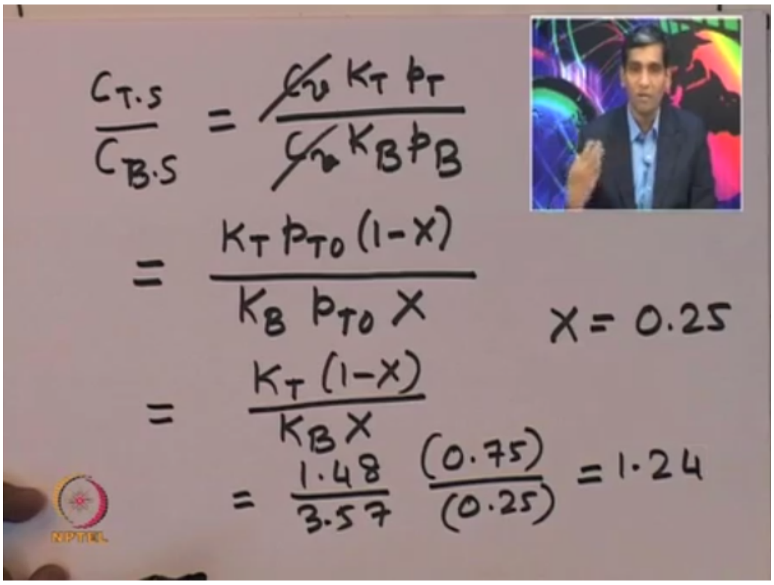

$$\frac{C_{T.S}}{C_{B.S}} = \frac{\cancel{C_v} K_T p_T}{\cancel{C_v} K_B p_B}$$

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

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

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

For example, we can find out what is the ratio of the 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 C v multiplied by the corresponding equilibrium constant, adsorption desorption constant k toluene multiplied by the corresponding partial pressure.

So, using that expression, we can rewrite this as by substituting those expressions, we can rewrite this as C v K T into P T divided by C v K B into P B. So, that is given by, so therefore cancelling the vacant sites we will see that this is = K T into, if the total partial pressure at the inlet of the reactor is given by P T nought, then P T is given by P T nought multiplied by 1 – X, where X stands for the conversion of that particular reaction.

Divided by K B which is the corresponding adsorption desorption constant multiplied by P T nought into X. And this is = K T into 1 – X divided by K B into X. Suppose if the conversion X is about 0.25. That is, it is a 25% conversion. Then we can plug in these numbers and we will see that this is = 1.48 divided by 3.57 multiplied by 0.75 divided by 0.25. So, this is approximately = 1.24.

So, what this suggests is that the number of sites on which the toluene is adsorbed is actually about 25% 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 that one can actually deduce. So, if one needs to have a 25% conversion of X to be 0.25, then the 25% of this sites has to be greater than, excuse me.

The number of sites on which the toluene is adsorbed has to be greater than 25% greater than that of the number of sites on which the benzene is adsorbed. 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 parameters. That is, the parameters that is involved in the rate law. So, the next step is actually to design a reactor. So, let us consider a tubular reactor filled with catalyst.

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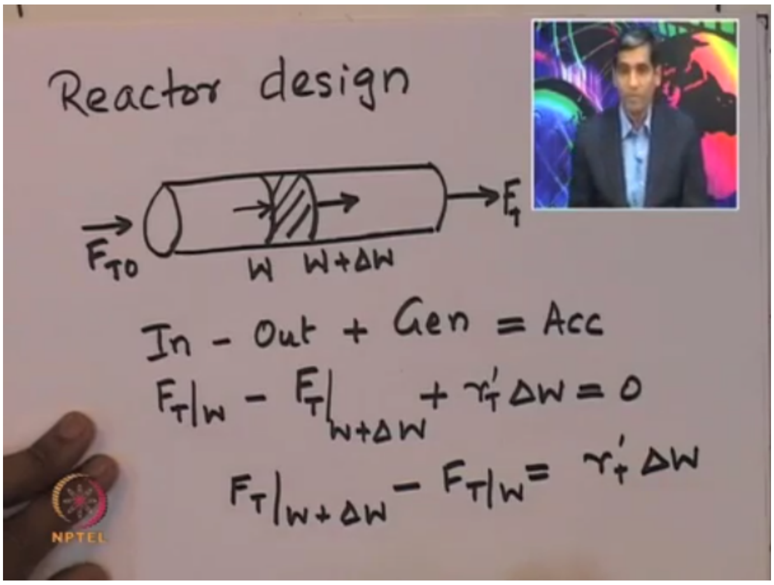

Reactor design

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, we get into the reactor design. So, let us consider a tube which is filled with catalyst. And if F T nought is the molar flow rate at which toluene is actually entering this particular reactor. And let us assume that F T 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 + 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 – what leaves this element + whatever is generated in this particular element, in this element, whatever is generated in this element should be = the amount of material that is being accumulated in that element. So, what enters that element?

It is the F T, that is the molar flow rate of T at W where the weight of the catalyst up to that point is W – the molar flow rate F T of toluene at W + delta W + if the reaction rate is – r T, then r T prime multiplied by delta W = 0. So, that is the rate law. So, where r T prime is the generation of, the rate at which the toluene is being generated. And delta W is basically the amount of catalysts which is packed in that particular element. So, we can simply rewrite this as F T W + delta W – F T W = r T prime into delta W.

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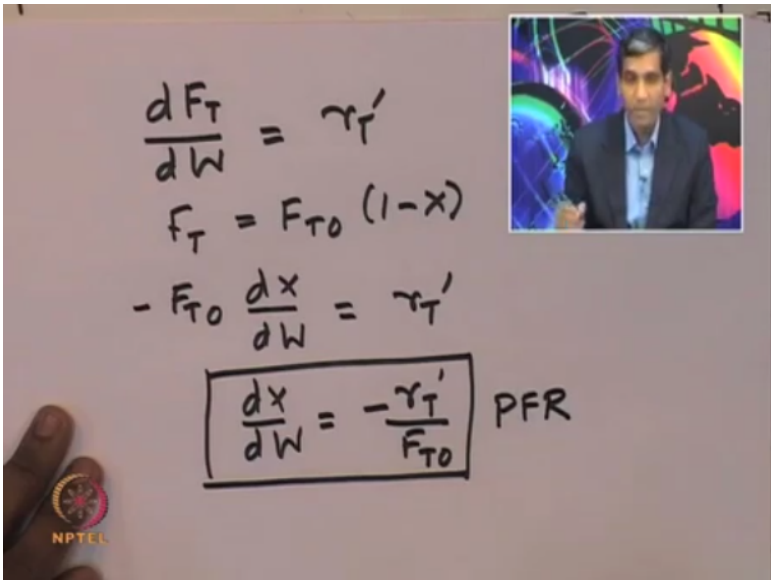

$$\frac{dF_T}{dW} = r_T'$$

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

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

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

And this can be rewritten as d F T divided by d W = r T prime. Now, F T can be written in terms of the conversion. That is = F T nought into 1 – X. So, substituting the expression for the relationship between the molar flow rate of toluene and conversion, we can rewrite this as – F T nought into d X by d W = r T prime. So, therefore, d X by d W = – r T prime divided by F T nought.

So, that is the performance equation. Now by assuming that it is a plug flow reactor, by assuming that the reactor is a plug flow reactor. The moment we find the, moment we write the model equation for the reactor, we need to now plugin the rate law.

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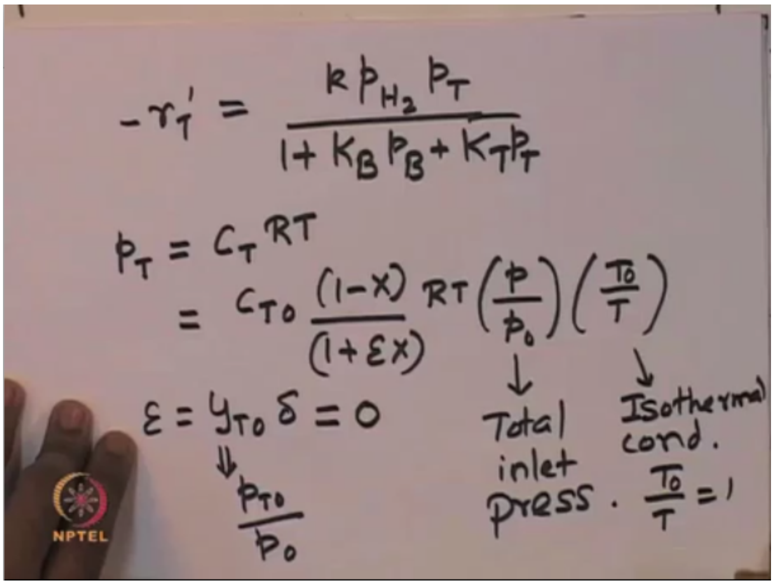

$$-r_T' = \frac{k\,p_{H_2}\,p_T}{1+K_B p_B + K_T p_T}$$

$$p_T = C_T RT$$

$$= C_{T0}\frac{(1-x)}{(1+\varepsilon x)} RT \underset{\substack{\downarrow \\ \text{Total inlet press.}}}{\left(\frac{p}{p_0}\right)} \underset{\substack{\downarrow \\ \text{Isothermal cond.}}}{\left(\frac{T_0}{T}\right)}$$

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

$$\Downarrow$$

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

$$\frac{T_0}{T} = 1$$

So, we know that the rate law is given by k into the partial pressure of hydrogen, partial pressure of toluene divided by 1 + K B into partial pressure of benzene + K T into partial pressure of toluene. So, we can now plugin 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 conversion. So, we can do that. So, partial pressure of toluene is given by the concentration of toluene multiplied by r into T using ideal gas law. And form stoichiometric relationship this can actually be expressed as C T nought into 1 – X divided by 1 + epsilon X into R T multiplied by P divided by P nought into T divided by T nought.

Where P nought is the total inlet pressure. And Epsilon is basically given by y T nought into delta, where y T nought 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. And so, because this particular, in this particular reaction these number of moles is actually 0. So therefore, this epsilon is = 0 which accounts for the change in the volume.

And if we assume that it is isothermal, if we assume that the reaction is conducted at isothermal conditions, then T by T nought is = 1. So now, using these assumptions, we can now rewrite the, we can now express the pressure, partial pressure of toluene in terms of the conversion as:

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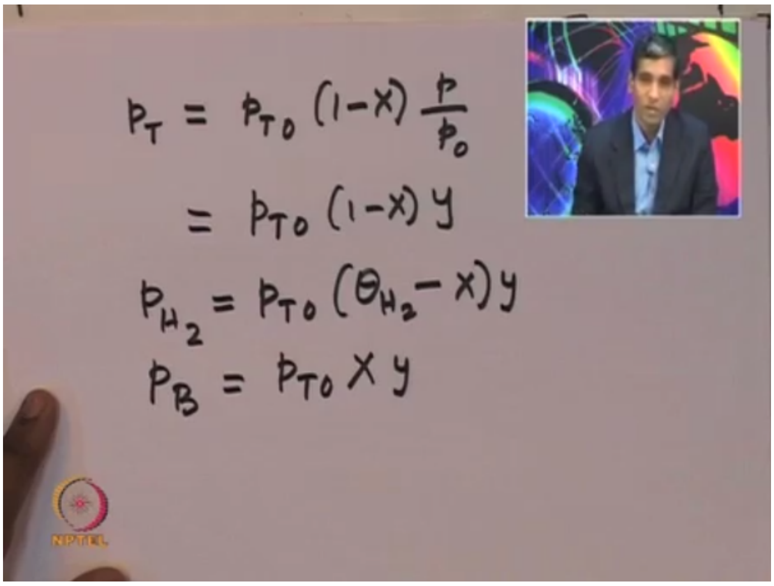

$$p_T = p_{T0}(1-X)\frac{p}{p_0}$$

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

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

$$p_B = p_{T0}Xy$$

P T nought multiplied by 1 – X into P by P nought. Now P is essentially the pressure at that particular location. And so, if I call that as y. So now, we can write this as P T nought into 1 –

X into y 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 P T nought multiplied by theta H 2 – X into y.

And partial pressure of benzene can be written as P T nought into X where theta H 2 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 present in the feed. So, in order to find the conversion profile as a function of the catalyst weight;

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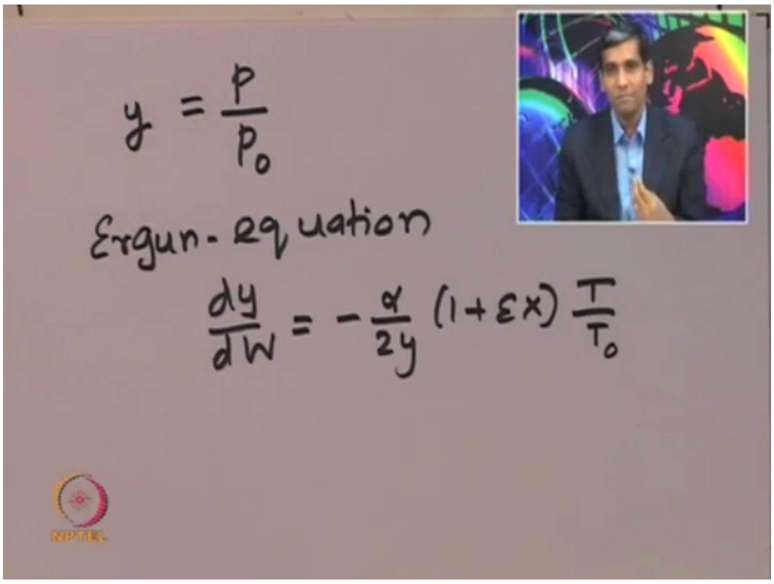

$$y = \frac{P}{P_0}$$

Ergun- equation

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

We 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 the quantity y. So, the Ergun equation can actually be written as d y by d W = – alpha by 2 y into 1 + epsilon X into T by T nought. 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, 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 a, 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.