Chemical Reaction Engineering II
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Lecture - 5
Heterogeneous data analysis for reactor design – II

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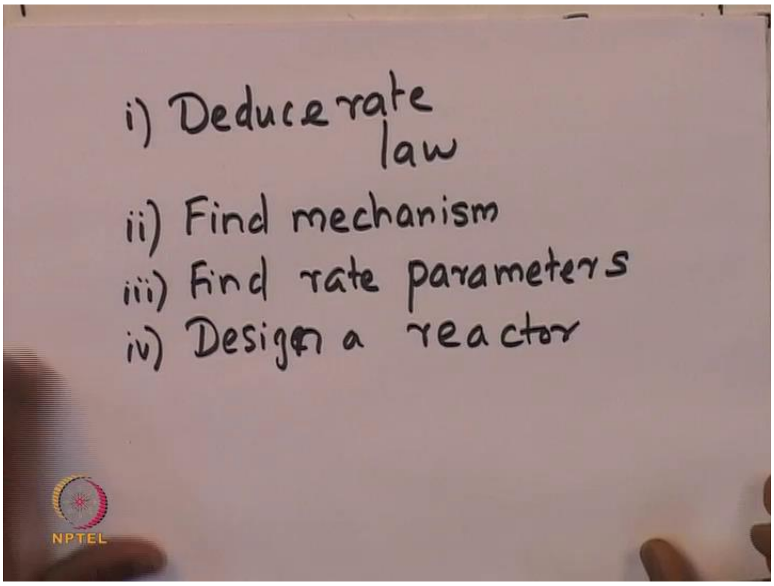

i) Deduce rate law
ii) Find mechanism
iii) Find rate parameters
iv) Design a reactor

Friends, let us summarize what we have learnt in the last lecture. So, we have learnt how to if there is a heterogeneous catalytic reaction; we have learnt how to deduce the rate law from experimenter data. Deduce the rate law; we have learnt the second step how to find mechanism. How to find the mechanism behind a certain catalytic reaction? We found for a particular example we found the rate parameters; we found the rate parameters and then we initiated discussion on how to design a reactor. In particular, we considered the example of hydroxymethylation of toluene on solid mineral catalyst containing a certain material called cleanotilite. We looked up the experimental data for that particular reaction and then we try to deduce the mechanism and try to estimate the rate parameters.

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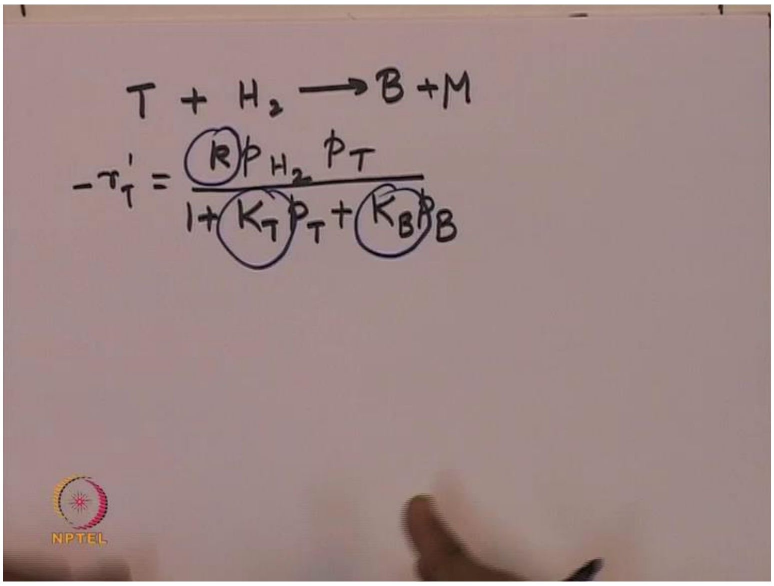

$$T + H_2 \longrightarrow B + M$$

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

We found that for the toluene reacting with the hydrogen leading to benzene and methane formation. So, for that reaction we deduce that the rate of the reaction can be represented as the rate of consumption of the toluene can be written as some rate constant k, multiplied by the partial pressure of hydrogen, multiplied by the partial of toluene, divided by 1 plus the absorption constant for toluene, multiplied by the partial pressure of toluene, plus the absorption constant for benzene, multiplied by the partial pressure of benzene.

So, then we use the experimental data in order to perform a linear regression analysis and estimate these parameters k estimates the parameters K estimates the parameters K T and also K B from experimental data. Then, we initially discussion on a design of a reactor using this rate law; so while designing the reactor we wrote a mole balance and found what is the balance equation that represents the captures the conversion in the reactors as a function of the weight of the catalyst.

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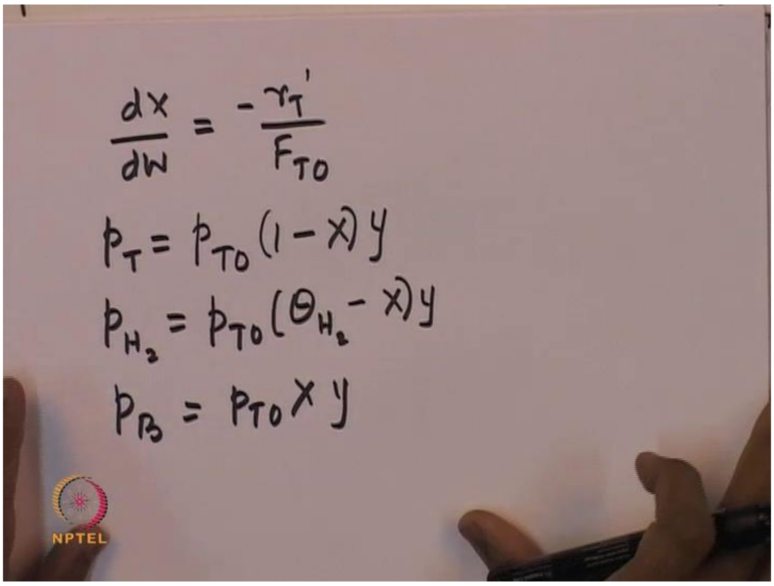

$$\frac{dX}{dW} = -\frac{r_T'}{F_{T0}}$$

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

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

$$p_B = p_{T0}Xy$$

So, that turned out to be dX by dW, X is the conversion and W is the weight of the catalyst in the reactor equal to minus r T prime divided by F T 0, where minus r T prime is the rate at which toluene is actually being consumed in the reaction and also F T 0 is the initial field molar weight of toluene species, which is participating in the reaction. You also found that the partial pressure of toluene can actually be expressed as the partial pressure of toluene of the inlet p T 0 multiplied by 1 minus the conversion into y which is the mole fraction.

Similarly for partial pressure of hydrogen, which is expressed as p T 0 into the field ratio of hydrogen to toluene minus the conversion into mole fraction and for benzene it will be p T 0 into X into y. So, we will continue from there today.

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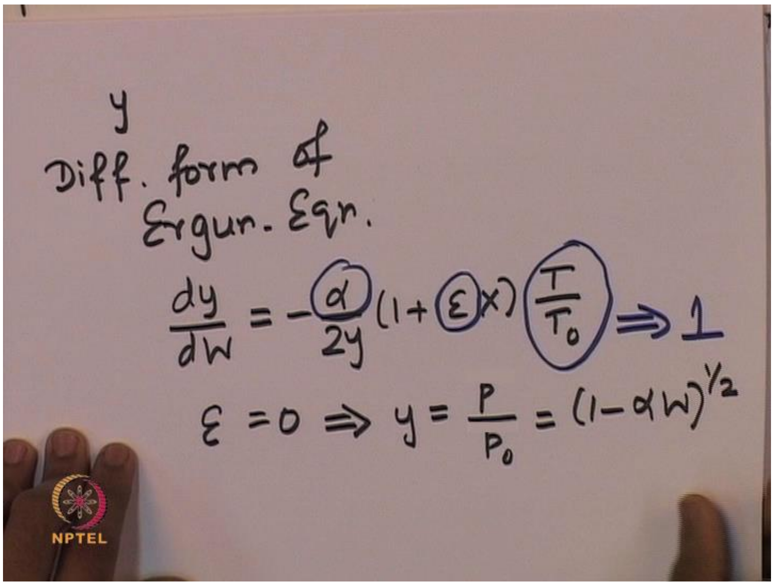

y

Diff. form of Ergun. Eqn.

$$\frac{dy}{dW} = -\frac{\alpha}{2y}(1+\varepsilon X)\left(\frac{T}{T_0}\right) \Rightarrow 1$$

$$\varepsilon = 0 \Rightarrow y = \frac{P}{P_0} = (1-\alpha W)^{1/2}$$

So, the first the first exercise is to find out what is this expression for what is y that is what is the mole fraction and that can be obtained; what is the relationship of mole fraction and the and the other and the conversion inside the reactor. This can actually be found out using the differential form of organic region, differential form of organic region. This is, which can be written as dy dW that is equal to minus alpha by 2 y multiplied by 1 plus epsilon X into T by T naught, where alpha is the pressure drop parameter; alpha is the pressure drop parameter; epsilon is the epsilon is the total fractional change in the number of moles and X is the conversion and T is the temperature at that location and T naught is the inlet temperature.

If we assume that it is an isothermal condition then T by T naught is equal to 1; if we assume that it is an isothermal the reactors actually reaction is under isothermal condition. Then, the temperature in the reactor is same as the inlet temperature of the fluid string and therefore, T by T naught we will be equal to 1. For the chosen reaction the epsilon, this is the total change in the number of moles; because of the reaction is equal to 0 because the net stoichiometric coefficient is 0. From here we can solve the differential organic equation and obtain the present for y as a function of the other parameters, which is P by P naught equal to 1 minus alpha times W to the power of half, where alpha is the pressure drop parameter and W is the weight of the catalyst.

So, the mole fraction at any location in the reactor will now depend upon how much catalyst is present in that location and the corresponding pressure drop parameter. So, now we can actually plug this into the model equation and then we can attempt to find out what is the conversion as a function of the weight of the catalyst.

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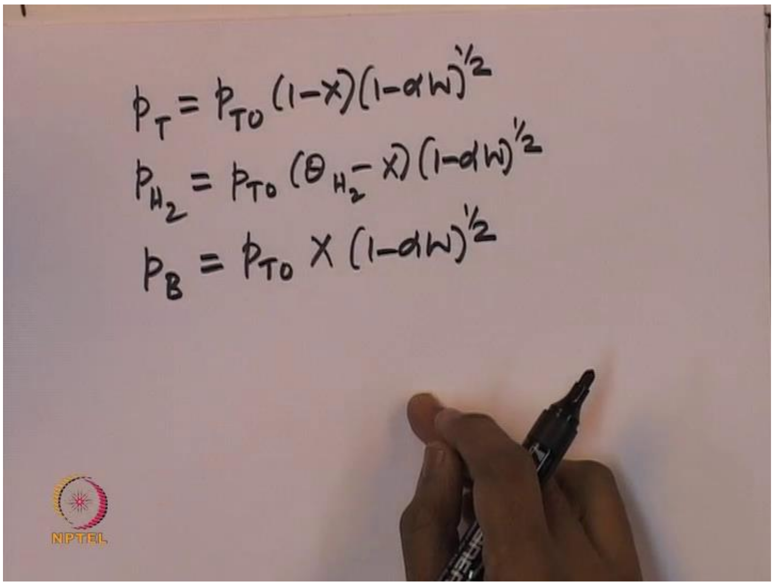

$$p_T = p_{T0}(1-X)(1-\alpha W)^{1/2}$$

$$p_{H_2} = p_{T0}(\Theta_{H_2} - X)(1-\alpha W)^{1/2}$$

$$p_B = p_{T0}\, X\, (1-\alpha W)^{1/2}$$

So, therefore, the partial pressure of toluene is now given by p T 0, which is the total partial pressure of toluene at the inlet multiplied by 1 minus X, which is the conversion into 1 minus alpha W to the power of half. Similarly that of a partial pressure of hydrogen is given by p T 0 into one theta H 2, which is the feed ratio of hydrogen versus toluene minus the conversion into 1 minus alpha W to the power of half. The partial pressure of benzene is given by P T 0 into conversion into 1 minus alpha W to the power half. So, now, we have all the information that we need to solve the equation. So, let us look at how to let us put them all together.

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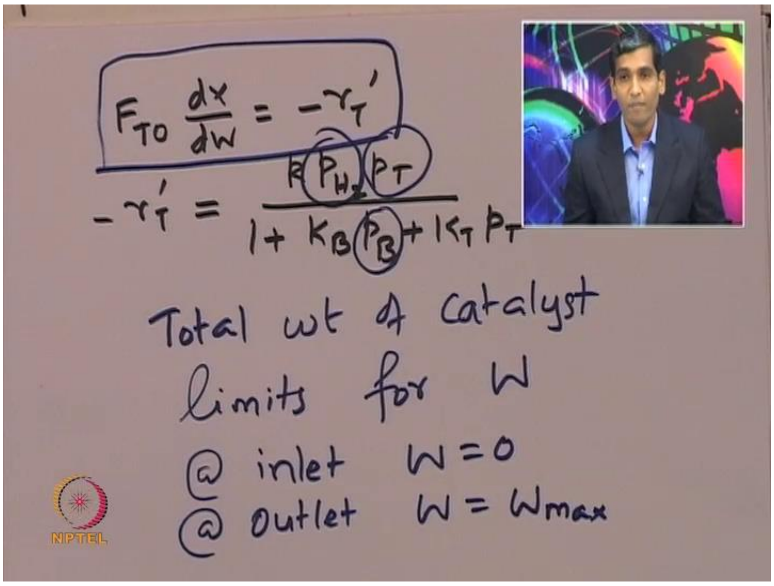

$$\boxed{F_{T0}\frac{dx}{dW} = -r_T'}$$

$$-r_T' = \frac{k P_{H_2} P_T}{1 + K_B P_B + K_T P_T}$$

Total wt of catalyst

limits for W

@ inlet $W = 0$

@ outlet $W = W_{max}$

So, the model equation that relates the conversion with the with the with catalyst is given by F T 0 multiplied by dX by dW that is equal to minus r T prime, which is the rate of generation of toluene. We know from the rate mechanism that the rate of generation is given by K into partial pressure of hydrogen, into partial pressure of toluene, divided by 1 plus K B into partial pressure of benzene plus K T into partial pressure of T toluene. So, now what we need to know is what are the limits of the integration, we know what is we know the expressions for partial pressure of hydrogen in terms of conversion; we know the expression for partial pressure of toluene in terms of conversion.

We know the expression for partial pressure of benzene in terms of conversion. Now once we know this in order to integrate the only piece of information that is required is; what is total weight of the catalyst in the reactor weight of the catalyst in the reactor. Now, why we need this because we need to in order to integrate this expression here in order integrate the expression, which is present here; we need to know what are the limits for the limits for W, which is the weight of the catalyst.

So, of course, at the inlet at the inlet the weight of the catalyst is zero. But at the outlet let us assume that there is W is given by some maximum weight of the catalyst. Now, how do we find this maximum weight of the catalyst. So, we know the expression for the mole faction as a function of the weight of the catalyst. So, what we can do is suppose if we assume that the reactor these fluid stream exits the reactor at atmosphere pressure.

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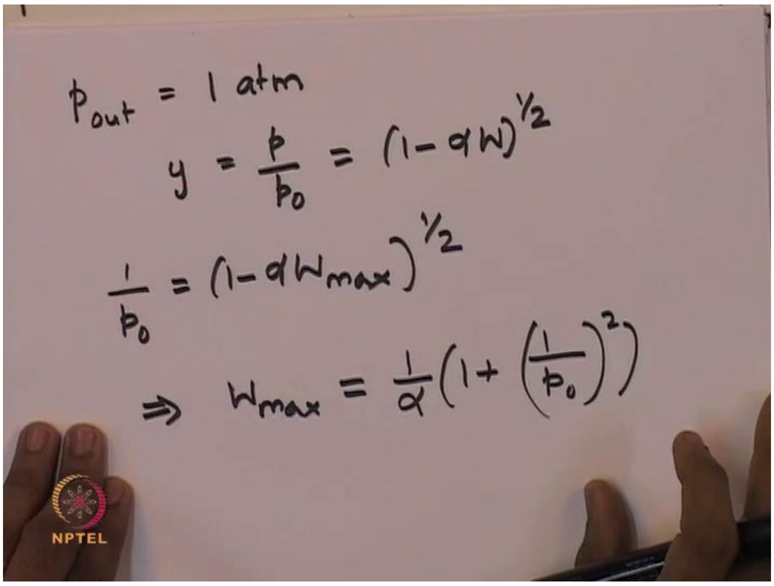

$p_{out} = 1$ atm

$$y = \frac{p}{p_0} = (1-\alpha W)^{1/2}$$

$$\frac{1}{p_0} = (1-\alpha W_{max})^{1/2}$$

$$\Rightarrow W_{max} = \frac{1}{\alpha}\left(1+\left(\frac{1}{p_0}\right)^2\right)$$

So, suppose the pressure at which the fluid stream needs the reactor is one atmosphere. Then, we will be able to estimate what is the maximum weight, because we know the relationship between the mole faction y which is p by p naught that is equal to 1 minus alpha times W to the power of half. So, from this expression we can now substitute the pressure at the exit of the reactor and find out what is the weight of the catalyst in terms of the other parameters.

So, therefore, 1 by p naught equal to 1 minus alpha W max to the power of half; so this means that the maximum weight of the catalyst, if the pressure at the outlet is one atmosphere that will be equal to 1 by alpha into 1 plus 1 by p naught whole square. So, now, we have all the required information in order to integrate the model equation.

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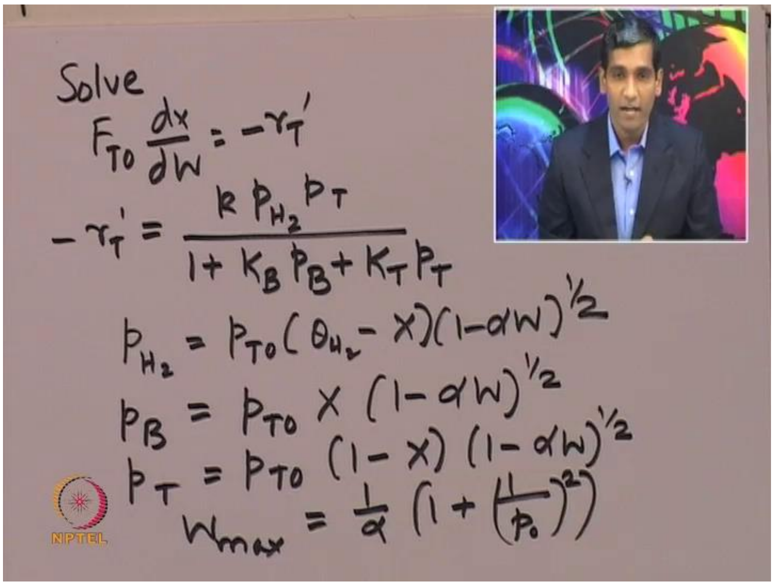

Solve

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

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

$$p_{H_2} = p_{T0}(\theta_{H_2} - X)(1-\alpha W)^{1/2}$$

$$p_B = p_{T0}\,X\,(1-\alpha W)^{1/2}$$

$$p_T = p_{T0}\,(1-X)\,(1-\alpha W)^{1/2}$$

$$W_{max} = \frac{1}{\alpha}\left(1 + \left(\frac{1}{p_0}\right)^2\right)$$

So, let us look let us put them all together. So, we need to solve we need to solve this equation F T naught into dX by dW equal to minus r T prime with the rate of the equation being the rate of the generation of species toluene being k into partial pressure of hydrogen, partial pressure of toluene divided by 1 plus the equilibrium constant for be benzene, multiplied by the partial pressure of benzene plus the equilibrium constant of toluene, multiplied by the partial pressure of toluene. We know that partial pressure of hydrogen is equal to p T naught into theta H 2 minus X into 1 minus alpha W to the power of half.

Then, the partial pressure of benzene is given by the inlet partial pressure of toluene multiplied by the conversion into 1 minus alpha W to the power of half and the partial pressure of toluene is given by p T 0 into 1 minus X into 1 minus of alpha W to the power of half and the maximum weight of the catalyst is given by 1 by alpha into 1 plus 1 by p 0 to the power 2. So, this gives you this captures the model equations and all the others necessary relationship between the partial pressures and the conversion in order to find the conversion as a function of the weight of the catalyst.

So, remember that the weight of the catalyst at the inlet of the reactor zero and at the outlet of the reactor is the maximum weight that can be packed, maximum catalyst that can be packed inside the reactor. So, let us look at how the solution is going to look like. So, if you have the numbers and if we have the quantities all the required quantities then in principle, we should be able to integrate this expression and find the profile of conversion as a function of rate of the catalyst.

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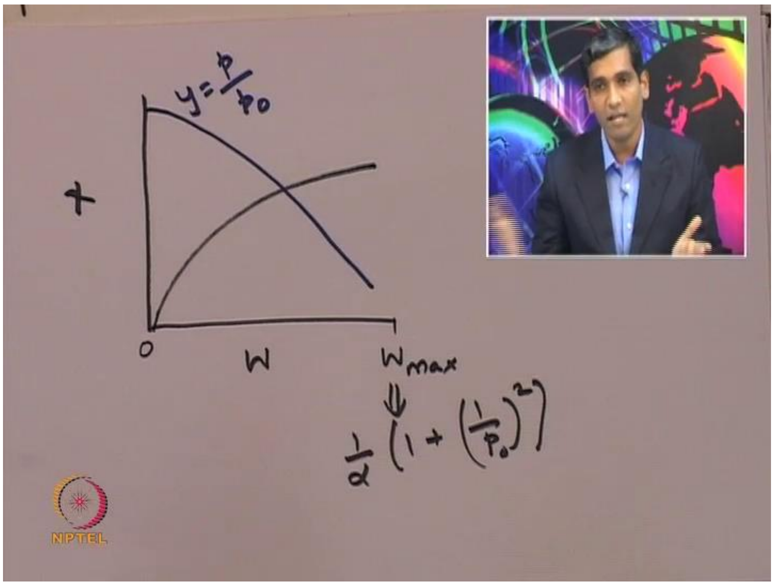

So, let me just sketch here I will sketch the profile of the conversion as a function of weight of the catalyst. So, suppose in the X axis I have the weight of the catalyst going from 0 to the maximum weight. So, remember that the maximum weight is given by 1 by alpha into 1 plus 1 by p naught the whole squares. If I plot X, which is the conversion then the conversion as you go into the reactor as the fluid streams is mole capitalist; you see that there is an increase in the a conversion as a function of the weight of the catalyst. While if you look at the pressure drop inside the mole fraction inside the reactor the mole faction why the overall mole faction why actually goes down.

So, this is y equal to p by p naught. So, that actually goes down because the reaction is being the action is being conducted and the reaction is happening as the fluid stream go through the reactor. We can there we can actually get much more information than this. So, we can actually look at the how the partial pressure changes with the weight of the catalyst.

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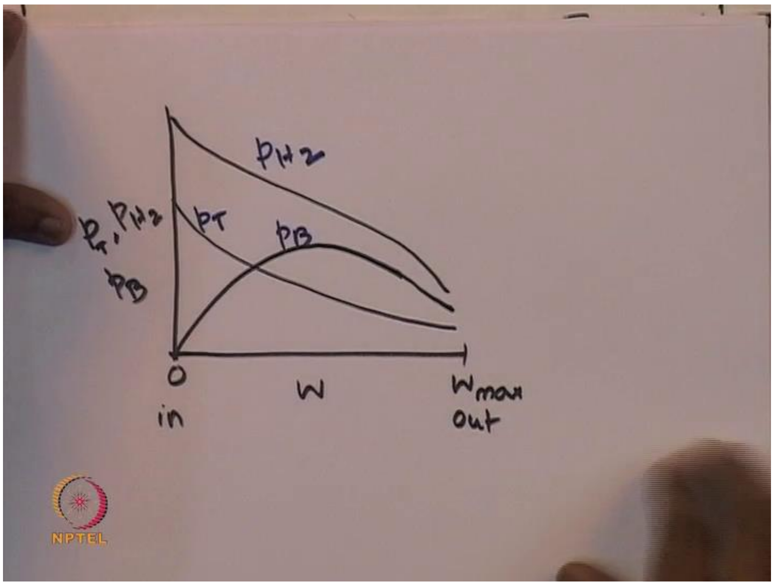

So, if I plot that is the maximum weight of the catalyst that is the exit of the reactor. So, this is the inlet stream and this is the outlet stream that is the outside location of the reactor. So, if I plot the partial pressures of toluene, partial pressure of hydrogen and partial pressure of benzene for typical set of parameters will see that the partial pressure of hydrogen has a profile its looks like this and then we have a toluene partial pressure which actually decreases. Because the toluene is being consumed and then the benzene partial pressures this is the kind of profile that is observed.

Now, the reason for to this is for this is the partial pressure for hydrogen, partial pressure for toluene and the partial pressure of benzene. Now, the reason why the partial pressure of benzene goes through a maxima because we set that the outside pressure is the pressure of at which the stream leaves the reactor is one atmosphere. So, there is clearly a pressure drop, and then and the pressure drop actually causes the partial pressure of benzene to go through a maximum and then towards the exit of the reactor its stop falling down. So, this sort of captures systematically the method for designing a reactor starting from experimental data.

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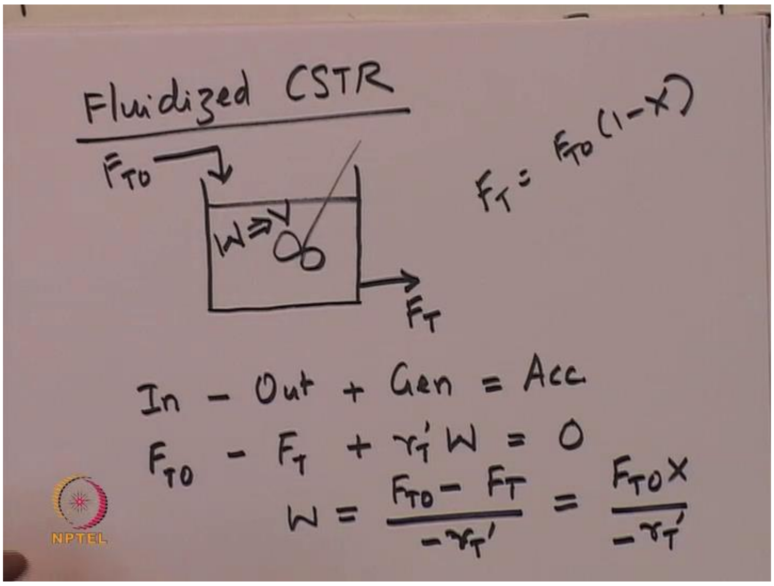

Fluidized CSTR

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

In − Out + Gen = Acc

$F_{T0} - F_T + r_T' W = 0$

$W = \frac{F_{T0} - F_T}{-r_T'} = \frac{F_{T0} X}{-r_T'}$

So, let us look at what happens if the if we conduct the reaction a fluidized CSTR. So, suppose if we take a fluidized CSTR. So, CSTR is a essentially a tank and this a fluid that goes into the CSTR and its well mixed and there is a fixed volume and as an outlet stream. Generally, for a fluidized the inlet is at the bottom and exit at the top. Just for the sake of convenience we assumed other way here. So, the question is how much catalyst weight of the catalyst or how much catalyst that is needs to be packed, which you directly correlate to the volume of the reactor.

So, how much catalyst has to be packed inside the CSTR in order to obtain the same conversion. So, if F T naught is deemed a law flow rate of toluene at the inlet at the inlet stream of the CSTR and F T is the law flow rate at which the toluene leaves that the reactor. Then as a simple mass balance can be mole balance can be return in order to estimate the amount of catalyst, which is required for obtaining the same conversion in a fluidized CSTR. So, the simple mass mole balance suggest that the rate at which the stream enter the reactor minus the rate at which things leave plus the generation should be equal to the accumulation.

So, now what the rate at which moles enter the CSTR is given by F T naught toluene minus the rate at which leaves is F T plus the rate at which it is generated is given by r T prime, which is basically the moles of toluene consumed per gram of catalyst per unit time multiplied by weight of the catalyst and that should be equal to 0 if it is steady state.

So, we can now rewrite this equation and we can say that the weight of the catalyst is given by F T 0 minus F T divided by minus r T prime. So, from here we know that F T, which is the rate molar rate at which the molar flow rate at which the species leaves the reactor is related to the conversion because F T is given by F T naught into 1 minus X.

So, therefore, we can rewrite this expression as F T naught into X divided by minus r T prime. So, if we know what the conversion in the packed bed reactor, then we should be able to use that conversion and if it is the same conditions that is the same flow rate molar flow rate at which the species enters the CSTR. Then, we will be able to estimate what is the weight at which the same conversion can be obtained if you use a fluidized CSTR and this provides an important parameter in terms of designing the reactor.

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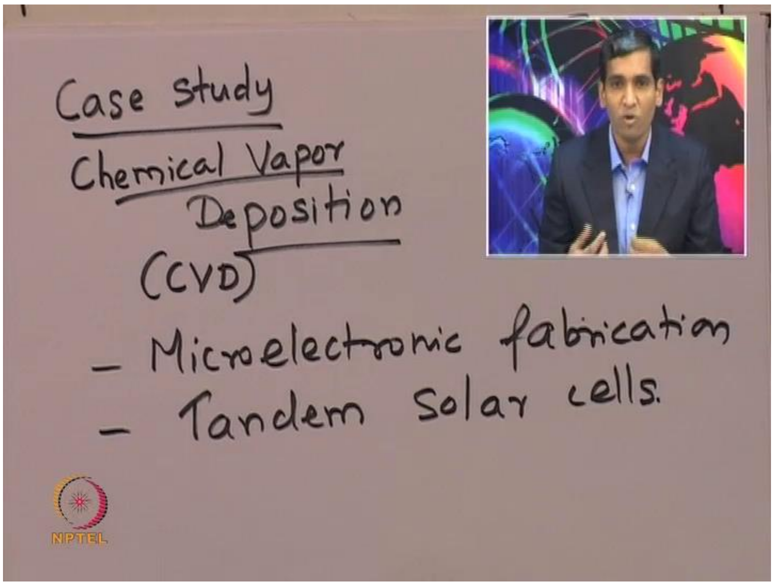

Case study

Chemical Vapor Deposition (CVD)

- Microelectronic fabrication
- Tandem Solar cells.

So, let us next look at a specific case study. So, we look at the chemical vapor deposition process; I will take the example of chemical vapor deposition process, which here after I will refer to as CVD. So, chemical vapor deposition is actually an important process in the microelectronic fabrication and it actually plays a strong role in in manufacturing the tandem or the multi-layer solar cells. So, the chemical vapor deposition is essentially depositing a particular material on a given substrate.

So, it is very similar to the heterogeneous catalysis process and it has a several applications in a microelectronic fabrication, microelectronic fabrication and it has applications in a manufacturing of tandem solar cells. So, we will take a specific case of a chemical vapor deposition, which is applicable to microelectronic fabrication. See, how it can be viewed as a heterogeneous catalytic system? How it can be molded in order to obtain certain design parameters?

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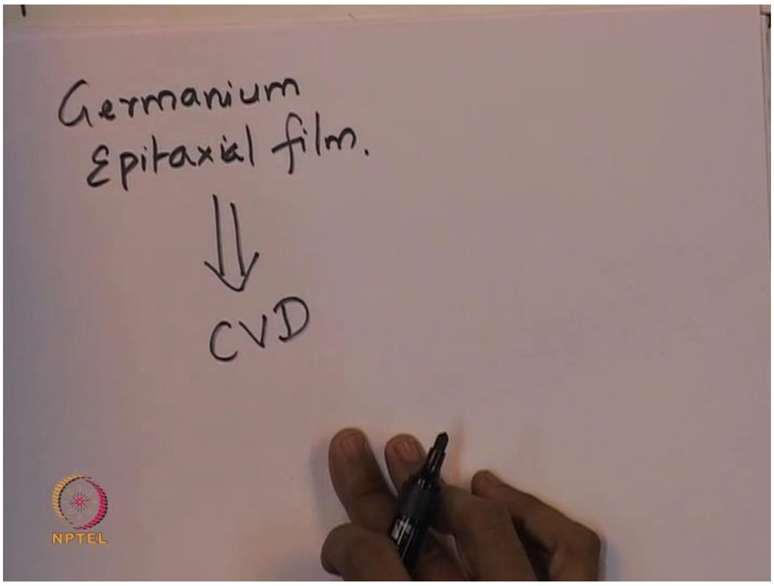

An interesting example of that is a growth of germanium epitaxial film; germanium epitaxial film is actually interesting example. So, while manufacturing in microelectronic fabrication it is important to have different layers between the gallium arsenide and silicon. So, germanium epitaxial film is servers a very good purpose of acting as an intern layer between the silicon layer, which is present and on top of it will be the gallium arsenide. it also acts as a good contact layer. So, the growth of this epitaxial film is actually obtained by using this process called the chemical vapor deposition. So, the mechanism that actually governs such a deposition process is actually very similar to that of the heterogeneous catalytic reaction.

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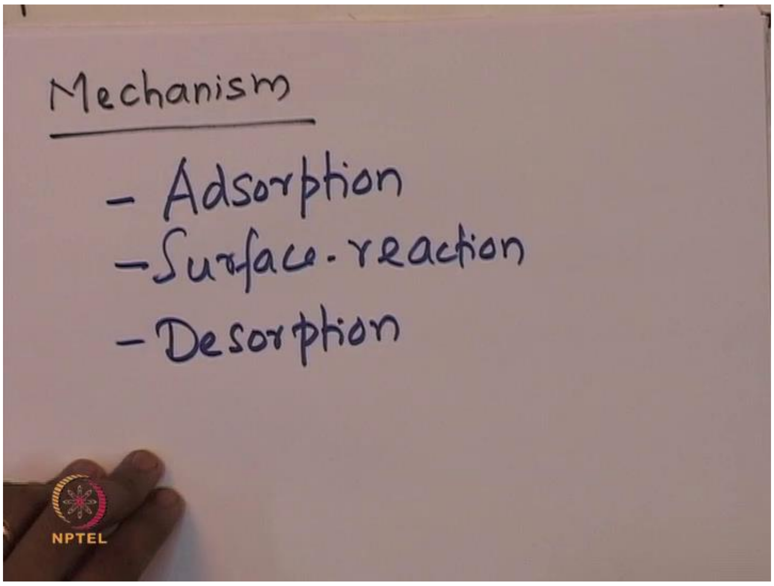

Mechanism

- Adsorption
- Surface reaction
- Desorption

So, if you look at the mechanism it is very similar to that of the heterogeneous catalytic systems. So, it involves the classical three processes is one is the adsorption, adsorption of the reactants onto the surface of a substrate and followed by a substrate reaction followed by a surface reaction and then followed by desorption; in addition to this may be gas phase reactions. So, it is the adsorption of reactance onto a substrate followed by a surface reaction and then followed desorption depending upon the nature of the reaction in some cases there may not be desorption and some cases that may be desorption step. So, it is very similar to the catalytic heterogeneous catalysis processes that we have we have learnt so far. So, we will use those principles in order to model this epitaxial film growth process.

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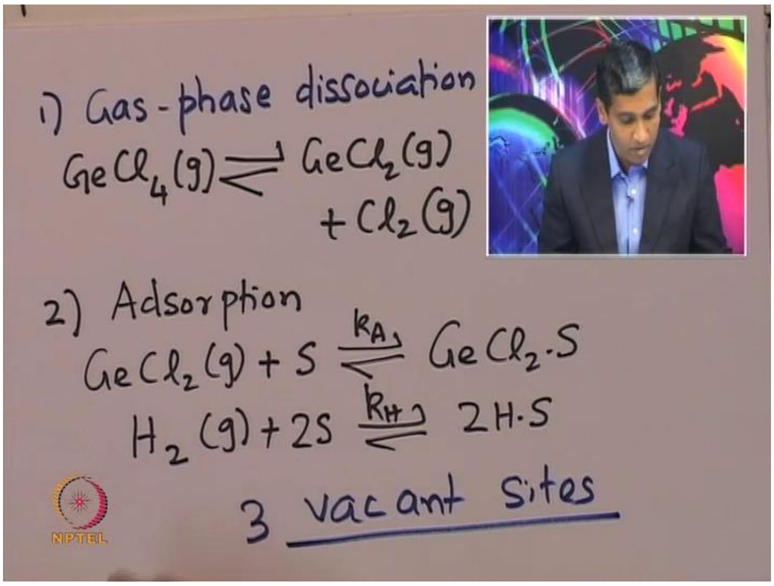

1) Gas-phase dissociation

$$GeCl_4(g) \rightleftharpoons GeCl_2(g) + Cl_2(g)$$

2) Adsorption

$$GeCl_2(g) + S \overset{k_A}{\rightleftharpoons} GeCl_2 \cdot S$$

$$H_2(g) + 2S \overset{k_H}{\rightleftharpoons} 2H \cdot S$$

3 vacant sites

So, the mechanism it involves three steps; the first step is the actually four steps, first step is the gas phase dissociation, gas phase dissociation step. Now, in the gas phase dissociation what happens is that the germanium chloride G e c l 4 G e c l 4 in the gas phase. Now, that reversibly gets converted into the germanium c l 2 the gas phase plus c l 2 plus chlorine. The second step is the adsorption process, where the germanium chloride G e c l 2 in the gas phase it adsorbs on to the catalyst site. It is an equilibrium process, if K a is the specific constant corresponding to that and G e c l 2 dot S, which is which basically represents the adsorption of germanium chloride onto the catalytic site.

Now, here germanium chloride actually reacts with the hydrogen and so in this particular case the hydrogen gas in the gas phase also get adsorb to the catalyst site. So, it actually interacts with two catalyst two vacant catalyst site. So, if I if there specific constant for that particular forward step or by adsorption step is k H, then it leads to that. So, one molecule of hydrogen actually by ends two sides to vacant site, which is available.

So, there are now three sites which are actually so there are three catalyst sites are actually involved; three vacant sites are required. Three vacant sites are required for these processes, this process this catalytic process and so then the next step is basically the surface reaction.

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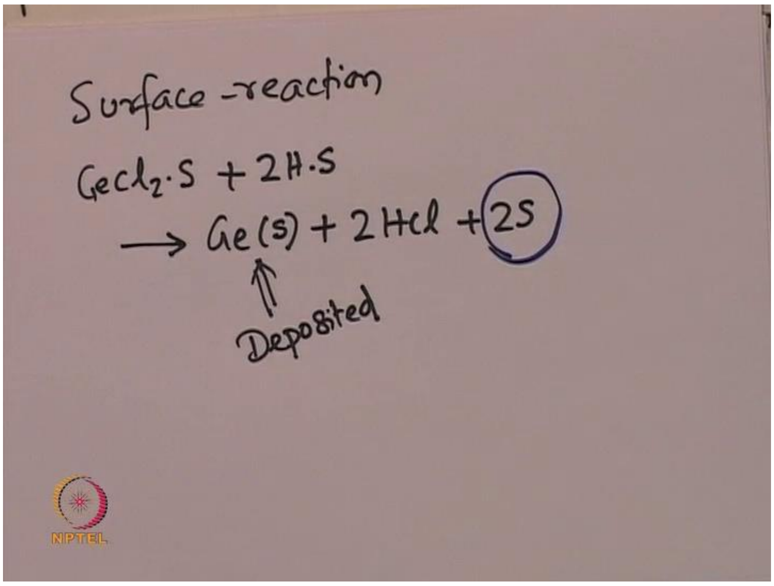

Surface -reaction

$GeCl_2 \cdot S + 2H \cdot S$

$\longrightarrow Ge(s) + 2HCl + \boxed{2S}$

$\Uparrow$

Deposited

So, the next step is the surface reaction process where it is the surface reaction process, where the germanium chloride which is now adsorbed to the catalysts site interacts with the hydrogen atoms, which are actually adsorb it two vacant sites, two sites leading to formation of germanium. In the solid form, this is actually deposited on the surface of the substrate plus 2 H c l plus 2 vacant sites. Now, so basically this is the one which is deposited the germanium which is formed because of this reaction is the one which is deposited on the substrate. After the reaction, it may appear that there are only two vacant site, which are actually left out it may appear that there only two vacant sites.

Now, that is not true because the germanium, which is deposited also becomes active. So, subsequently the deposited germanium in its solid form also acts as a as an active site for binding of germanium chloride or the hydrogen atom itself. So, therefore, in addition to the two vacant sites, which are creates the germanium deposit also acts as an active site. So, totally there are three vacant sites three active sites that are actually created because of the reaction. So, really there is no loss of active sites on the catalyst because of the action.

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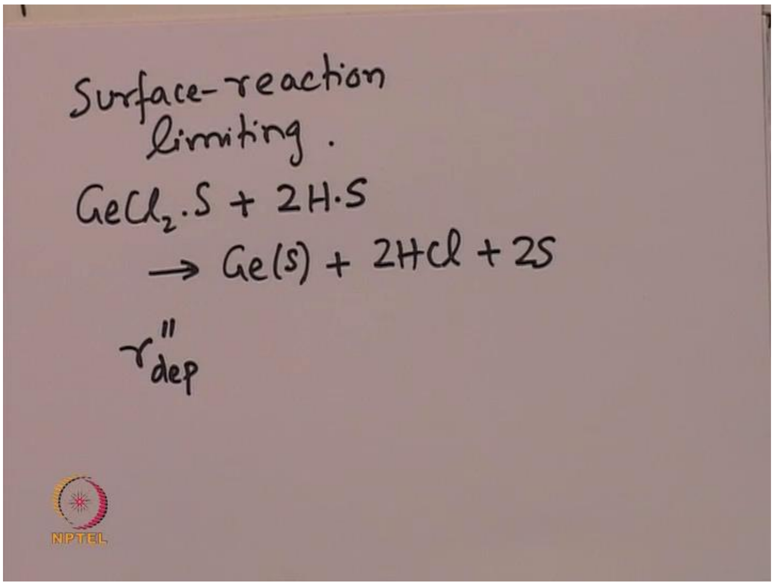

Surface-reaction limiting.

$$GeCl_2\cdot S + 2H\cdot S \rightarrow Ge(S) + 2HCl + 2S$$

$$r''_{dep}$$

So, now if I assume that the surface reaction is the limiting reaction. Then, I can write or I can find out what is the rate of deposition of germanium? So, the surface reaction is G e c l 2, which is adsorbed to the surface plus the two hydrogen atoms, which adsorbed to the surface leads to the deposition of germanium in the solid form, plus 2 H c l plus 2 vacant sites.

So, now based on this reaction we can actually write a rate of deposition of germanium. So, rate of deposition of germanium must be a function of the total number of active sites, which are actually present and total number of active sites on which the germanium chloride adsorbed and also the total number of active sites on which the hydrogen atoms are adsorbed.

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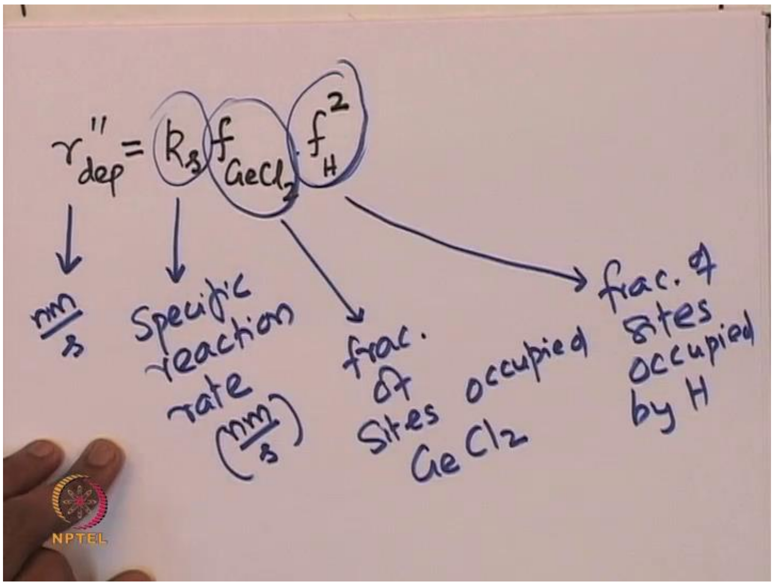

So, therefore, we can write this reaction rate as r deposition is equal to the specific reaction rate multiplied by the fraction of sites, which are occupied by the germanium chloride multiplied by the fraction of sites, which has occupied by the hydrogen atom and thus square of that. So, the reason why there is a square here because for every reaction, every surface reaction which is assume irreversible. There are two catalytic sites are actually involved in the surface reaction. Two catalytic sites containing adsorbed hydrogen atoms are actually involved in the reaction.

Therefore, the rate of deposition has to be some constant reaction specific reaction rates multiplied by the fraction of sites on which the germanium chloride is adsorbed and multiplied by the square of the fraction of sites on which the hydrogen atom is adsorbed. The unit of the rate is actually nanometers per second, so that is the rate this can actually be converted into the molar units by multiplying the molar density. This is the specific reaction rate and the units are nanometers per second, and this is the fraction of sites occupied by germanium chloride and this is the fraction of sites occupied by hydrogen atom.

So, this sort of captures the rate of deposition of germanium on the substrate. So, now the exercises to find out what is the fraction of germanium chloride, which is absorbed onto the surface and what is the faction of the hydrogen atom, which is adsorbed on to the surface. So, this can be obtained by looking at the expression looking at the adsorption process. So, the adsorption steps, so let us look at a little more deeply into the adsorption steps there are two adsorption steps; one is the germanium chloride, which adsorbs on to the vacant sites and the hydrogen adsorbs on two vacant sites.

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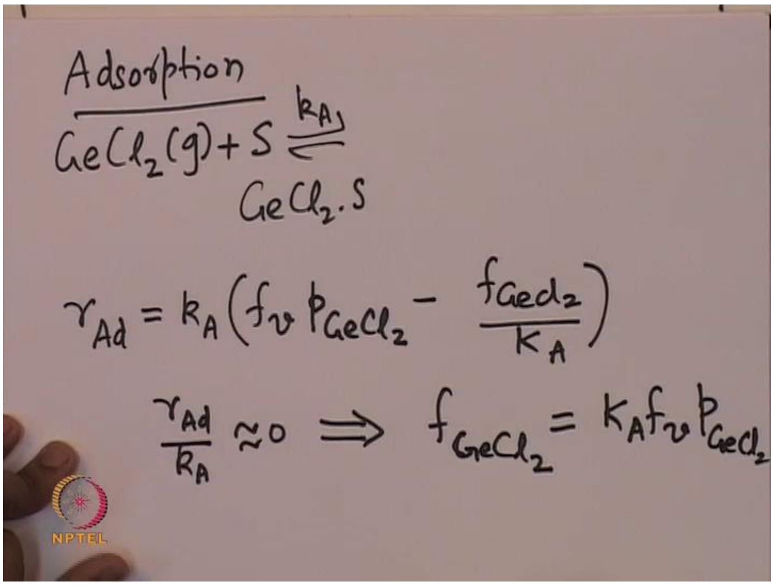

Adsorption

$$GeCl_2(g) + S \underset{}{\overset{k_A}{\rightleftharpoons}} GeCl_2.S$$

$$r_{Ad} = k_A \left(f_v \, p_{GeCl_2} - \frac{f_{GeCl_2}}{K_A} \right)$$

$$\frac{r_{Ad}}{k_A} \approx 0 \Rightarrow f_{GeCl_2} = K_A f_v \, p_{GeCl_2}$$

So, the first absorption step is G e c l 2 in the gas phase plus a particular vacant site reversibly; it is an equilibrium process and if the k A is the corresponding specific constant gets adsorbed and leads to the adsorbed germanium chloride adsorb to the active site. So, the rate of adsorption is given by k a multiplied by the fraction of vacant sites f v, multiplied by the partial pressure of the germanium chloride in the gas phase minus the fraction of sites on to which the germanium chloride is absorbed divided by the corresponding equilibrium constant.

Now, because we assume that the surface the action is the limiting the action, the rate of absorption has to be approximately zero. So, therefore, the rate of absorption divided by k A is approximately 0 from which one can estimate that the fraction of sites on which the germanium chloride is adsorbed is given k A into fraction of the vacant site multiplied by the partial pressure of germanium chloride in the gas phase.

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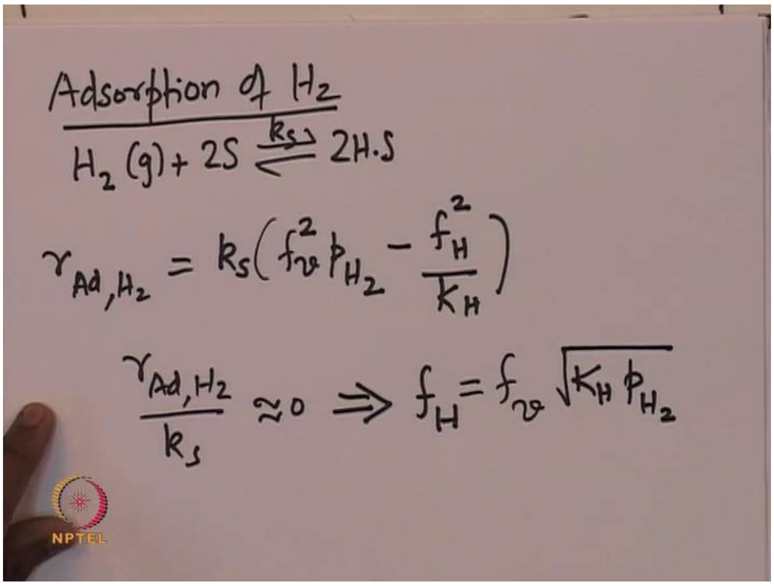

Adsorption of H_2

$$H_2(g) + 2S \overset{k_s}{\rightleftharpoons} 2H.S$$

$$r_{Ad,H_2} = k_s\left(f_v^2 p_{H_2} - \frac{f_H^2}{K_H}\right)$$

$$\frac{r_{Ad,H_2}}{k_s} \approx 0 \Rightarrow f_H = f_v \sqrt{K_H p_{H_2}}$$

Similarly, we can look at the other adsorption process, which is the adsorption of hydrogen which is the adsorption of hydrogen. So, this the reaction that corresponds to the adsorption desorption step is hydrogen plus two catalytic vacant sites if k s is the corresponding specific constant leads to two sites in which the hydrogen atoms are bound. So, now the rate of adsorption of hydrogen is given by a specific constant k s multiplied by so it needs two vacant sites. So, rate will be given by f v square multiplied by the partial pressure of hydrogen minus the fraction of sites that are actually occupied by the hydrogen atom f h square divided by the corresponding equilibrium constant.

Because we assume that the surface reaction is a limiting reaction; we can actually say that the rate of adsorption of H 2 divided by k s is approximately 0. From here, one can estimate that the fraction of sites to which the hydrogen atoms is bound is given by the vacant sites f v multiplied by square root of the equilibrium constant for hydrogen adsorption multiplied by the partial pressure in the gas phase of hydrogen in the gas phase. So, now the total number of sites which is present in the catalyst is actually a constant because it is a conservation property.

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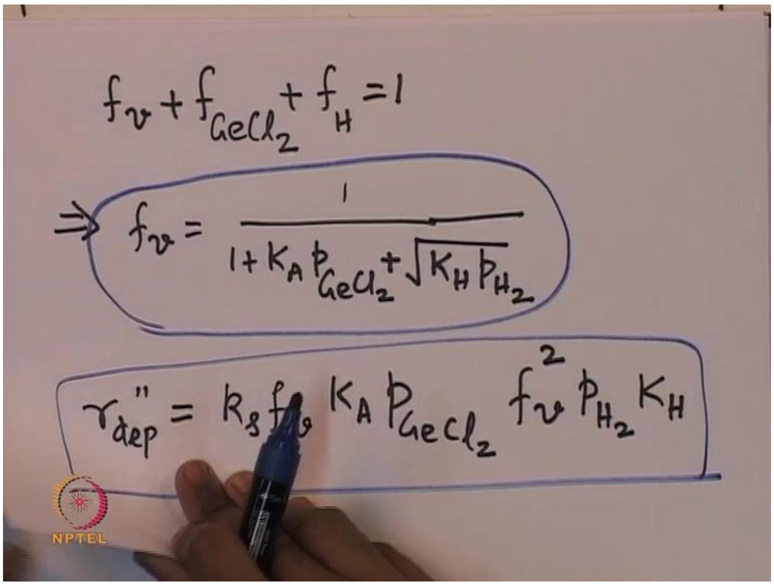

$$f_v + f_{GeCl_2} + f_H = 1$$

$$\Rightarrow f_v = \frac{1}{1 + K_A p_{GeCl_2} + \sqrt{K_H p_{H_2}}}$$

$$r''_{dep} = k_s f_v K_A p_{GeCl_2} f_v^2 p_{H_2} K_H$$

So, therefore, that can be written the conservation property can be written as f v, which is the total fraction of vacant sites side sites plus the sites on which the germanium chloride is bound plus the total the fraction of sites on which the hydrogen atom bound that should be equal one. Because the total number of sites which is present in the catalyst is a constant and from here we can express that f v equal to. So, we can find we can substitute the fractional sites, on which the germanium chloride is bound and the factional sites on which the hydrogen is bound.

From this conservation property, we can estimate that the fraction of vacant sites, which is present is given by 1 divided by 1 plus k A into partial pressure of germanium chloride in the gas phase plus square root of the equilibrium constant for hydrogen adsorption multiplied by the partial pressure of hydrogen in the gas phase. So, now, we can plug all these expressions into the rate of deposition. So, the rate of deposition is now given by k s into f v into K A, f v is the vacant site number of vacant sites, which is present multiplied by the equilibrium constant for adsorption on germanium chloride multiplied by the square of the number of vacant sites, which is present multiplied by the partial pressure of hydrogen in the gas phase into the equilibrium constant for hydrogen.

So, now we know that is the relationship between the vacant site, which is available and the partial pressure of the germanium chloride in the gas phase and the partial pressure of hydrogen in the gas phase. So, we can relate we can plug in this expression in the reaction rate deposition rate expression.

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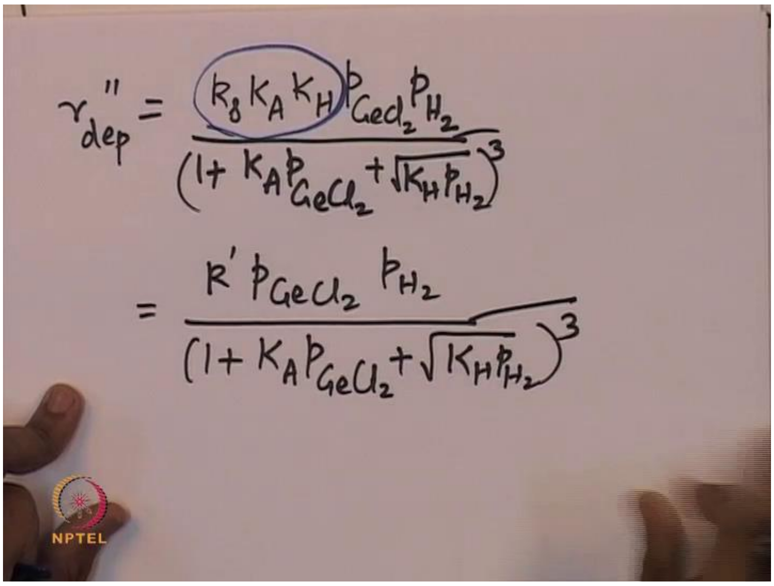

$$r''_{dep} = \frac{\boxed{k_s K_A K_H} p_{GeCl_2} p_{H_2}}{\left(1 + K_A p_{GeCl_2} + \sqrt{K_H p_{H_2}}\right)^3}$$

$$= \frac{k' p_{GeCl_2} p_{H_2}}{\left(1 + K_A p_{GeCl_2} + \sqrt{K_H p_{H_2}}\right)^3}$$

We can rewrite the we can rewrite the deposition rate expression as r deposition is equal o k s K A K H multiplied by the partial pressure of germanium in gas phase multiplied by the partial pressure of hydrogen in the gas phase divided by 1 plus K A partial pressure of germanium chloride in the gas phase plus square root of K H into p H 2 whole cube. So, now we can plug in we can collate these three constants again; we can collate three constants together and we can write it as one constant k prime. So, that will be k prime into partial pressure of germanium chloride into partial pressure of hydrogen in the gas phase divided by 1 plus K A into partial pressure of germanium chloride whole cube.

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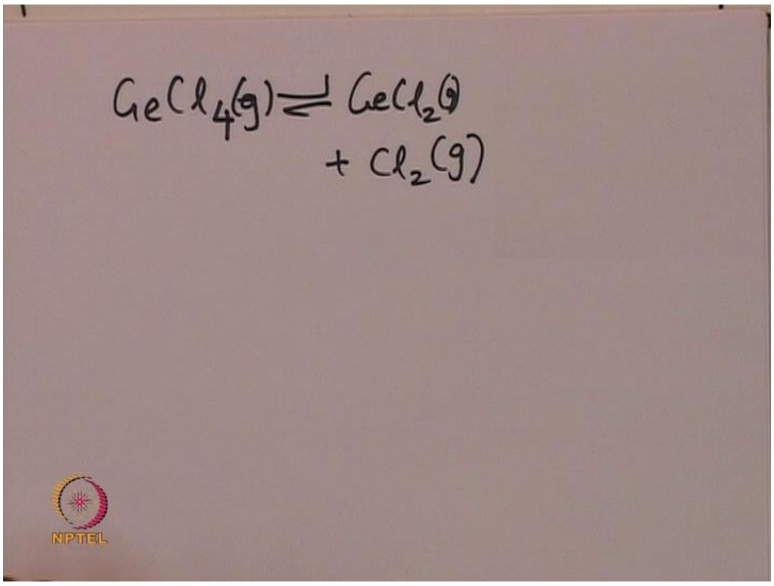

$$GeCl_4(g) \rightleftharpoons GeCl_2(g) + Cl_2(g)$$

So, now when we the germanium chloride is actually in the form of G e c l 4 c l 4 and not in G e c l 2, which is the one which gets absorbed onto the surface. So, now, there is a gas phase reaction, which actually is responsible for the conversion of are transformation of G e c l 4 into the c l 2 form. So, the gas phase reaction is given by G e c l 4 in the gas phase, c l 2 plus chlorine. So, that is the gas phase reaction. Now, one can write to an expression relating the gas phase partial pressure of the germanium chloride G e c l 4 and the germanium chloride G e c l 2. So, that can simply be to turn as because it is in an equilibrium conditions.

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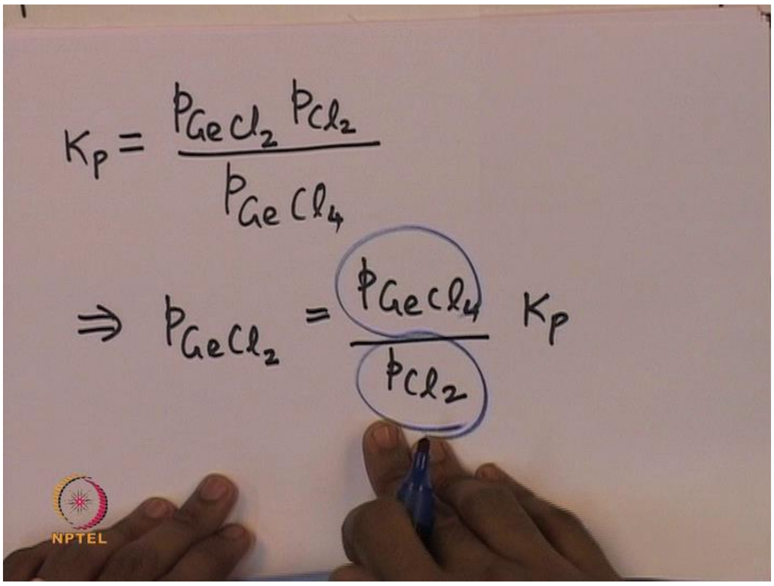

$$K_p = \frac{p_{GeCl_2}\, p_{Cl_2}}{p_{GeCl_4}}$$

$$\Rightarrow p_{GeCl_2} = \frac{p_{GeCl_4}}{p_{Cl_2}} K_p$$

We can write it as K p, which is the corresponding constant and that should be equal to partial pressure of G e c l 2 multiplied by partial pressure of chlorine divided by partial pressure of germanium c l 4. So, from here we can find out what is the partial pressure of germanium G e c l 2, which is given by c l 4 divided by partial pressure of c l 2 multiplied by K p. So, this is require to complete the problem, because what is practically measurable the quantity is actually the partial pressure of G e c l 4 and the partial pressure of chlorine. So, therefore, it is required to express the partial pressure of G e c l 2 in the gas phase in terms of the measurable quantities.

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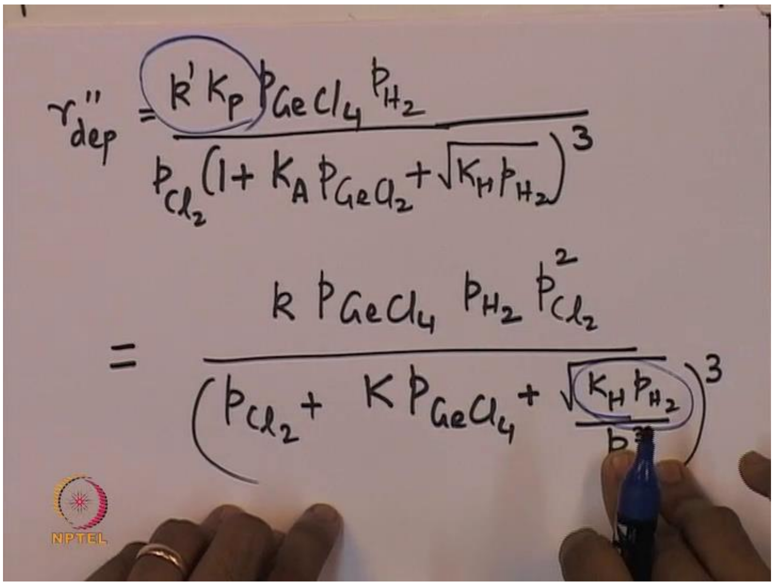

$$r''_{dep} = \frac{k' K_p \, p_{GeCl_4} \, p_{H_2}}{p_{Cl_2}\left(1 + K_A \, p_{GeCl_2} + \sqrt{K_H \, p_{H_2}}\right)^3}$$

$$= \frac{k \, p_{GeCl_4} \, p_{H_2} \, p^2_{Cl_2}}{\left(p_{Cl_2} + K \, p_{GeCl_4} + \frac{\sqrt{K_H \, p_{H_2}}}{p^{3}}\right)^3}$$

So, plugging in these measures these expressions, we can find that the net rate of deposition r dep net deposition rate is actually given by k prime K p into partial pressure germanium chloride G e c l 4 into partial pressure of hydrogen divided by partial pressure of c l 2 into 1 plus equilibrium constant K A multiplied by partial pressure of G e c l 2 plus square root of K H into partial pressure of hydrogen the whole cubes. So, we can easily rewrite this expression as with a little bit of algebra; we can rewrite this expression as k, which is basically k prime into K p.

So, we can club we can club these two constants here into one constant K multiplied by the partial pressure of G e c 4 multiplied by the partial pressure of H 2 into partial pressure of c l 2 square divided by the partial pressure of c l 2 plus constant K into partial pressure of G e c l 4 plus the square root of K H into partial pressure of H 2 divided by partial pressure of c l 2 cube the whole cube. So, now suppose if the partial pressure of hydrogen in the K H into partial pressure of hydrogen is very small suppose; if this quantity is very small then we can rewrite this expression.

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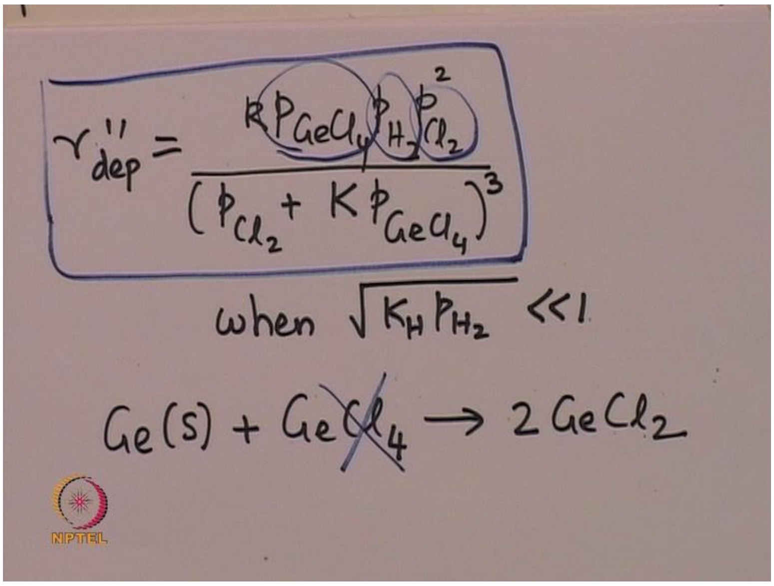

$$\boxed{r''_{dep} = \frac{k p_{GeCl_4} p_{H_2} p_{Cl_2}^2}{(p_{Cl_2} + K p_{GeCl_4})^3}}$$

when $\sqrt{K_H p_{H_2}} \ll 1$

$$Ge(s) + Ge\cancel{Cl_4} \rightarrow 2\,GeCl_2$$

We can rewrite this expression as r deposition the deposition rate is given by k into partial pressure of germanium chloride 4 multiplied by partial pressure of hydrogen multiplied by partial pressure of chlorine square divided by partial pressure of chlorine plus modified constant K multiplied by the partial pressure of germanium chloride 4 in the gas phase whole cube. This is valid only when only when square root of K H p H 2 is much smaller than one. So, let us see it this equation. So, we will see that now we have expressed the rate of a deposition as a function of the gas phase partial pressure of germanium chloride, which is a measurable quantity.

Then, the partial pressure of hydrogen, which is again a measurable quantity and then partial pressure of chlorine, which is again a measurable quantity; so from here we can find out what is the expression for the rate of deposition of germanium on the substrate. Now, there is another process which can actually occur along with this the germanium, which is deposited onto the surface because of the reaction can actually react with the germanium chloride in order to form 2 germanium c l 2. So, this has actually being ignored in the current a framework, but in principle this can actually occur in reality. So, let us summarize what we have learnt today. So, what we have seen is we have completed the reactor design that we initiated in the last lecture.

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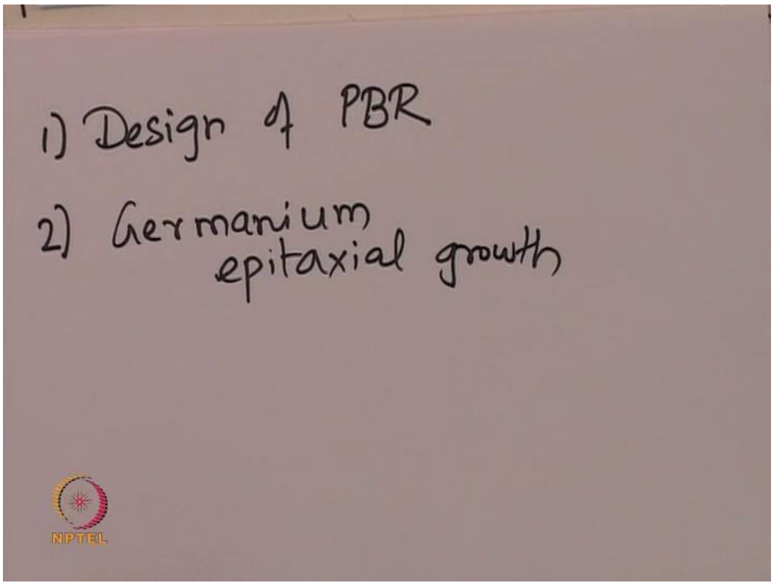

1) Design of PBR

2) Germanium epitaxial growth

So, we looked at the design of design of a packed bed reactor and then we looked at how the conversion can be expressed in terms of the weight of the catalyst, which is packed inside the reactor. Then, we also looked at what should be the performance equation for a CSTR in case, we want to find out what is the weight of the catalyst, which is required to obtain the same conversion as that obtained in the packed bed reactor. Then, we went on to describe a case study of the germanium epitaxial film growth. So, germanium epitaxial film growth, which also is can be modeled as a heterogeneous catalytic process.

So, with these two examples of hydroxymethylation of toluene and the germanium epitaxial growth, what we have learnt is a systematical way to start from first principles by determining, what is the mechanism of a particular catalytic reaction. Find out, what is the surface what is the limiting step in both these cases. We assume that it is see surface reaction, which is the limiting step and in principle the adsorption or desorption also can be a limiting step.

So, it is important to note that the only the seventy percent of the heterogeneous catalytic reactions are actually surface reaction limiting. So, in principle the same procedure can be followed if the adsorption and desorption step where to be the limiting step. So, using these rate laws for hydroxymethylation of toluene; we estimated the rate parameters and then we went ahead to design a simple pack bed reactor modeled to find the relationship between the conversion and the weight of the catalyst that is actually packed inside the reactor.

Thank you.