Chemical Reaction Engineering - II
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Module - 2
Lecture - 7
Rate Controlling Steps and Rate Law

In the last lecture we looked at how to find the rates for different steps in the catalytic reaction. In today's lecture we will start looking at how to find out what is the actual rate or what is the rate limiting step and how to find out the rate of reaction, taking into account the rate limiting step in the catalytic reaction.

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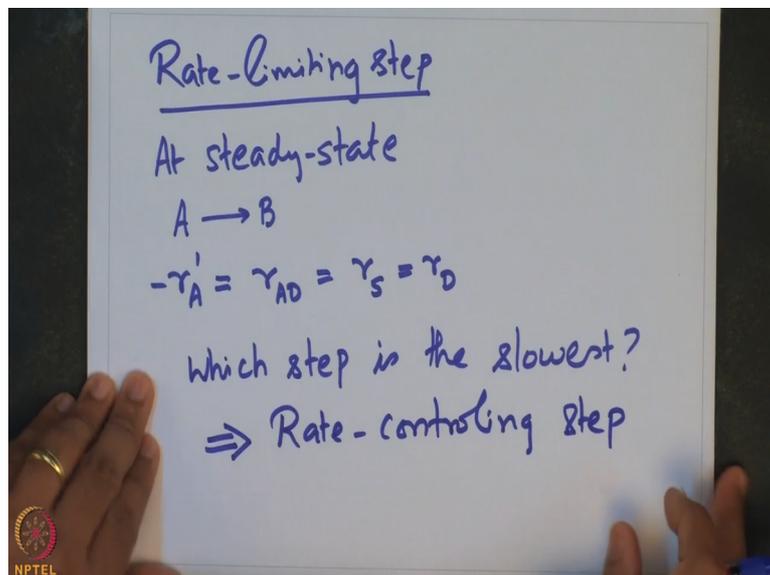
So, at steady-state supposing if the species A is going to products B. At steady-state, the rate at which the species is actually being consumed, that should be = the adsorption rate, that should be = rate at which the surface reaction is happening and that should be = rate at which the desorption is happening. Now, the question is which one is actually controlling the overall reaction.

So, in fact, it turns out usually that one of these steps is actually the slowest step in the catalytic reaction. And infect, if the slowest step is identified, then one can think of how to accelerate the slowest step. And accelerating the slowest step would actually accelerate the overall conversion of species, reactant species into the products. That is because all the other steps are faster than this one.

And they do not really control the overall reaction rate. So, the overall reaction rate can be tweaked and controlled and accelerated only if we identify which one is the slowest step in that particular reaction. So, let us look at that. So, which step is the slowest? And automatically this implies that, if you identify which one is the slowest, that will be the rate controlling step. So, let us look at a few examples.

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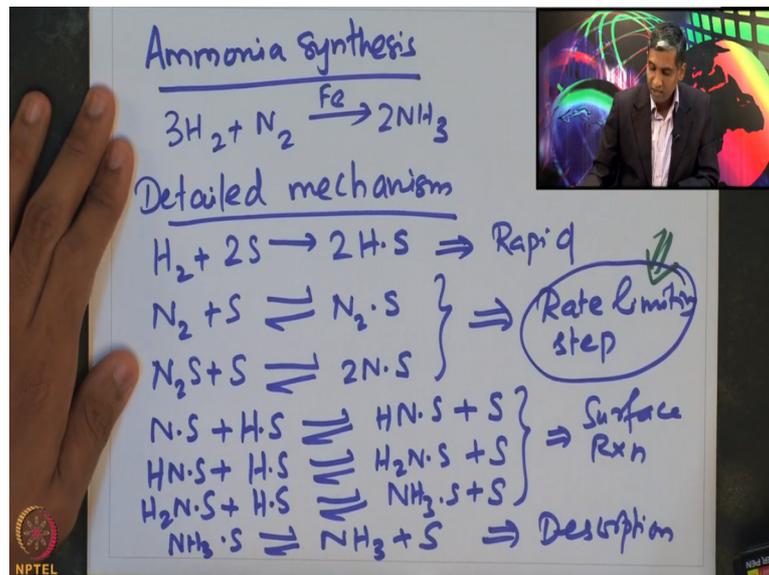
Ammonia synthesis for instance. So, the overall reaction is given by the step where hydrogen N 2, in the presence of iron catalyst gives ammonia. And the detailed mechanism that governs this ammonia synthesis process is essentially given by hydrogen which actually gets adsorbed onto the catalyst site and nitrogen also gets adsorbed onto the catalyst site. And then, N 2 S uses another site to form 2 N S.

And then, N dot S that is nitrogen adsorbed onto the catalyst site reacts with the hydrogen adsorbed onto the catalysts site which gives H N S + leaves out another site. And then H N S reacts with another molecule of the hydrogen molecule bound to the active sites. And it gives H 2 N dot S + S. And then H 2 N dot S + another H S gives N H 3 S + S. And this N H 3 S essentially desorbs from the catalyst site and gives out a free site.

So, this step is actually known to be a rapid strep which is basically the adsorption process, one of the adsorption steps. And then this adsorption step of nitrogen is actually known to be the rate limiting step. And these 3 are the surface reaction steps. And this is the desorption step. So, note that in this example, I have meant, I have said that the rate limiting step is

basically the adsorption of nitrogen onto the catalyst sites and not necessarily the adsorption of hydrogen onto the catalyst site.

And in fact, you should also observe that I have actually put a single side arrow. In fact, the hydrogen adsorption onto the catalyst site. It turns out is actually an irreversible step in this particular detailed mechanism. And in fact, this mechanism is known to be the mechanism that supports the ammonia synthesis using this process. So, in this case the adsorption is actually the rate limiting step here.

So, this is the, the adsorption of N 2 is actually the rate limiting step. And so, the overall reaction is essentially controlled by this particular rate limiting step of the ammonia synthesis process. So, let us look at another example where the surface reaction is actually the rate limiting step.

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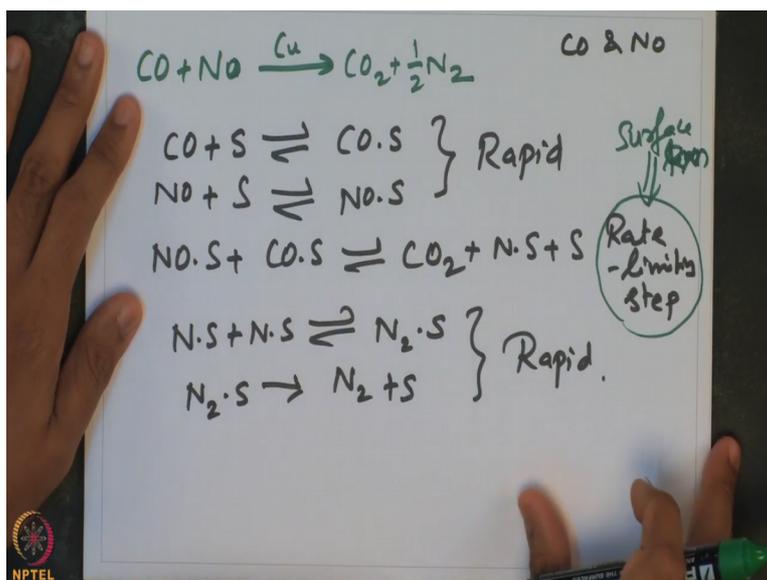
So, let us look at the reaction C O + N U, C O + N O in the presence of copper catalyst gives C O 2 + half N 2. And in fact, C O and N O are known to be the noxious automobile exhaust gases. And this cannot be let, these 2 are actually not environmentally very friendly. So, they need to be converted into C O 2 and N 2 in order to be let out into the atmosphere. So, this is a very important reaction which is usually conducted on copper catalyst.

And the detailed mechanism is C O + S reversibly binds to the catalyst site in the molecular form. Note that this is non-dissociated adsorption onto the catalyst site. And these 2 are known to be rapid steps. So, which means that the adsorption is actually not the rate

controlling step here. And the reaction between the adsorbed species; this is actually known to be the rate limiting step.

The surface reaction here is actually known to be the rate limiting step. And then the desorption process. These 2 are actually known to be rapid steps. So, in this case the surface reaction is actually the rate limiting step. Surface reaction is actually the rate limiting step that actually controls the overall rate of the reaction. So, let us look at how to actually synthesise a rate law once we know which one is the rate limiting step.

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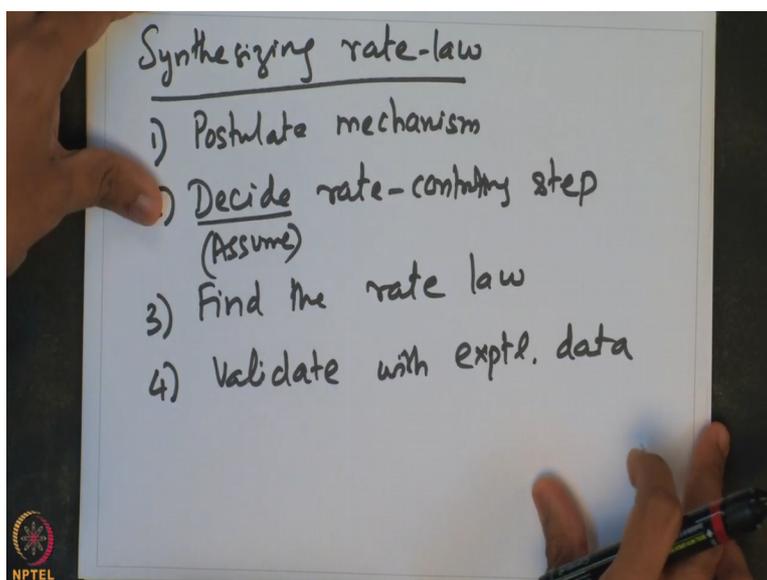
Synthesising rate law. So, the first step in synthesising a rate law is essentially to postulate what should be the mechanism with which the reaction is happening. And once the mechanism is decided, we propose as to or postulate what is the rate controlling step. And then we use that to determine what should be the rate law that actually controls the overall reaction rate. So, let us look at each of these cases.

Let, we will take a specific example and we will look at each of the cases of weather adsorption is rate controlling, surface reaction is late controlling or desorption processes actually rate controlling. So, step number 1 is to postulate the mechanism. And then decide on which one is the rate controlling step or rather assume and verify later. And find the rate law. And validate with experimental data.

If the proposed postulates, if the proposed mechanism or the assumption of which one is the rate controlling step which leads to a certain rate law does not satisfy the experimental data,

then we need to iterate on this repeat this process till we get the right model and the correct rate law that actually governs the particular process we are looking at.

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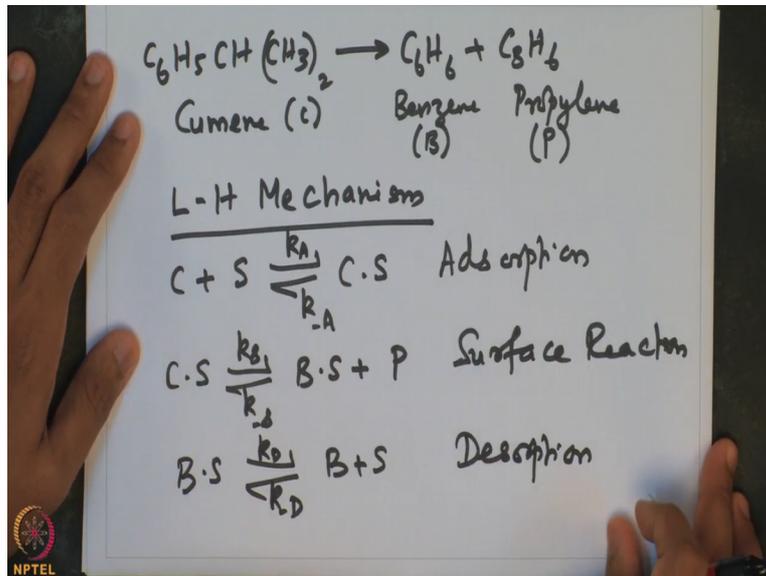
So, we will synthesise the rate law for a specific example of cumene getting converted to; so, this is cumene, we will refer to this as c. And then we will, this gets converted to benzene. Let us write this as B, refer to this as B. And propylene, let us refer to the species as P. Let us assume that Langmuir Hinshelwood mechanism is valid. Let us assume Langmuir Hinshelwood mechanism.

Remember that we have to first postulate a mechanism, then assume a certain, whichever is the rate controlling step followed by, find out or synthesise the rate law and then validate with experiments. So, let us start by assuming that the Langmuir Hinshelwood mechanism is a mechanism that captures this reaction, a catalytic reaction or C giving B + P where C is cumene, B is benzene and P is propylene.

So, let the detail mechanism be cumene which actually adsorbs onto the active site. So, that is the adsorption step. And let us say that the corresponding adsorption and desorption constants are k a and k − a. C S k s and k − s are the corresponding forward and backward rate constants. So, this is the surface reaction. And then we have, this is the desorption step. So, what we are going to do now is, we are going to write the rate law for, rate for each of these steps.

And one by one we are going to assume, if adsorption is the rate limiting step, what will be the overall rate law; if surface reaction is the rate limiting step, what will be the overall rate law; and if desorption is the rate limiting step, what will be the rate law. So, we will see each of these cases separately.

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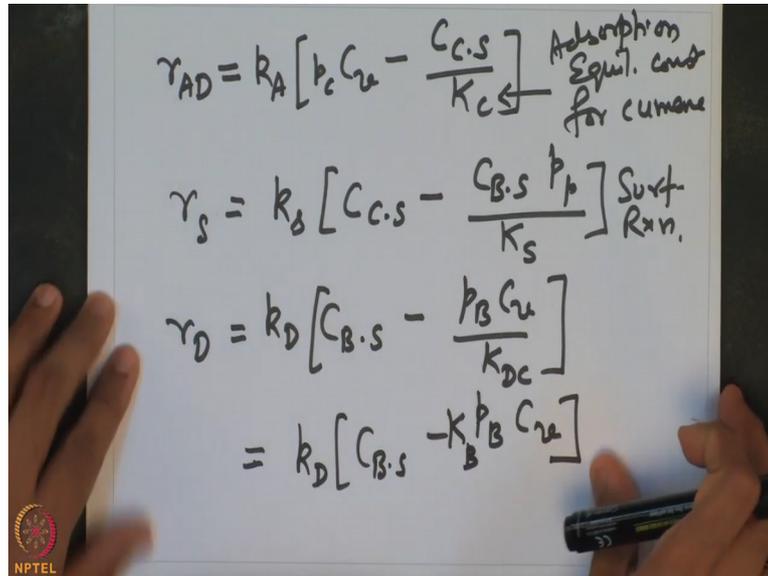
So, the rates of each of these step, r A D is = k A p c C v – C C dot S divided by K C where for adsorption step, the rate is essentially given by the adsorption process which depends on the partial pressure of cumene and the concentration of the vacant sites. And then we have the desorption step or detachment step which depends on the concentration of the cumene which is adsorbed onto the active sites.

And note that K C is the equilibrium constant, adsorption equilibrium constant for cumene. Similarly, for surface reaction, it is k s into C C dot S – C B S into partial pressure of propylene, divided by K S. And this is for surface reaction. And then we have r D which is the desorption step which is k D into C B dot S – P B C v divided by K D C. This is the desorption equilibrium constant.

But that is also =, this is the desorption equilibrium constant for benzene and that is also = 1 by the adsorption equilibrium constant for the same species. Therefore, we can rewrite this rate as k D into C B S – P B C v into K B.

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

$$= C_v + \frac{K_B P_B P_p C_v}{K_S} + K_B P_B C_v$$

$$\Rightarrow C_v = \frac{C_t}{1 + \frac{K_B P_B P_p}{K_S} + K_B P_B}$$

$t=0$
$P_B = P_p = 0$

$$-r_c' = r_{AD} = k_A\left[P_c - \frac{P_B P_p}{K_P}\right]\frac{C_t}{1 + \frac{K_B P_B P_p}{K_S} + K_B P_B}$$

$$K_P = \frac{K_S k_C}{K_B}$$

initially $\Rightarrow -r_c' = k_A P_c C_t$

So, let us assume that adsorption is the rate limiting step. So, if adsorption is rate limiting step, then the surface reaction and the desorption process are relatively faster. So essentially these 2 steps would quickly reach to an equilibrium. So, we can assume that these 2 steps are in equilibrium are which means that the rate of the surface reaction and the rate of desorption are essentially = 0.

So, if we impose these conditions. That is r S = 0 and r D = 0, then we will see that C C S is essentially = C B S into partial pressure of propylene divided by K S and C B S is = K B P B into C v. What we have done is, essentially, we have taken these 2 expressions. This expression and we have taken this expression. And then we have assumed that because this is a faster step, we have assumed that these 2 steps are in equilibrium and therefore the rates are = 0.

And by assuming that the rates are = 0, we essentially estimated what is C C S and C B S. So, from here we will see that C C S is = k B P B P propylene C v divided by K S. All I have done is I have substituted C B S into this expression. Now, the rate of, the overall reaction rate, let us say if I want to write overall reaction rate as r c prime which is the overall reaction rate with respect to cumene species.

And that is essentially now given by the adsorption rate of that particular species. And that is = k A into partial pressure of cumene into vacant sites – K B P B P P C v divided by K S into K C. And that, so the unknown quantity here, which is cannot be measured is the

concentration of the vacant site. So, now we are going to use the conservation rule to essentially eliminate the concentration of the vacant sites.

So, C T is the total concentration of the sites, is = C v + C C S + C B S which is the concentration of the sites occupied by cumene and concentration of sites occupied by benzene. So, that is = C v + K B P B partial pressure of propylene into vacant sites divided by K S + K B P B into C v. So, from here C v is = C t divided by 1 + K B P B partial pressure of propylene divided by K S + K B into P B.

So, if we substitute C v into the rate, we will see that – r c prime is = k A P C – P B by into partial pressure of propylene divided by K P. So, we have, we can define K P as the equilibrium constant with respect to pressure. So, that will be K S K C divided by KB. And that is =, and that multiplied by C t divided by 1 +, divided by K S, K B into P B. So, this essentially gives the overall rate at which the reaction is actually happening because it is adsorption control.

All we have done is, we have assumed that the other steps are actually at equilibrium and we have eliminated those terms which may be present there. And then we found out what is the overall rate. So, let us stare at this expression a bit. So, suppose if at the initial, initially if the benzene and propylene which are the product species are not present, then the partial pressures of these 2 are likely to be 0.

So, if the, if at initial time t = 0, partial pressures of benzene and partial pressure of propylene is = 0, then this expression essentially boils down to; so, this term goes to 0, this term goes to 0 and the first term goes to 0. So, therefore the at t, and the initial phase, so initially, – r c is essentially given by K A P C into C t. So, the initial rate is essentially a linear function of the partial pressure of cumene.

And so, we can now sketch this behaviour. So, if the, in the initial phase, initially if I now plot P C versus the r c prime, essentially one actually has a linear profile. The reaction, overall reaction rate, it actually depends linearly on the partial pressure of cumene in the initial phase. So, let us now take the second case where we want to look at the situation where the surface reaction is actually rate limiting.

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2. Surface rxn. is rate-limiting

$$r_{AD} = 0, \quad r_D = 0$$

$$\Downarrow \qquad\qquad \Downarrow$$

$$C_{C \cdot S} = P_C C_v K_C \qquad C_{B \cdot S} = K_B P_B C_v$$

$$C_t = C_v + P_C C_v K_C + K_B P_B C_v$$

$$= C_v \left[1 + P_C K_C + K_B P_B \right]$$

$$\Rightarrow C_v = \frac{C_t}{1 + P_C K_C + K_B P_B}$$

So, let us say that surface reaction is rate limiting. So, in this case we can assume that the rate of adsorption, that is actually in equilibrium and rate of desorption is actually in equilibrium. So, now because of this, we will see that C C S which is the concentration of cumene attached to the sites is essentially given by P C C v into K C. And this gives that C B S is = K B P B into C v. So, from here, we can substitute in the conservation rule.

So, that will be C V + P C C v into K C + K B P B into C v. So, that should be = C v into 1 + P C into K C + K B into P B. So, from here, C v is = C t divided by 1 + P C K C + K B into P B. So, now we can plug this expression into the rate of, rate at which the surface reaction happens.

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$$r_C' = r_S = k_S \left[C_{C \cdot S} - \frac{C_{B \cdot S} P_P}{K_S} \right]$$

$$= \frac{k_s K_c C_t \left[P_C - \frac{P_B P_P}{K_P} \right]}{1 + K_c P_C + K_B P_P}$$

initially P_B & P_P are negligible
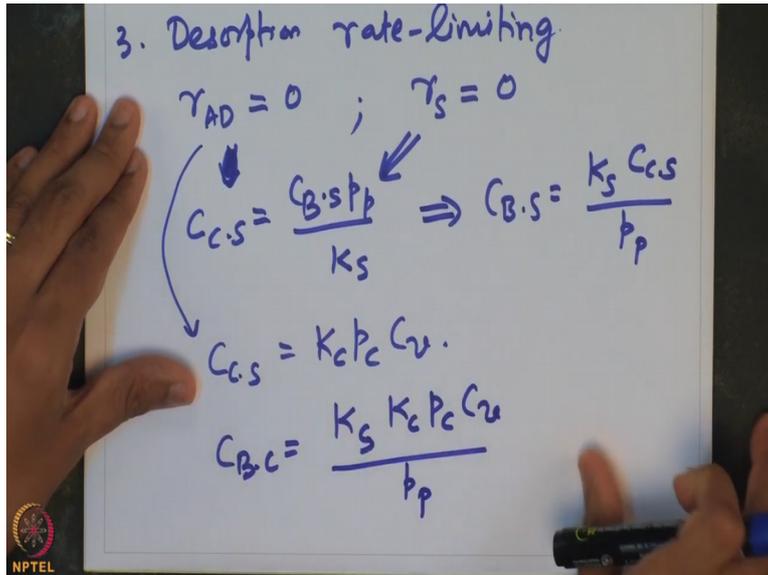
Initially,

$$-r_C' = \frac{k_s K_c C_t P_C}{1 + K_c P_C}$$

So, the overall reaction rate of cumene is essentially given by the rate at which the surface reaction happens. And that should be $= k_s$ into C C S into C B S which is the concentration at which, concentration of benzene attached to the sites, multiplied by partial pressure of propylene divided by K S. And that should be $=$, when we substitute the expression for C C S, C B S and C v we will see that the rate is $= k_s$ K C C t multiplied by P C $-$, by K P, divided by $1 + $ K C P C $+$ K B into P B.

So, all that is required is just substitute the concentration of C C S that we found few minuets, few moments ago and concentration of C B S in terms of the partial pressures and the equilibrium constants. And substitute for the concentration of the vacant sites. Then we can see that, after little bit of algebra, we can see that the rate at which the, you know, overall reaction happens is essentially given by this expression.

So, once again let us say initially P B and P P let us say are negligible. So, by setting these 2 $= 0$, we will see that initially $- r_c$ prime is $= k_s$ into K C into C t into P C divided by $1 + $ K C into P C. It is no more linear. So, if the overall rate is actually controlled by the surface reaction, then the dependence of the overall rate on the partial pressure of cumene is no more linear as was observed for the case when the adsorption is rate limiting.

So, let us try to sketch this. So, P C in the initial stages, initially and $- r_c$ prime; so, it will behave linearly for very small concentrations. And then slowly it will become like this. So, clearly the overall rate, dependence of the overall rate on the partial pressure when the surface reaction is limiting is not same as the overall dependence of the overall rate on the partial pressure of cumene. In the adsorption case is linear, while here you can see that it is not a linear relationship. Let us look at the third case where desorption may be the rate limiting step.
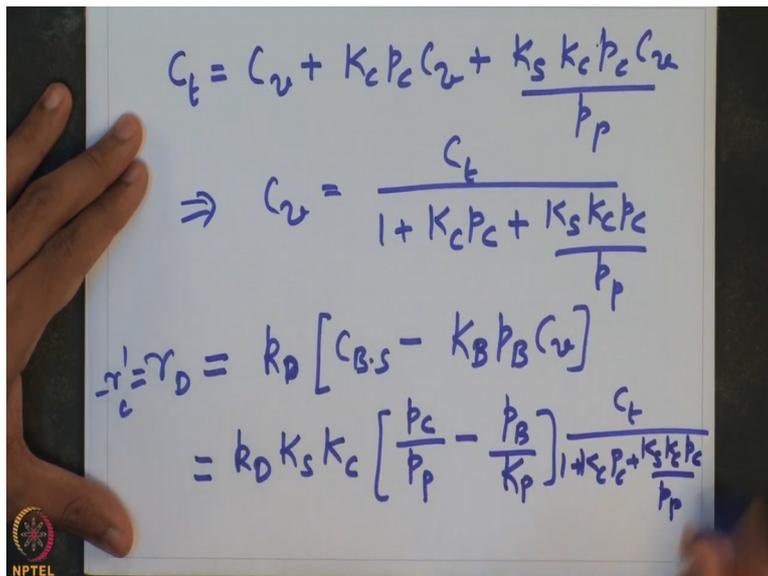
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3. Desorption rate-limiting

$$r_{AD} = 0 \quad ; \quad r_S = 0$$

$$\left(C_{C \cdot S} = \frac{C_{B \cdot S} \cdot p_p}{K_S} \Rightarrow C_{B \cdot S} = \frac{K_S \, C_{C \cdot S}}{p_p} \right.$$

$$\left. C_{C \cdot S} = K_C P_C \, C_v \right.$$

$$C_{B \cdot C} = \frac{K_S \, K_C \, P_C \, C_v}{p_p}$$

Desorption step is actually rate limiting. So, in this case clearly the adsorption rate should, adsorption is at equilibrium, so we can set r A D as 0. And the surface reaction is also at equilibrium, so we can set r s is 0. So, from here we will see that C S is = C B S into partial pressure of propylene divided by K S. So, that comes by, assume setting the reaction rate is = 0. And by setting the adsorption rate = 0, one will get that C C S is = K C P C into C v.

So, from here C B S is = K S into C C S divided by partial pressure of propylene. By substituting this expression, we will see that, is = K S K C P C into C v divided by partial pressure of propylene. So, once again we substitute these in the conservation rule.

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$$C_t = C_v + K_C P_C \, C_v + \frac{K_S \, K_C \, P_C \, C_v}{p_p}$$

$$\Rightarrow C_v = \frac{C_t}{1 + K_C P_C + \frac{K_S K_C P_C}{p_p}}$$

$$-r_C' = r_D = k_D \left[C_{B \cdot S} - K_B P_B \, C_v \right]$$

$$= k_D K_S K_C \left[\frac{P_C}{P_p} - \frac{P_B}{K_p} \right] \frac{C_t}{1 + K_C P_C + \frac{K_S K_C P_C}{p_p}}$$

So, we will find that the total concentration of the sites is = vacant sites + K C P C into C v + K S K C P C C v divided by partial pressure of propylene. And, from here, C v is = C t

divided by 1 + K C into P C + K S K C P C divided by partial pressure of propylene. So, now we can substitute this in the rate of desorption which is = the rate at which the overall reaction happens. And that should be = K D multiplied by C B S – K B P B into C v.

So, substituting the expression for C B S and C B, we find that this is = k D K S into K C multiplied by P C divided by partial pressure of propylene – P B divided by K P and that into C t divided by 1 + K C P C + K S K C P C divided by partial pressure of propylene.

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So, we can further simplify this expression to get that r D is = k D K S into K C, that into P C – P B partial pressure of propylene divided by K P multiplied by C t, the whole divided by partial pressure of propylene + K C P C into partial pressure of propylene + K S K C into P C. And that will be the overall rate. So, in the initial phases, initially when partial pressure of benzene and partial pressure of P are negligible. We substitute that here.

So, r D which is = – r c prime will essentially be = k D K S K C P C C t divided by K S K C into P C. So, we can cancel out these. So, this is essentially = k D into C t. So, which means that it is not a function of the partial pressure of cumene. So, if I now plot the rate, – r c prime versus P C in the initial phase, then the curve will essentially be constant. So, clearly you can see that when adsorption is rate limiting, the initial reaction rate is actually a linear function of partial pressure of cumene.

And if the surface reaction is rate limiting is no more a linear function. And if desorption is rate limiting the rate is essentially constant is independent of the partial pressure of cumene in

the initial stages. So, as one can see from this example that depending upon which ever step is the rate limiting step, the overall reaction rate is likely to be different. And for every reaction that needs to be, every catalytic reaction that needs to be characterised, one needs to assume what is the rate limiting step.

And then, we need to make such a derivation by first assuming the mechanism and then deciding which one is the rate controlling step and find out what is the overall reaction rate. And this needs to be validated with the experimental data to be to gain confidence on if the mechanism that is assumed is correct and also the rate limiting step that is assumed is correct. Thank you.