Chemical Reaction Engineering - II
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Module - 2
Lecture - 8
Rate Law: Pseudo-Steady State Hypothesis

Let us summarise what we have seen in the last couple of lectures. We looked at the different steps which are involved in catalytic reaction. We observed that there are 7 steps that are involved. There is external diffusion, there is internal diffusion, there is adsorption of the gas species onto the catalyst site. And there is a surface reaction. Then there is desorption, Then, we have internal diffusion which carries the product species to the external surface of the pellet.

And from there, there is external diffusion which takes the product species to the bulk gas phase. And we also looked at what happens if the different, each of these different steps could be the rate limiting step. And we looked at how to synthesise rate law by taking decomposition of cumene example to see how the different overall reaction rate is different when each of these different steps are actually controlling, or rate controlling or is a rate limiting step. So, this idea of synthesising rate law.

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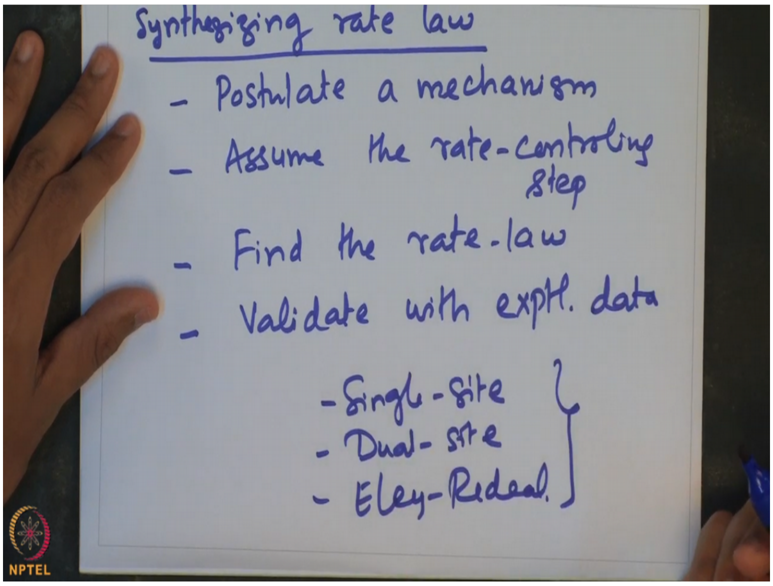

Synthesizing rate law

- Postulate a mechanism
- Assume the rate-controlling step
- Find the rate-law
- Validate with exptl. data
  - Single-site
  - Dual-site
  - Eley-Rideal

The procedure that we prescribed in the last class where we first postulate a mechanism. Assume the rate controlling step, find the rate law and validate with experiments. So, this procedure can actually be followed for any different mechanism that is actually used. So, for instance in the previous lectures we have looked at single site mechanism, we have looked at dual side mechanism, we have looked at Eley-Rideal mechanism.

So, each of these can actually be used in the mechanism. And one can actually follow these steps to actually find the rate law and validate with experimental data. So, it turns out that different reactions actually satisfy different mechanisms, in fact different mechanisms govern different reactions. And so, one can actually try different combinations of these mechanisms and synthesise the rate law and actually compare it with the experimental data.

Recall that the experimental data typically will be experiment done at a specific temperature or may be at different temperature. So, you fix a temperature and then change the partial pressure of the gas and measure the, you know, observables and we can validate the model or the rate law that is actually derived using the method proposed here with the experimental data. And that will actually give confidence whether the assumed mechanism and the rate controlling step that is assumed is actually correct for the reaction that is being considered. So, let us look at another case now.

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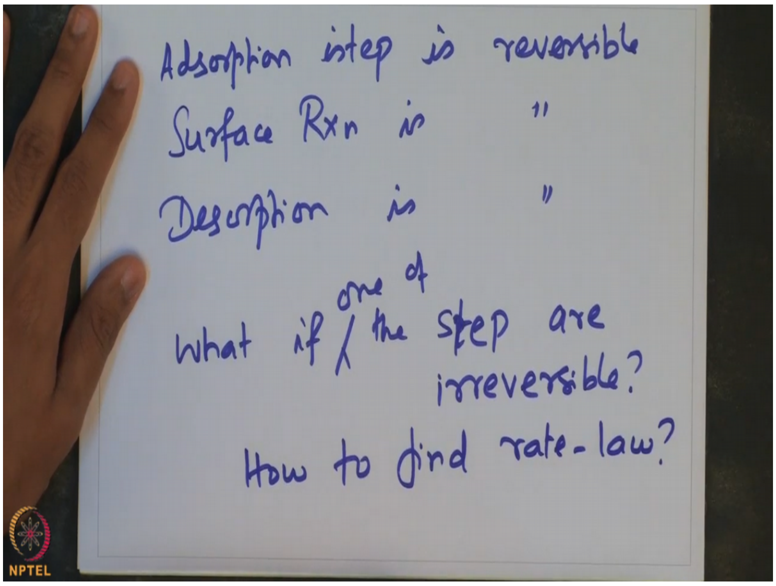

Adsorption step is reversible
Surface Rxn is "
Desorption is "

What if one of the step are irreversible?

How to find rate-law?

So, in all the earlier examples and the mechanism we have considered, we assume that the adsorption step is reversible. We assume that surface reaction is also a reversible step. We assume that desorption step is also a reversible step. We in fact observed in the example of ammonia synthesis where one of the adsorption step was actually an irreversible step. So, we will see an example now as to what if one of the steps or may be more steps are actually is irreversible.

How do we, so, how to find rate law in these cases. How to find rate law when one or more steps which are involved in catalytic reaction are actually irreversible. So, what we will see in this lecture is to understand how to actually synthesise rate law when there is an irreversible step that may be present.

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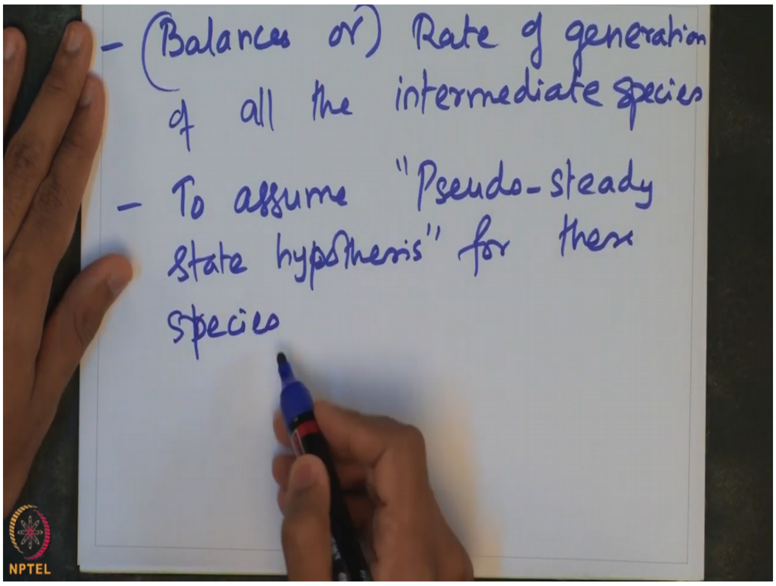

- (Balances or) Rate of generation of all the intermediate species
- To assume "Pseudo-steady state hypothesis" for these species

So, the strategy here is to look at the balances for or look at the rate of generation of all the intermediate species and to assume pseudo-steady state for these. So, one can assume a pseudo-steady state hypotheses for these species. And once we assume a pseudo-steady state hypothesis we can assume that the rate of generation of each of these intermediate species whichever is relevant, we can assume that each of these rates are actually 0.

And that approximation can be used to find the rate law. So, this is a method which can be used when there are irreversible steps which are actually present in the catalytic reaction. If one of these 7 steps that we outlined earlier, if some of these are actually irreversible, for example adsorption, surface reaction and desorption which are at, these 3 are actually, any one or more of these 3 are actually irreversible steps, then one can actually use a pseudo-steady state hypothesis.

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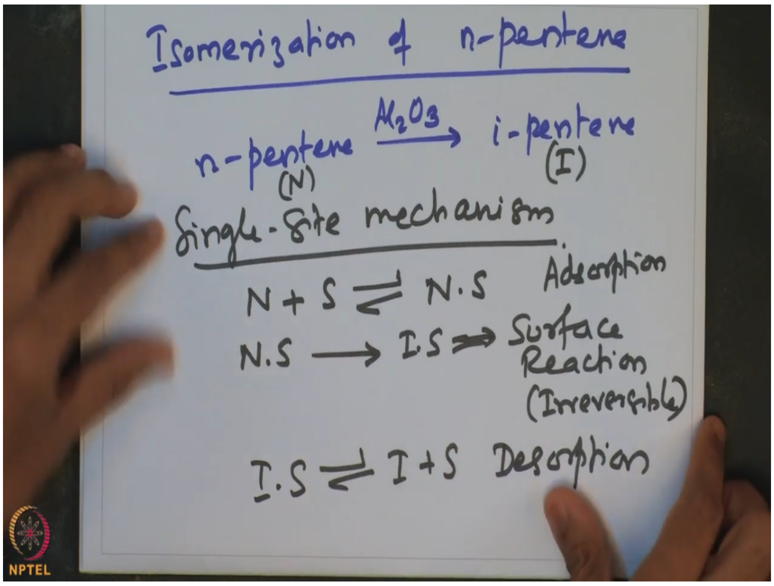

Isomerization of n-pentene

$$\underset{(N)}{\text{n-pentene}} \xrightarrow{Al_2O_3} \underset{(I)}{\text{i-pentene}}$$

Single-site mechanism

$N + S \rightleftharpoons N \cdot S$ Adsorption

$N.S \longrightarrow I.S \Rightarrow$ Surface Reaction (Irreversible)

$I.S \rightleftharpoons I + S$ Desorption

Let us take a specific example of isomerization of n-pentene. So, the reaction is n-pentene forms isomerized form, isomerization. And, actually happens over alumina catalyst. So, the mechanism is actually a single-site mechanism. So, use a single-site mechanism. So, let us say that n-pentene is represented as N and i-pentene is isomerized pentene is represented as I. And N adsorbs onto the site which is actually, it is a reversible adsorption step.

And then we assume that N S irreversibly forms I S. And this is the surface reaction. And assume that it is irreversible surface reaction, irreversible step. And then we assume that I S actually reversibly undergoes a desorption process. We assume that the n-pentene actually interacts with the active sites and forms the bound species N dot S. And we assume that this adsorption step is actually reversible.

And we assume that the adsorbed species irreversibly undergoes a surface reaction. And then we assume that the adsorbed product species I S actually reversibly desorbs from the active sites leaving the active site free. So, let us look at how to generate the, how to synthesise the rate law for this particular case.

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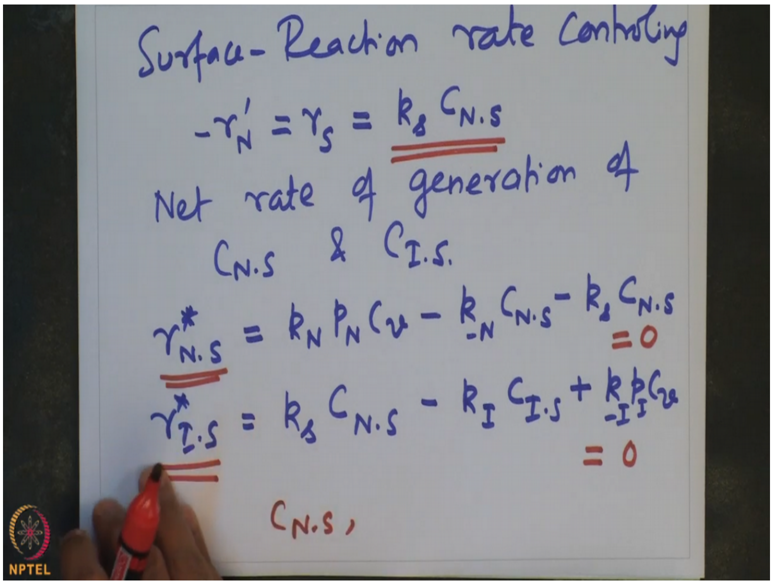

Surface-Reaction rate Controlling

$$-r'_N = r_S = \underline{\underline{k_s C_{N.S}}}$$

Net rate of generation of

$C_{N.S}$ & $C_{I.S}$

$$\underline{\underline{r^*_{N.S}}} = k_N P_N C_v - k_{-N} C_{N.S} - k_s C_{N.S} = 0$$

$$\underline{\underline{r^*_{I.S}}} = k_s C_{N.S} - k_I C_{I.S} + k_{-I} p_I C_v = 0$$

$C_{N.S}$,

So, let us assume that surface reaction is rate controlling. And since the reaction is actually a irreversible reaction, then the overall rate is essentially given by the surface reaction which is given by K S into C N S. Let us assume that its first order. And then the, suppose let us say we consider the net rate of generation of the other species. So, r N S is essentially given by, this is an intermediate, so, if I put a star to represent the intermediate, rate of generation of the intermediates.

So, k N into partial pressure of n-pentene into vacant sites. This is the rate at which the species is getting adsorbed onto the site – the desorption step which again affects the total species – the surface reaction actually takes the species attached to the sites to a product form. And let us say that similarly for I S, it is given by K S into C N S. That is the rate at which the species is formed. And let us assume that the adsorption desorption step is k I into C I S +, into C V.

So, that is the rate at which the desorption process is happening. So, the first equation here, the first rate is the rate of formation of this intermediate species N S. And this is the rate of formation of this intermediate species. So, in pseudo-steady state hypothesis method we assume that the rate at which the intermediates are formed is actually = 0. So, from here we will find out what is C N S. And we will find out what is C N S and substitute that in this expression. And then we are done. We will be able to find what is the overall rate of reaction. So, let us do this exercise.

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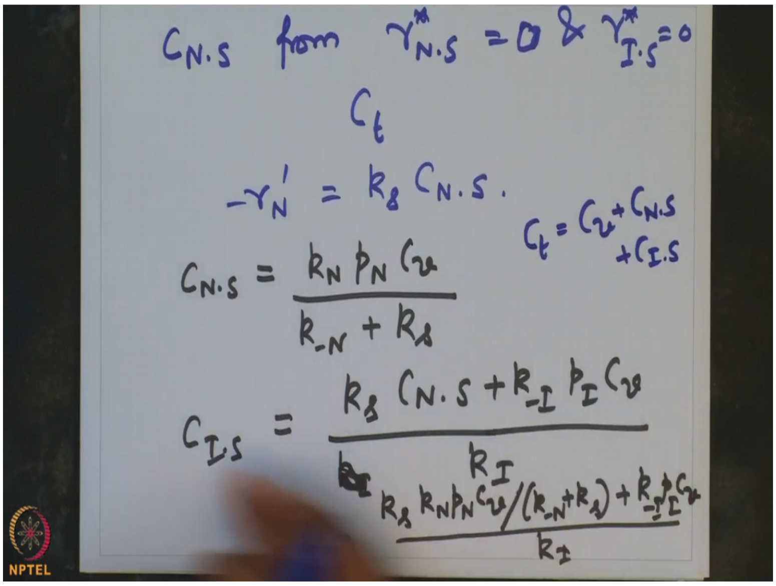

$C_{N.S}$ from $r^{*}_{N.S} = 0$ & $r^{*}_{I.S} = 0$

C_t

$$-r_N' = k_s C_{N.S}.$$

$$C_t = C_v + C_{N.S} + C_{I.S}$$

$$C_{N.S} = \frac{k_N p_N C_v}{k_{-N} + k_s}$$

$$C_{I.S} = \frac{k_s C_{N.S} + k_{-I} p_I C_v}{k_I} = \frac{k_s k_N p_N C_v/(k_{-N}+k_s) + k_{-I} p_I C_v}{k_I}$$

So, what we need to find is, we need to find C N S from the expression = 0 and 0. And also, we can use the conservation rule, we will use the conservation rule for the total number of sites. And once we find C N S then we are at, we can actually find out what is the rate at which the overall reaction rate which is essentially given by K S into C N S. So, let us do this exercise. So, from the pseudo-steady state equations we can find out that C N S is essentially given by k N into P N into C v divided by k – N + k s.

So, this essentially comes from this expression here. So, C N S is essentially given by this divided by sum of these 2 coefficients. And in a similar fashion we can find out that C I S is essentially given by k s into C N S divided by k I, k s into C N S + divided by k I. But we know what C N S is. So, we can substitute that here. So, that will be = k s k N P N C v divided by k – N + k s – I P I into C v divided by k I.

So, we now know what is C N S and we know what is C I S. And we know that the conservation rule is essentially given by C t C v + C N S + C I S. So, we will substitute this in the conservation rule. And by substituting this in the conservation rule we can find out what is the expression for C v.

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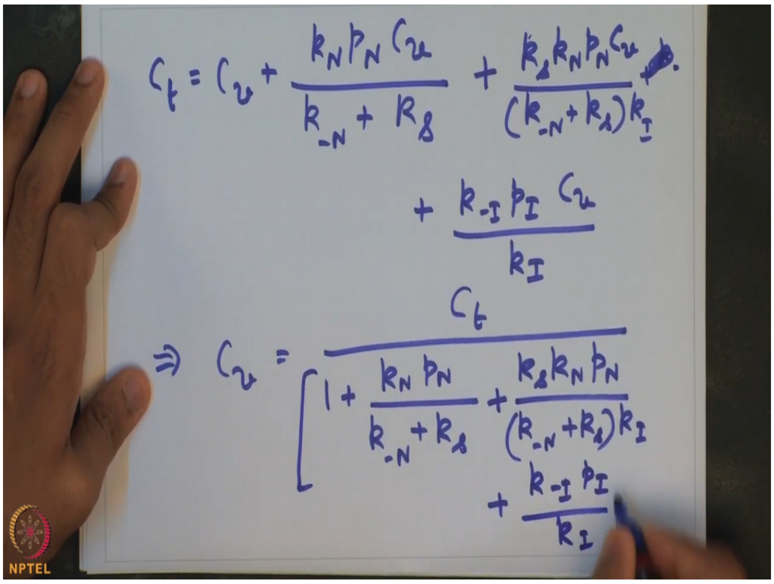

$$C_t = C_v + \frac{k_N p_N C_v}{k_{-N} + k_s} + \frac{k_s k_N p_N C_v}{(k_{-N}+k_s)k_I} + \frac{k_{-I} p_I C_v}{k_I}$$

$$\Rightarrow C_v = \frac{C_t}{\left[1 + \frac{k_N p_N}{k_{-N}+k_s} + \frac{k_s k_N p_N}{(k_{-N}+k_s)k_I} + \frac{k_{-I} p_I}{k_I}\right.}$$

So, C t is = C v + k N P N into C v divided by k – N + k s. That + k s k N P N C v divided by k s into k I + k I P I into C v divided by k I. So, from here, we can find out that C v is = C t divided by 1 + k N P N divided by k – N + k s + k s k N P N divided by k – N + k s into k I + k – I P I divided by k I. We can simplify this and rewrite this as C v is =;

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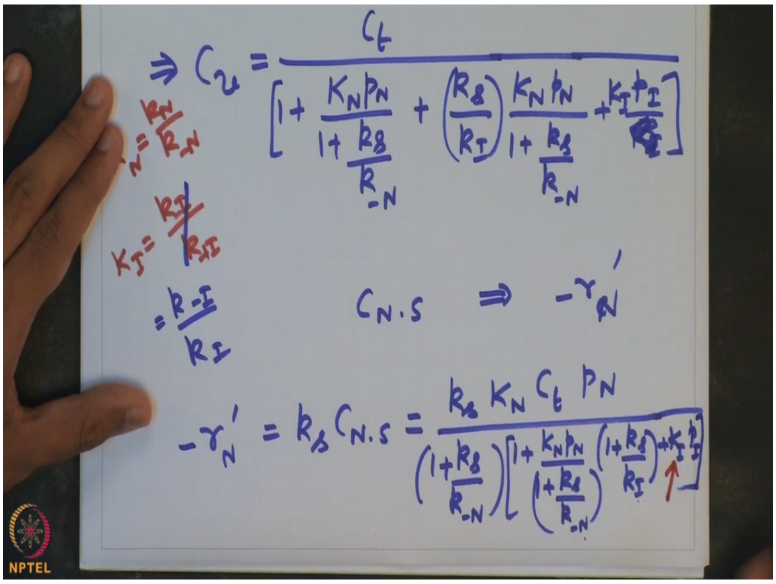

$$\Rightarrow C_v = \frac{C_t}{\left[1+\frac{K_N p_N}{1+\frac{k_s}{k_{-N}}} + \left(\frac{k_s}{k_I}\right)\frac{K_N p_N}{1+\frac{k_s}{k_{-N}}} + \frac{K_I p_I}{\cancel{k_I}}\right]}$$

$_N = \frac{k_N}{k_{-N}}$

$K_I = \cancel{\frac{k_I}{k_{-I}}} = \frac{k_{-I}}{k_I}$

$C_{N.S} \Rightarrow -r_N'$

$$-r_N' = k_s C_{N.S} = \frac{k_s K_N C_t p_N}{\left(1+\frac{k_s}{k_{-N}}\right)\left[1+\frac{K_N p_N}{\left(1+\frac{k_s}{k_{-N}}\right)}\left(1+\frac{k_s}{k_I}\right)+K_I p_I\right]}$$

We can simplify this and write C v = C t divided by 1 + capital K N which is essentially given by ratio of small k n by; so, if I define capital K N as small k N by k – N which is essentially the equilibrium, adsorption equilibrium constant. So, that is = P N divided by 1 + k s by k – N + k s by k I into K N P N divided by 1 + k s by k – N + P I divided by K I. So, if I define K I as; if I define capital K I as k – I + k I, then I can essentially write this, if K I is the adsorption equilibrium constant of species I, so, essentially this is k – I by k I.

I can write this as k – I by k I. So, this C v I can substitute now back in C N S. And that I can substitute in the expression for r N overall rate, reaction rate. So, overall reaction rate will essentially be = k s into C N S. And that is = k s into K N into C t into P N divided by 1 + k s by k – N, multiplied by 1 + capital K N P N divided by 1 + k s by k N multiplied by 1 + k s divided by k I + capital K I into P I.

So that will be the expression for the overall reaction rate. So, let me repeat. It will be = k s which is the rate at which the surface reaction happens. K N is the adsorption equilibrium constant for n-pentene. C t is the concentration, total concentration of the sites. P N is the partial pressure of n-pentene. 1 + ratio of the rate constant for the surface reaction. Remember that the surface reaction is irreversible here. And divided by the disorption constant of the n-pentene.

And then we have 1 + K N P N divided by 1 + k s by k – N, 1 + k s by k I + K I into P I where this is the equilibrium constant for equilibrium adsorption constant for species I. So, now from this expression one can actually see what are the limiting cases. So, these, this is the actual expression that actually governs the rate at which the overall reaction is happening. Suppose we assume that, suppose if we assume that k s by k N is very small.

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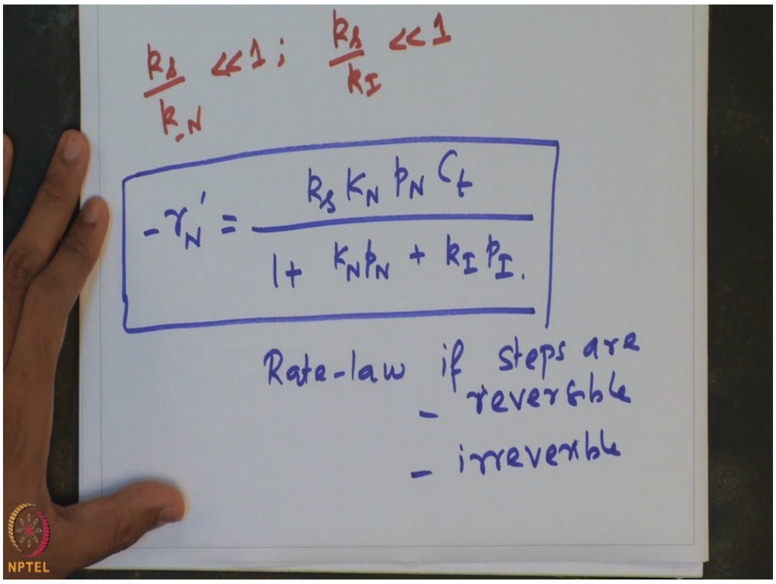

$\frac{k_s}{k_{-N}} \ll 1$; $\frac{k_s}{k_I} \ll 1$

$$\boxed{-r_N' = \frac{k_s K_N p_N C_t}{1 + K_N p_N + k_I p_I}}$$

Rate-law if steps are
- reversible
- irreversible

Suppose we assume that k s by k N is much smaller than 1 and we also assume that k s by k I is much smaller than 1, then we will see that the overall rate is essentially boils down to k s K N P N C t divided by 1 + K N P N + k I into P I. So, one can actually look at such limiting cases. And such limiting cases would actually tell you what is the overall rate law for different situations. One can actually obtain the same expression by assuming the rates of each of these steps and assuming that the surface reaction is the rate controlling step.

And one can actually find the same expression. But using pseudo-steady state hypothesis method actually provides a elegant way of finding rate law when some of these steps are actually irreversible. So, what we have seen so far is we have actually seen what is, how to synthesise rate law if steps are reversible. We have seen how to do it if there are irreversible steps. So, if rate, we have looked at how to find the rate law any or more of these steps are actually reversible. Any or more of these steps are actually irreversible.

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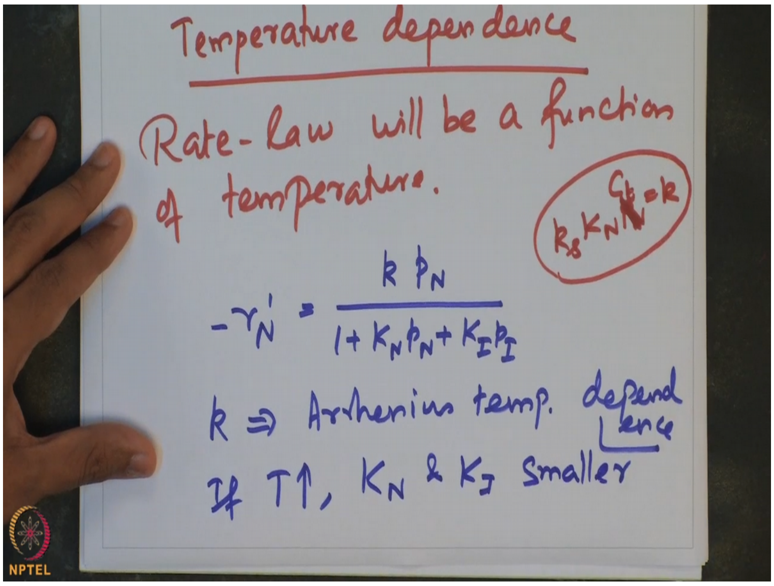

Temperature dependence

Rate-law will be a function of temperature.

$k_s K_N \cancel{P_N} C_t = k$

$$-r_N' = \frac{k\,p_N}{1 + K_N p_N + K_I p_I}$$

$k \Rightarrow$ Arrhenius temp. dependence

If T↑, K_N & K_I Smaller

So, let us now briefly look at the temperature dependence. So, rate law is of course a function of temperature, will be a function of temperature. So, let us look at what could be the temperature dependence for the case that we have just looked at. So, the rate law for let us say isomerization that we arrived at, let us say that r N prime is essentially given by some rate constant k into P N which is the partial pressure of n-pentene divided by 1 + K N P N + K 1 K I P I.

What we have done is we have essentially pooled in the different rate constants in the numerator. We said that k s K N P N is = k. So, we have just assumed that these 3 constants, these 3 into C t. We have assumed that k s K N into C t where this is the total concentration of the active sites. That is = k. And clearly these, this rate law will certainly be a function of temperature.

And in fact, this k actually follows Arrhenius dependence. Whereas the adsorption of the species is also exothermic. So, if temperature increases, then K A K N and K I actually becomes smaller. So, that is the typical relationship with the temperature. And so, clearly, rate law also is a function of temperature. So, what we have seen in this topic so far is we have actually looked at catalysis. We have defined catalysis.

We have looked at various steps that are involved. We have looked at synthesis of rate law using 2 different methods. And these 2 methods can be used for different mechanisms. What we will see from the next lecture is to deduce the rate law from the experimental data. The challenge is once the experimental data is there, what should be the functional form of the rate law that would actually approximately govern the experimental observations.

Because mechanism can be very detailed and there can be many many steps, there are many many ways to formulate mechanism. And it is not possible to do all combinations. So, the next best option is given an experimental data can we approximately deduce what should be the mechanism that governs the given experimental observations. And what could be the proposed or approximately what should be the functional form of the rate law. Can it be deduced from the experimental data using intuitive methods. So, this is what we will start seeing from the next lecture. Thank you.