# Chemical Reaction Engineering - II

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## Module - 2
## Lecture - 6
## Surface Reaction

Hi. In the last lecture we looked at adsorption isotherm which is essentially the third step in the catalytic reaction. And we started discussion on the fourth step which is the surface reaction. Particularly that of, after the species is adsorbed onto the active sites, we want to look at how the species, adsorbed species actually undergoes reaction. There are many different ways in which the adsorbed species can undergo reaction.

And we will look at a few cases. And we outlined in the last lecture what are the few cases that we are going to look at. So, let us start with the first one.

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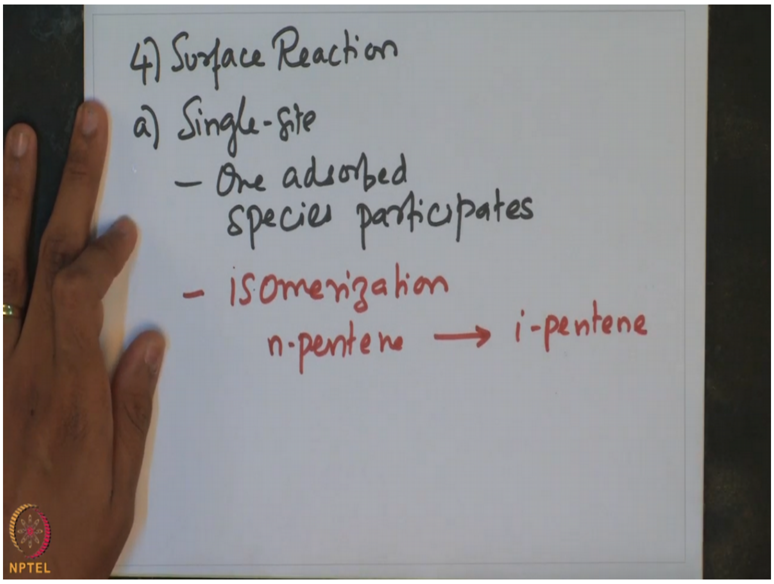

4) Surface Reaction

a) Single-site

– One adsorbed species participates

– isomerization

n-pentene $\rightarrow$ i-pentene

So, it is a single site reaction where only 1 adsorbed species participates in the reaction. A good example of this where there is only 1 species that actually participates in the reaction; a good example of this is, let us say isomerization reaction. For example, if n-pentene actually leads to isomerized-pentene form, isomerized form. And that is a good example of a surface reaction where 1 species just essentially gets converted into the isomerized form of the same species which is now the product species. So, one can actually represent this, one can depict this process.

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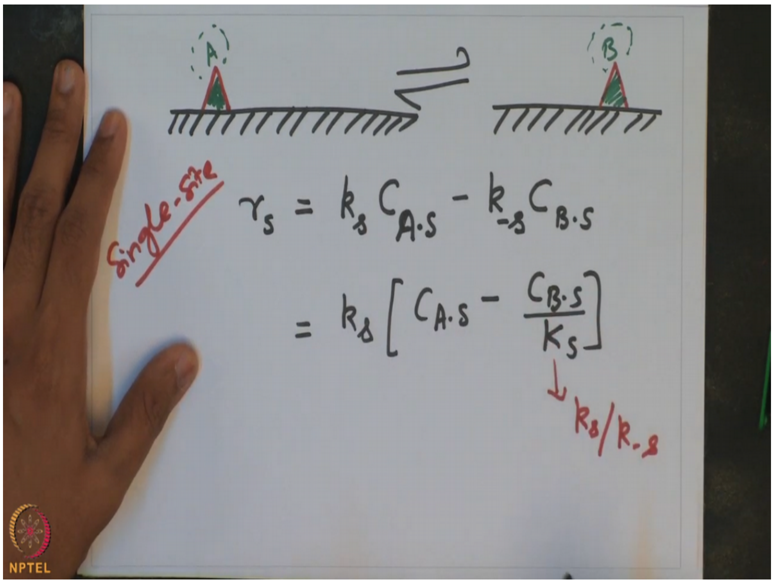

Single-site

$$r_s = k_s C_{A\cdot S} - k_{-s} C_{B\cdot S}$$

$$= k_s \left[ C_{A\cdot S} - \frac{C_{B\cdot S}}{K_S} \right]$$

$$\downarrow k_s/k_{-s}$$

Let us say that we have a catalyst surface. And this is the site at which species A is present. And this can actually reversibly get converted, let us say isomerized in this case, if you look at specific example. Or in general it gets converted into the product species. And after it gets converted into the product species, the species continues to remain adsorbed onto the catalyst site. So, now one can, and it is a reversible process.

And therefore, on can actually write the rate at which this reaction happens. Rate at which this reaction happens is essentially given by k s into concentration of the adsorbed species onto the active sites, which is essentially the rate at which the forward reaction happens – k – s into C B S which is the concentration of the adsorbed product species. With this right, this second term is essentially the rate at which the adsorbed product species may go back in and form the reactant product itself.

So, it can, it could be a reversible step. And we could write this as k s into C A S – C B S divided by K S which is essentially the equilibrium constant. So, k s is nothing but k s divided by k – s, in this case. So, if there is a single site reaction where there is only 1 adsorbed species which is participating in the reaction, then the rate can essentially be represented as k s into C A S – C B S divided by the corresponding equilibrium constant. Let us look at the next case of dual site reactions.

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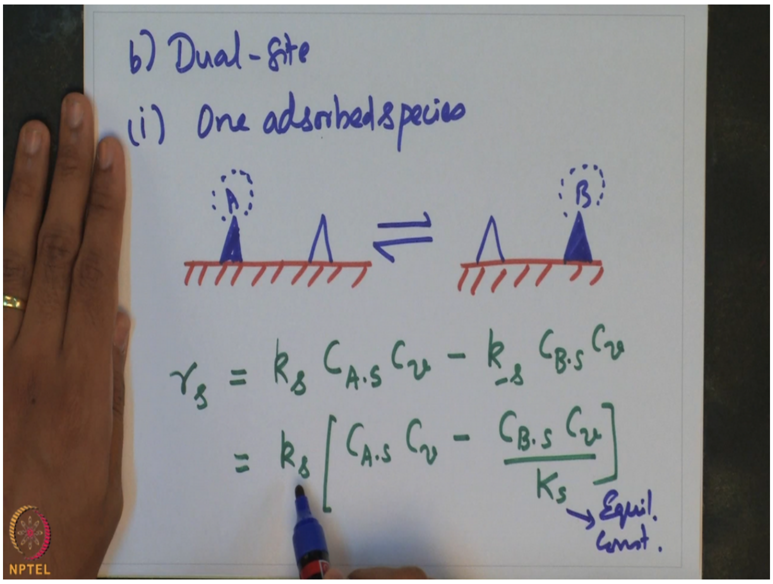

b) Dual-site

(i) One adsorbed species

$$r_s = k_s C_{A\cdot S} C_v - k_{-s} C_{B\cdot S} C_v$$

$$= k_s \left[ C_{A\cdot S} C_v - \frac{C_{B\cdot S} C_v}{\underset{\searrow \text{Equil. Const.}}{K_s}} \right]$$

Let us take the case of dual site mechanism, where you have 2 sites or adsorbed species in 2 sites or adsorbed species in 1 site somehow interacts with another site that may actually form products. So, there are 3 specific sub cases in this. Let us look at the first case where there is only 1 adsorbed species. And one can depict this as, if this is the catalyst surface and we have the active sites sitting here.

And let us say that species A is adsorbed onto this site. And there is a vacant site which is present. So, this 1 adsorbed species dual site is essentially the case where you have 1 species which is adsorbed onto the surface. And there is a second vacant site. And somehow these 2 actually interact with each other in order to form the product species. And the product could be that, we have the catalyst surface sitting here.

And then, we have 2 sites. And let us say that the, after the interaction, after the reaction, the product species is formed on the vacant site and the original site on which the reactant species A was adsorbed, will actually come out empty. And so, essentially, 1 active site, extra site is used. And to form the product species. And it leaves out another empty site back. So, we can, let us now try to write the rate expression for this particular mechanism.

So, the rate at which the reaction happens is given by k s which is the forward rate. Concentration of species at adsorbed species A, multiplied by vacant site, because now a vacant site is also involved. So, we need to account for the concentration of the vacant sites as well. – k – s into C B S into C v. So, essentially this is = k s multiplied by C A S into C v – C B S into C v, divided by K S, where K S in now the equilibrium constant.

So, for 1 adsorbed species dual site case the rate is given by k s which is the forward rate constant, multiplied by C A S into the vacant site concentration – the C B S into C v divided by K S. So, let us now look at the second case of dual site mechanism;

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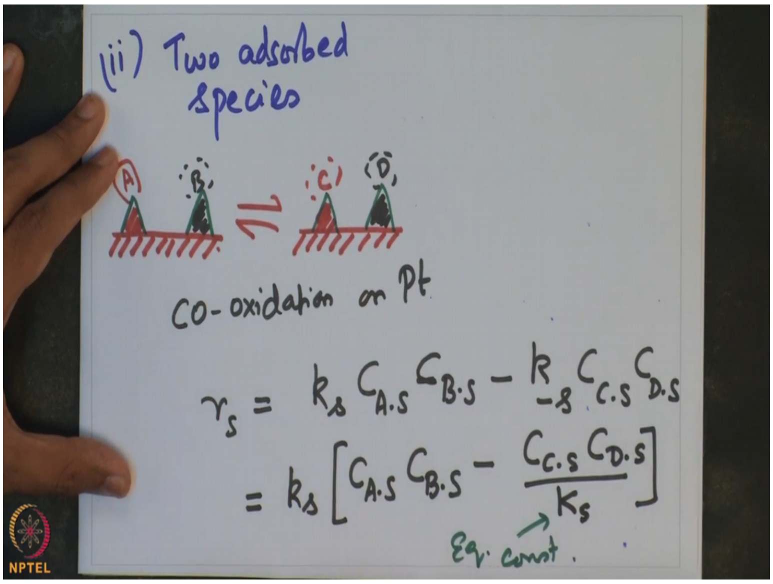

(ii) Two adsorbed species

CO- oxidation on Pt

$$r_s = k_s C_{A\cdot S} C_{B\cdot S} - k_{-s} C_{C\cdot S} C_{D\cdot S}$$

$$= k_s \left[ C_{A\cdot S} C_{B\cdot S} - \frac{C_{C\cdot S} C_{D\cdot S}}{\underset{\nearrow}{K_s}} \right]$$

Eq. const.

Where there are 2 adsorbed species that are participating in the catalytic reaction. And this can now be represented as, suppose let us say this is the catalyst surface. And we have 2 sites, where you have, let us say species A is sitting here and say species B is occupying this site. And now, these 2 would undergo a catalytic reaction reversibly to form let us say some product C and another product D.

Now this, a very good example of this particular case is the C O oxidation on platinum catalyst where you have C O which may be present here and oxygen which may be present here. And once they react they may form C O 2 let us say D corresponds to C O 2. And it might leave an empty vacant site. But, let us say for a general purpose or for generalisation, we can say that A, species A which is adsorbed onto 1 site and species B, it is adsorbed onto the second site.

Could actually reversibly lead to 2 product species C and D, which are actually adsorbed onto the 2 sites that is actually initially having 2 adsorbed reactant species. So, let us try to write the rate expression for this. So, r s is essentially given by k s into C A S into C B S – k – s into C C S into C D S. So, this we can rewrite as k s into C A S into C B S – C C S into C D S divided by the equilibrium constant K S. So, this is essentially the equilibrium constant.

So, C O oxidation, this is the mechanism that is known to actually happen when the C O is actually oxidised under rare conditions, where C O is reacting with oxygen on the surface of the catalyst in order to form C O 2. C O oxidation actually is a very very very common reaction, because C O is one of the very well-known and common by products of the combustion of any of the organic species.

And C O is not an environmentally friendly molecule. So, it needs to be converted into C O 2 form before it can be let out into the atmosphere. So, C O oxidation which is typically happening on platinum catalyst is actually a very good candidate for a, for such kind of a 2 adsorbed species dual site mechanism. That is typically the mechanism that satisfies the observed data.

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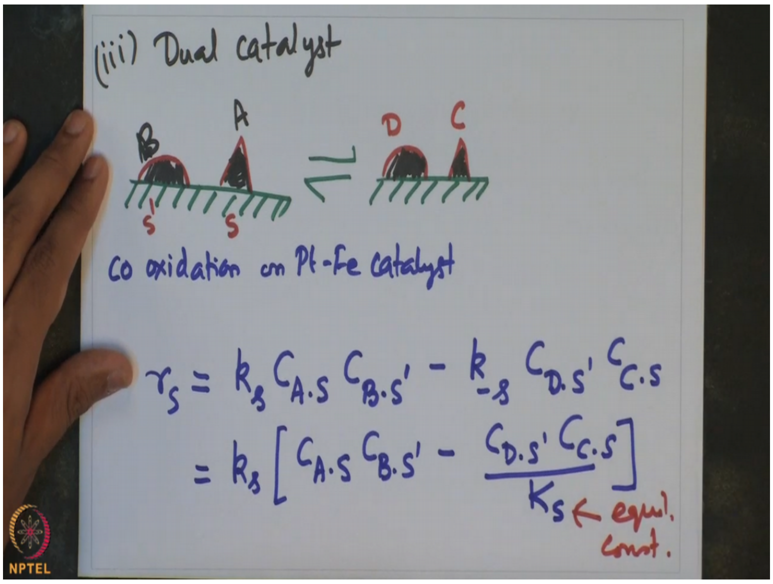

(iii) Dual catalyst

CO oxidation on Pt-Fe catalyst

$$r_s = k_s C_{A.S} C_{B.S'} - k_{-s} C_{D.S'} C_{C.S}$$
$$= k_s \left[ C_{A.S} C_{B.S'} - \frac{C_{D.S'} C_{C.S}}{K_s} \right]$$

$K_s \leftarrow$ equil. const.

So, let us look at a third case, dual catalyst. So, there are many situations where you have multiple species which are actually participating in the reaction. And 1 species may have a specific or special affinity to a particular catalyst. And the rate at which the species is binding to that catalyst could be very high at the given temperature in which the reaction has to happen. And unfortunately, the other species may not have a good affinity or it may not adsorb well onto the same catalyst site at that temperature.

So, one way to address this issue is where you have 2 catalysts, 2 active catalyst species which is actually impregnated onto the support. And 1 species has special affinity to 1 particular catalyst at that temperature in which the reaction happens. And the other species has affinity to the other catalyst. Remember that we said that the temperature is very important here because the adsorption is also an exothermic process and the reaction has to be conducted in the temperature range at which the species has, the species is able to adsorb onto the catalyst site.

So, therefore the temperature plays an important role and the operating temperature is necessary to, one needs to keep in mind what is the operating temperature. One way to circumvent this issue where 2 different species have different levels of affinity for a catalyst is essentially to use 2 different catalyst material, where each of these species have specific affinities to each of these 2 at that operating temperature.

So, what is the mechanism. And this is also a dual site, in some sense a dual site. And so, let us try to understand how that mechanism works and what is the rate at which the reaction happens for this particular case. So, we can depict this as: here is the catalyst surface. And let us say that 1 catalyst we depict as a mount and the other one let us say is a cone. And let us say that species A is bound to a cone and species B is bound to the mount.

And let us say that the occupied species is here. A good example of such a system is where you have C O oxidation on platinum F e catalyst where the species actually adsorbs onto platinum. C O adsorbs onto platinum and oxygen adsorbs onto iron catalyst. And then the species actually interact with each other. So now, this reversibly can lead to product D which is actually attached to, let us say catalyst, 1 particular catalyst let us say depicted by the mount.

And product C which is attached to the catalyst which is actually depicted by a cone. Now, suppose I call this as S prime. And this catalyst which is used for the cone type of a active site is called as S. So now, I can write the rate expressions for this. So, the rate of reaction is essentially given by the forward rate constant multiplied by the concentration of A which is bound to the active site whose catalyst is of type S multiplied by concentration of B whose catalyst site is essentially of the type S prime – k – s into C D S prime into C C S.

So, I can rewrite this as k s into C A S C B S prime – C D S prime into C C S divided by capital K S, where K S is the equilibrium constant. So, what we have seen in the dual site mechanism is 3 specific cases. And these 3 specific cases are the rate at which these 3 specific mechanisms are described. That type of kinetics is what is called as the Langmuir Hinshelwood Kinetics.

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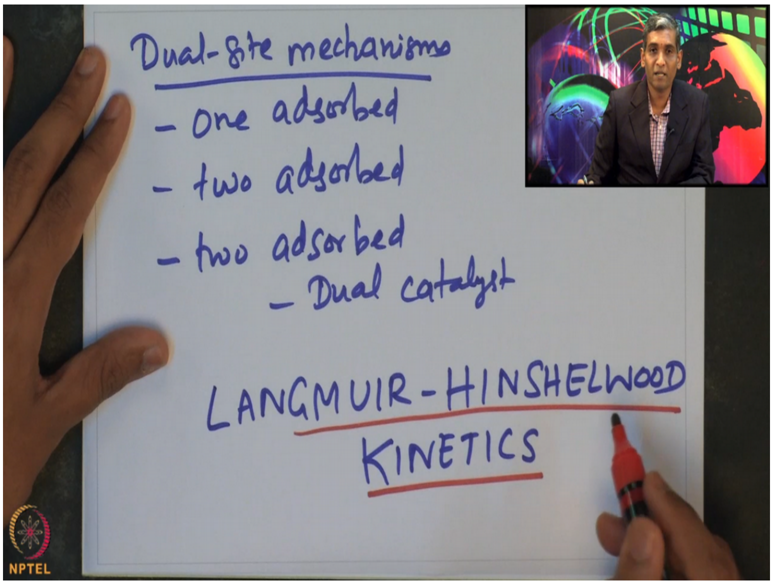

Dual-site mechanisms
- one adsorbed
- two adsorbed
- two adsorbed
  - Dual catalyst

LANGMUIR-HINSHELWOOD KINETICS

So, the dual site mechanism has 3 sub types, where you have once adsorbed species, 2 adsorbed species and 2 adsorbed species on dual catalyst. These are the 3 cases we looked at. Of course, there are many other possible things, many other possible ways by which the dual site mechanism can happen. And these 3 types, the kinetics that we actually derived for these 3 types is what is classically called as Langmuir Hinshelwood Kinetics.

So, it is a very very famous kinetic model, Langmuir Hinshelwood Kinetics. And we will be using this Langmuir Hinshelwood Kinetics in many examples in this course. So, let us look at a third case which is called the Eley-Rideal mechanism.

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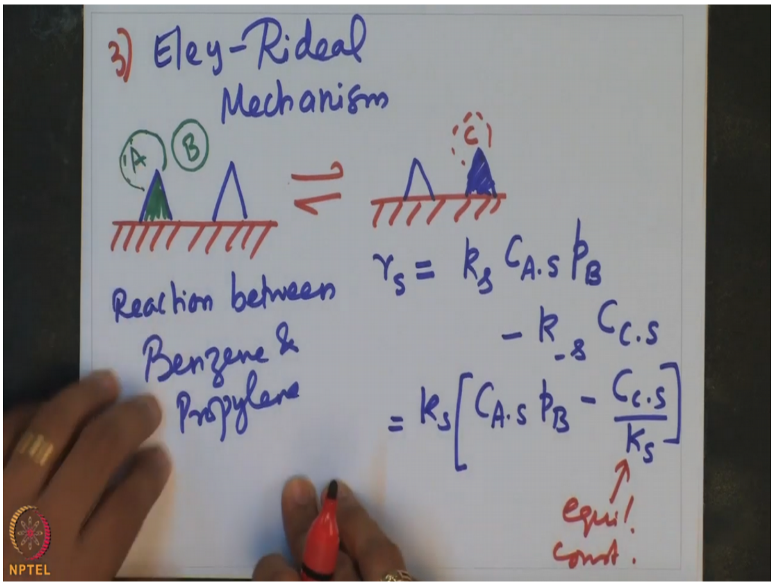

3) Eley-Rideal Mechanism

Reaction between Benzene & Propylene

$$r_s = k_s C_{A.s} p_B - k_{-s} C_{C.s}$$

$$= k_s \left[ C_{A.s} p_B - \frac{C_{C.s}}{K_s} \right]$$

equil. const.

This is a very special case where there may be a situation where the species which is adsorbed, 1 species which is actually adsorbed onto the catalyst site. And there may be another species which is actually present in the gas phase and not adsorbed onto the catalyst site. And the species adsorbed onto the catalyst site might react with the species which is present in the gas phase in order to form the necessary products.

So, this kind of a mechanism is very different from what we saw in the earlier case of single site and dual site. Where in each of these cases all the species is reacting or actually adsorbed onto the active sites. So, let us see how this works. So, we have a catalyst site, surface. We have a catalyst surface. And let us say that there are 2 sites that are depicted by cone. And let us say species A which is bound to this site here.

And species B is present close to it in the gas phase. Now, this kind of a mechanism is actually quite prevalent in the case of reaction. A good example of this is reaction between benzene and propylene where the benzene molecule is actually adsorbed onto the sites and the propylene molecule is available freely. And because of the reaction between the benzene molecule which is adsorbed onto the site with the propylene molecule which is in the gas phase.

These 2 actually join together, the reaction happens between them. So, it is a different mechanism. And let us try to see how to write the rate expression for this particular case. So, r s will be =; before that let us try to depict the reversible reaction here in the cartoon. So, here is the surface. And you have empty sites. And after the reaction happens, species C is actually bound to this particular active site.

And let us say that it leaves 1 empty site after the reaction happens. And the rate can now be written as k s which is the forward reaction, multiplied by the concentration of species A which is bound to the site, multiplied by the partial pressure of species B. Note that the species B is in the gas phase. And therefore, we now have to look at how many molecules of species B is actually present next to these active sites.

Because now the reaction is happening because of collision between the species B which is present in the gas phase close to the active sites where species A is bound and species A which is actually bound to the active sites. So, therefore the rate at which the forward reaction happens must be proportional to the partial pressure of species B which is actually present close to the active sites containing species A.

So, therefore the forward rate is now given by k s multiplied by C A S into P B and the backward reaction is essentially given by K – S into C C S. So, we can rewrite this as k s into C A S into P B – C C S divided by the equilibrium constant. So, this is the equilibrium constant. So, next let us look at the fifth step in the process, fifth step in the catalytic reaction process.

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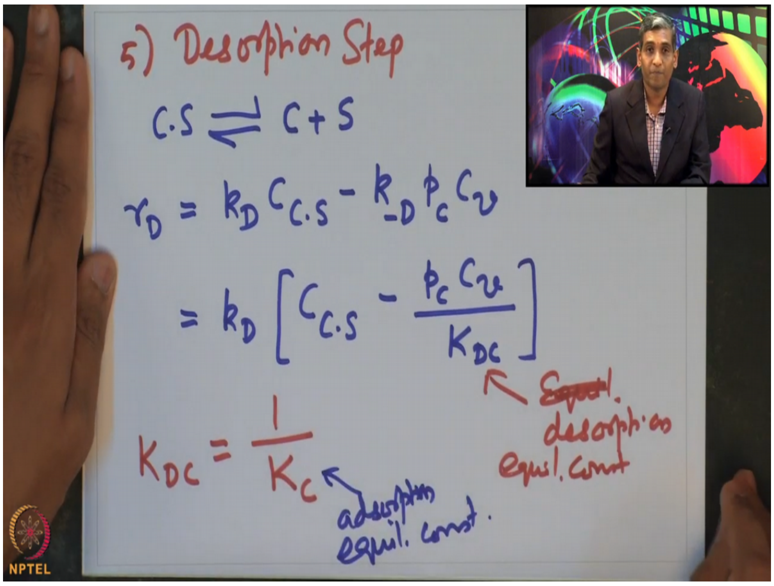

5) Desorption Step

$$C{\cdot}S \rightleftharpoons C + S$$

$$r_D = k_D C_{C \cdot S} - k_{-D} p_C C_v$$

$$= k_D \left[ C_{C \cdot S} - \frac{p_C C_v}{K_{DC}} \right]$$

~~Equil.~~ desorption equil. const

$$K_{DC} = \frac{1}{K_C}$$

adsorption equil. const.

So, step 5 is the desorption process. It is the desorption step. And that can be depicted in the form of a reaction where let us say species C which is bound to the site S. Now, species C is the product species. That should, that would reversibly lead to the product species in the gas phase and will leave out an active site. So, we can write the rate at which the desorption step happens.

r D as k D which is the forward desorption rate, rate constant multiplied by the concentration of the species, concentration of the active site containing species C – k – D into partial pressure of the species, product species C in the gas phase multiplied by the concentration of vacant sites. So, I can now rewrite this as k D into C C S – P C into C v divided by K D C which is the equilibrium desorption constant. It is the desorption equilibrium constant.

And so now, the desorption equilibrium constant will be = 1 by K C where K C will be the adsorption equilibrium constant. So, the desorption step, the rate at which the desorption step happens can easily be captured by this expression that is present here, where K D C is essentially the desorption equilibrium constant. And that should clearly be related to the adsorption equilibrium constant.

And it is related to adsorption equilibrium constant as 1 by K C. So, what we have characterised so far are these 5 steps which is actually present in the catalytic reaction. That is the external diffusion, we have characterised the internal diffusion, we have characterised the adsorption process, the reaction process, the desorption process.

Now, the external diffusion of the product species to the catalyst surface and the internal diffusion of the product species to the catalyst pellet surface, and the external diffusion of the product species from the catalyst pellet surface to the gas phase, that mechanism is very similar to what we saw for the reactant species that is diffusing from the bulk to the catalyst surface and from the catalyst surface all the way up to the surface of the, internal surface of the catalyst where the adsorption process happens.

So, in the next class what we will look at is we will look at how to determine what is the rate limiting step and what, how to find out what is the overall rate at which the particular reaction is happening, where there are multiple steps that is involved. Thank you.