

**Chemical Reaction Engineering - II**  
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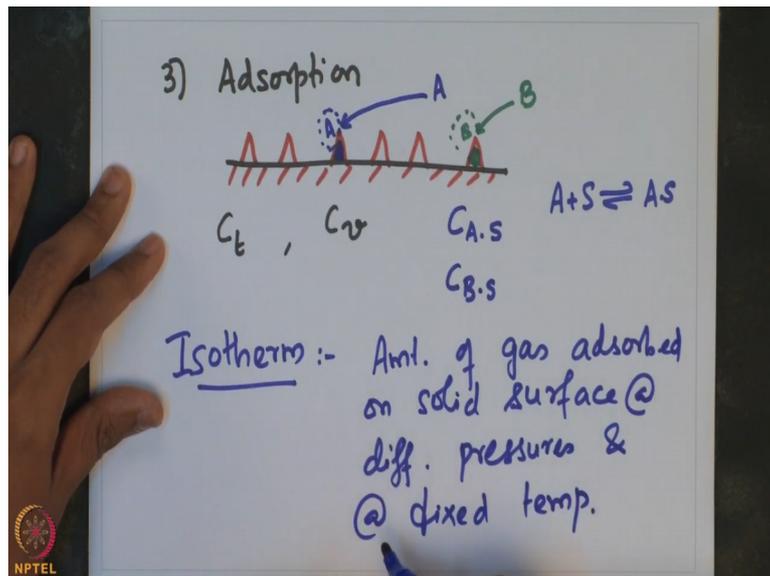
**Module - 1**  
**Lecture - 5**  
**Adsorption Isotherm**

Hi. Let us recap on what we looked in the last lecture. We looked that the different steps which are involved in catalytic reaction. We particularly observed there are 7 steps that are actually present, where step number 1 is the species from the bulk fluid diffuses and reaches the exterior surface of the pellet, due to external diffusion. And then, the species through the pores via the internal diffusion, reaches the surface of the catalyst which is actually step number 2.

And the species which reaches the surface of the catalyst actually gets adsorbed onto the active sites. And that is step number 3. And the adsorbed species undergoes reaction which is step number 4. And following which the products which are now sitting on the active sites get desorbed near the catalyst surface. And that is step number 5. And following which the species, product species diffuses back through the pores via the internal diffusion to the exterior surface of the pellet.

And the product actually from the exterior surface diffuses via the external diffusion to the bulk fluid. So, these are the 7 steps which are involved in catalytic reaction. And we attempted to find out what is the rate of reaction for the first 2, what is the rate for first 2 steps, that is the external diffusion and the internal diffusion. Now, we will start with the third step which is the adsorption.

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So, we will look at step 3 which is adsorption. We want to find the rate at which the species are actually getting adsorbed from the gas phase into the solid surface. And we drew a cartoon in last lecture. We said that, if this is the surface of the catalyst and there are these sites where the species can adsorb. And if, let us say that the empty hats are the vacant sites. And let us say species A which is actually gas species, which comes and adsorbs onto, let us say one of the empty sites.

And let us represent it by a filled hat. So, species A is now sitting on the site which is basically filled. Which means that, that site is actually occupied. And so, in order to quantify this process we defined a couple of terms. We defined what is called as  $C_t$  which is the total molar concentration of the active sites. We also defined what is  $C_v$  which is the concentration of the vacant sites.

Suppose there are 2 species, 2 gas species which are present, then it could be that species B which is also, which may also be participating in the reaction. They may come and sit in another site. They may come and occupy another site. So, let us now define concentration of species A which is sitting on the catalyst active site. That may be is  $C_{A.S}$  where  $A + S$  reversibly sits on the catalyst site.

So, if  $C_{A.S}$  is the concentration of the species which is actually sitting in the catalyst site or which is adsorbed onto the vacant catalyst site. And then,  $C_{B.S}$  let us say is the corresponding concentration of the species that is actually adsorbed onto a catalyst site. So,

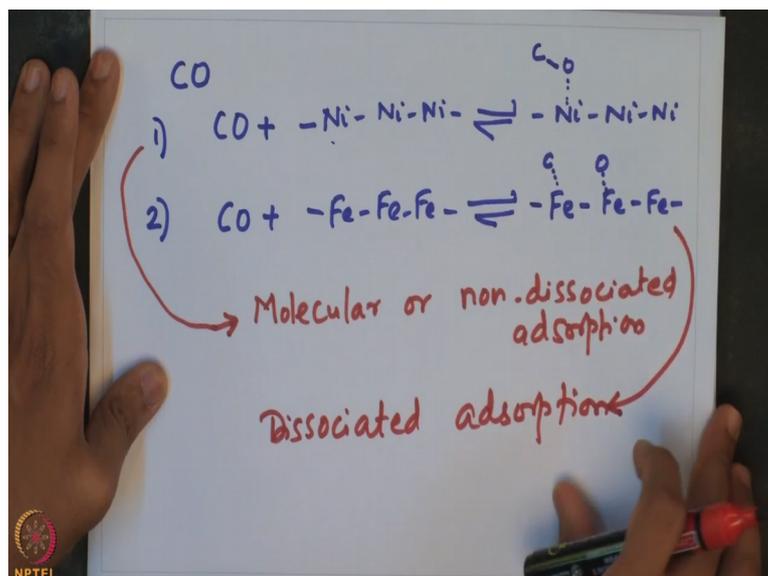
typically the adsorption is actually characterised by what is called as an isotherm. So, what we are going to spend most of today's lecturer is actually going to characterise the isotherm.

So, the definition of isotherm is that, it essentially refers to the amount of gas adsorbed on solid surface at different pressures and at fixed temperature. So, how do we find what is this isotherm? How do we find what is the relationship between the amount of gas adsorbed and the rate at which the species is actually getting adsorbed? So, let us look at what is, what really happens at the molecular level.

So, the gas species which is now coming and present close to the active site of the catalyst or the solid surface in the pores. So, the number of molecules which is actually present. Number of gas molecules that is present, they will collide with the species at the surface which is present, the catalyst species that is present. So, clearly the adsorption that is happening because of pollution is a strong function of the number of molecules of the gas species which is present close to the surface.

So, clearly, the rate at which the adsorption is going to happen is a function of, or is proportional to the partial pressure of the gas species that is present near the solid surface. So, let us try to quantify this. So, let us take a specific example of carbon monoxide.

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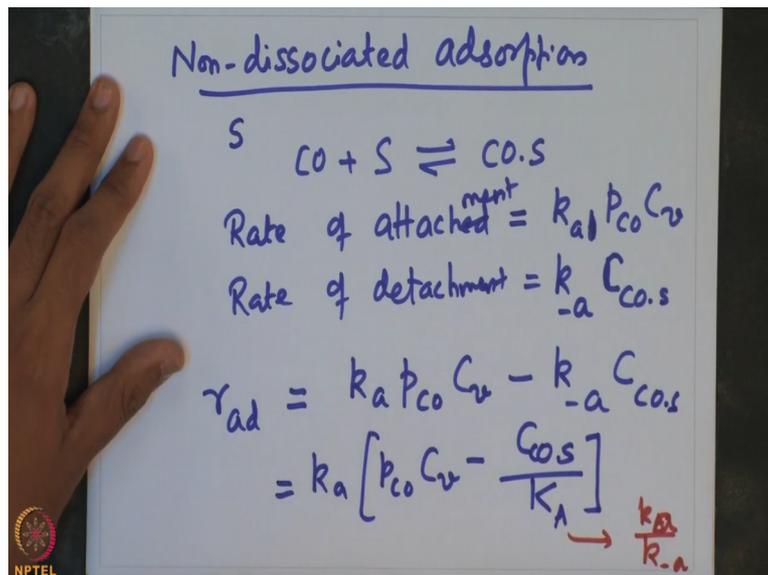
So, there are 2 possible cases where you may have C O which is actually reacting with let us say nickel catalyst. So, let us say these are the vacant sites in the nickel catalyst. And that will reversibly adsorb onto the surface where the whole molecule itself will adsorb onto the active

sites of the catalyst or it will form a bond with the nickel catalyst which is present. There may be another possibility where C O, let us say if it is in presence of iron catalyst, then the molecule may dissociate and the species would actually go and bind to different sites.

So, for instance F e, you may have carbon atom which is sitting here. And the oxygen is sitting in another site. So, there are 2 different ways by which the adsorption can happen. One could be because the whole molecule by itself could actually go and adsorb onto the active site or the molecule can dissociate itself and the individual species can go and adsorb onto the active sites. So, clearly there are 2 possible ways by which adsorption can happen.

One is called the molecular or non-dissociated adsorption, which is essentially the first case. And then, one can also have the second case where you have dissociated adsorption which is essentially the second case. So, we will find out the rate at which the adsorption can happen for both these cases. So, let us take the first one.

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So, let us say, non-dissociated adsorption. So, let us now say that S represents a vacant site. So, C O + S will give C O S which is actually adsorbed onto the vacant site. So now, the rate of attachment of the species onto the active site, clearly is a function of the partial pressure of the gas species which is actually adsorbing on site. So, that should be = k. Let us say that the attachment is a t multiplied by the partial pressure of C O multiplied by the concentration of the vacant sites.

Now, the rate of detachment will be  $k_d$  into concentration of the species which is actually present, concentration of the species which is actually bound to the active sites. So therefore, the rate of adsorption is essentially given by  $k_a P_{CO} C_v - k_d C_{CO,S}$ . So, this we can rewrite as  $k_a P_{CO} C_v - C_{CO,S}$  divided by an equilibrium, adsorption equilibrium constant called  $K_A$  which is essentially defined as the ratio of  $k_a$  by  $k_d$ .

So, this is the adsorption equilibrium constant. And now, we can actually use a conservation rule to actually understand how to define the rate of adsorption. Now, if you stare at the expression for the rate of adsorption, you will see that the quantity which we do not know is essentially this vacant site concentration. So, we will try to eliminate this in order to get the rate in terms of the measurable quantities. So now, we can use the conservation rule.

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The image shows a whiteboard with handwritten mathematical derivations. At the top, the total concentration of sites is given as  $C_t = C_v + C_{CO,S}$ , and the vacant site concentration is  $C_v = C_t - C_{CO,S}$ . To the right, a graph plots  $C_{CO,S}$  against  $P_{CO}$ , showing a curve that starts linearly and then levels off. The initial linear portion is labeled 'linear'. Below this, the rate of adsorption is given as  $r_{ad} = k_a \left[ P_{CO} [C_t - C_{CO,S}] - \frac{C_{CO,S}}{K_A} \right]$ . It is noted that at equilibrium,  $r_{ad} = 0$ . This leads to the equation  $\Rightarrow [P_{CO} C_t - P_{CO} C_{CO,S} - \frac{C_{CO,S}}{K_A}] = 0$ . Finally, the concentration of adsorbed species is derived as  $\Rightarrow C_{CO,S} = \frac{K_A P_{CO} C_t}{1 + K_A P_{CO}}$ , which is boxed in red.

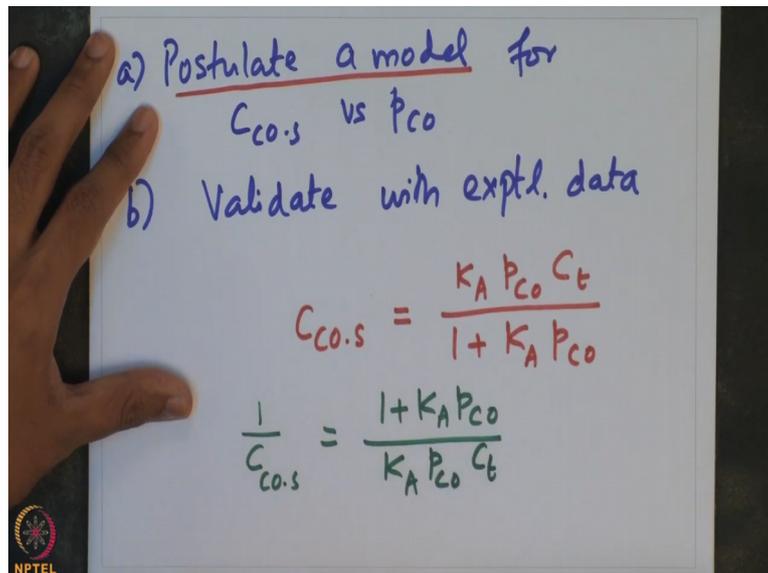
The conservation rule essentially is that the total concentration of the sites, active sites should be = the concentration of the vacant sites  $C_v$  + the concentration of the species adsorbed onto the sites. So therefore,  $C_v$  is essentially  $= C_t - C_{CO,S}$ . So, now if we plug this into the rate expression, we will see that  $r_{adsorbed}$ , rate of adsorption is = some  $k_a$  into  $P_{CO}$  into  $C_t - C_{CO,S} - C_{CO,S}$  divided by  $K_A$ .

So now, if at equilibrium the  $r_{adsorbed}$  is = 0. Which means that the attachment and detachment rates are equal. So, from here clearly,  $P_{CO} C_t - P_{CO} C_{CO,S} - C_{CO,S} = 0$ , that is = 0. So, from here, we can deduce that  $C_{CO,S}$  which is the concentration of the adsorbed  $CO$  onto the active sites, that should clearly be =  $P_{CO} C_t$  divided by  $1 + K_A P_{CO}$  into  $K_A$  here.

So, it is just a little algebra. So, once you do the algebra, you will find that the concentration of the species that is adsorbed onto the active sites is essentially given by this expression here. So now, let us try to see how this expression actually depends or what is its dependence on the partial pressure of the C O. So, suppose if I plot P C O versus C C O S. Then the typical curve is that you have initially it actually increases linearly and then actually remains constant.

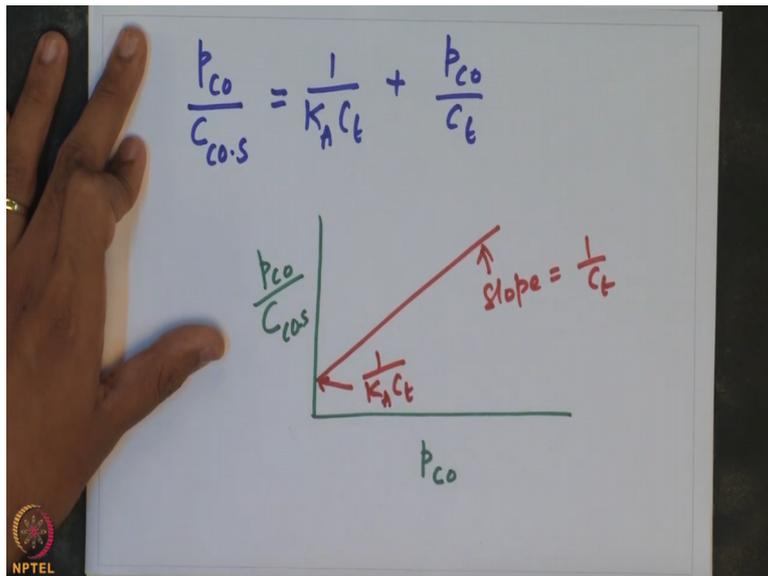
So, this region is actually linear. And as the partial pressure of C O increases further the concentration of the adsorbed species is no more a function of the concentration, partial pressure of the gas C O. So, initial phase where low concentration behaves linear, and that sort of can be seen from this expression. One can actually deduced from this expression that if P C O is very small, then K times K A times P C O is much smaller than 1, which essentially means that it behaves like a linear function with respect to P C O. So now if, how do we know what is the adsorption isotherm. The best way to do that is to postulate an isotherm.

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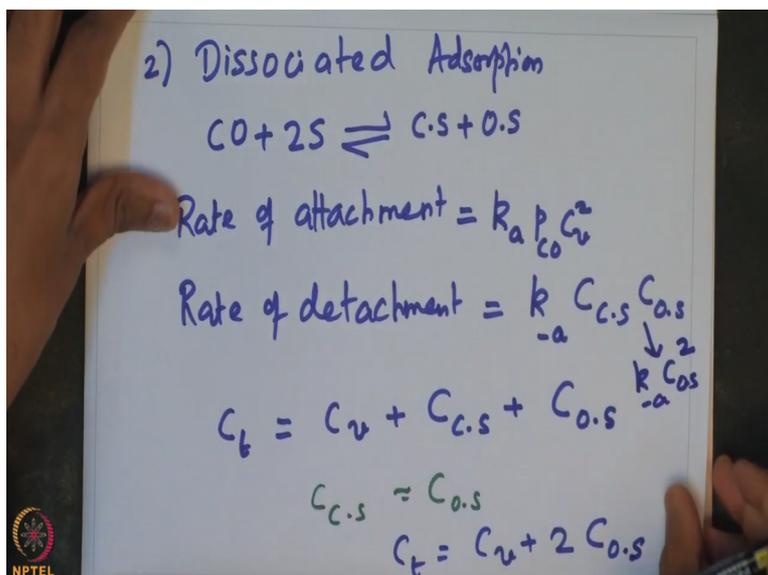
Postulate a model for C C O S versus the partial pressure of C O. And then validate with experimental data. So, the postulation of a model is what we just did a few minutes ago. And so, suppose let us say I have such a model, where C A, C C O S is essentially given by K A into P C O into C t divided by 1 + K A into P C O. Suppose I have this model, then I can actually rewrite this model, rewrite this expression in the form of, rewrite this expression by essentially taking 1 by C C O S, you take inverse of this, divided by C O into C t. And this, I can actually rewrite as, so, this expression can be simply rewritten as;

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P times, partial pressure of C O, divided by C C O S is = 1 by K A C t + P C O by C t. So now, if the experiments are done at different partial pressures of C O. So, I can now plot C O versus P C O divided by C C O S. And based on this expression I should actually get a straight line fit, I should get a straight line fit whose slope is = 1 by C t and the intercept should be = 1 by K A into C t. So, if the model that I propose is essentially the molecular non-dissociative form, then I can actually use that model and validate it with experiments using such a linear fit. So, let us now next look at the dissociative model.

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Let us look at the second case of dissociative adsorption. Let us look at dissociative adsorption. So, we can represent the adsorption of C O in a dissociated form, as a reaction, as a steps, as a reversible reaction step where we have C O + 2 S reversibly gives C S + O S. So

now, I can write the rate of attachment. Is essentially given by  $k_a$  into partial pressure of  $C O$  into  $C v$  square. And the rate of detachment will be given by  $k - a$  into concentration of  $C S$  into concentration of  $O S$ .

And the conservation rule now is  $C t$  will be = total concentration of sites, will be  $C v$  + the concentration of sites occupied by  $C$  + the concentration of sites occupied by  $O$ . Now, since the active sites containing  $C$  and  $O$  essentially comes from this species. For this case,  $C$  of  $C S$  should actually be =  $C$  of  $O S$ . And so, from here, we can see that the conservation rule is essentially =  $C v$  + 2 times  $C O S$ . And the rate of detachment is  $k - a$  into  $C O S$  square. So now, let us plug these in into the rate.

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The whiteboard shows the following handwritten equations:

$$r_{ad} = k_a P_{CO} C_v^2 - k_{-a} C_{OS}^2$$

$$= k_a \left[ P_{CO} C_v^2 - \frac{C_{OS}^2}{K_A} \right]$$

At equil.

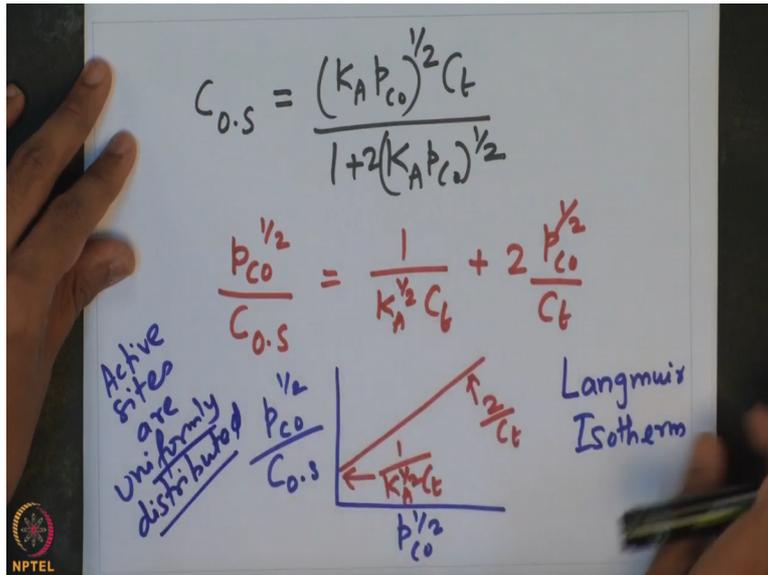
$$C_{OS} = (K_A P_{CO})^{1/2} C_v$$

$$C_t = C_v + 2(K_A P_{CO})^{1/2} C_v$$

$$\Rightarrow C_v = \frac{C_t}{1 + 2(K_A P_{CO})^{1/2}}$$

I can now write the rate of adsorption as  $k_a$  into  $P C O$  into  $C v$  square –  $k - a$  into  $C O S$  square. So, from here, I can actually rewrite this expression as  $k_a$  into  $P C O$  into  $C v$  square –  $C O S$  square divided by the adsorption equilibrium constant. So, at equilibrium  $C O S$  is essentially given by  $K_A$  into  $P C O$  to the power of half into  $C v$ . So, if I now plug this into the conservation rule, I will see that  $C t$  is =  $C v$  + 2 times  $K_A P C O$  to the power of half into  $C v$ . Or from here,  $C v$  is =  $C t$  divided by  $1 + 2 K_A P C O$  to the power of half. So, this I can now substitute in this expression here. So, if I substitute in this expression, what I find is that;

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$C_{O.S}$  is essentially  $= K_A \text{ into } P_{CO}$ , to the power of half into  $C_t$ , divided by  $1 + K_A, 2$  times  $K_A P_{CO}$  to the power of half. So, once again I can actually modify this equation to bring it into a linear fitting form. And the way to do that is, I once again take an inverse. And if I take an inverse, I will see that it will reduce to the form where it will be  $P_{CO}$  to the power of half divided by  $C_{O.S}$  is  $= \frac{1}{K_A \text{ to the power of half into } C_t} + 2 \text{ times } P_{CO}$  to the power of half divided by  $C_t$ .

So, I will get this linear relationship expression between the partial pressure of  $CO$  and the concentration of the oxygen molecule which is attached to the sites. So now, I can now draw a linear fit. Suppose if I have experimental data where I actually measure the concentration of the oxygen attached to the sites as a function of the partial pressure of  $CO$ , then I will be able to draw a fit, where I can actually draw  $P_{CO}$  on the axis here, to the power of half.

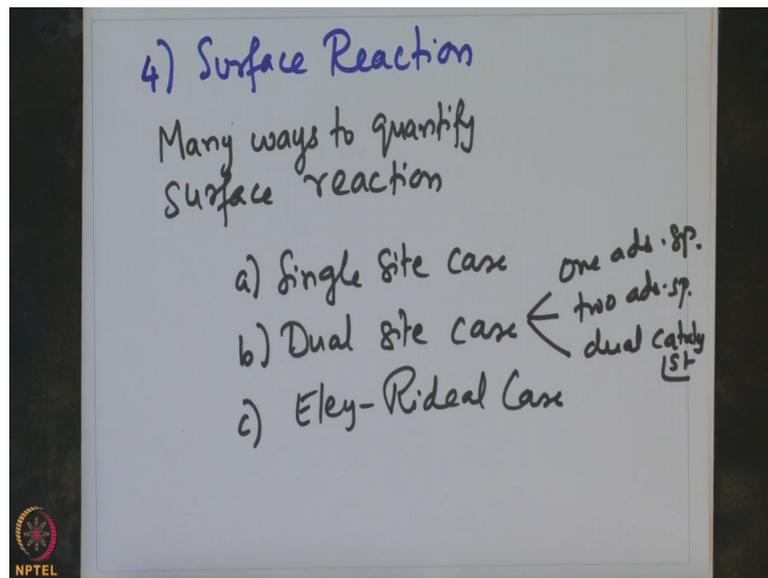
And  $P_{CO}$  to the power of half by  $C_{O.S}$ . And I should actually get a straight line fit, with the slope being  $2 \text{ by } C_t$  and the intercept being  $\frac{1}{K_A \text{ to the power of half into } C_t}$ . So, this is how one can actually measure the, use the experimental data and validate the postulated model. And if the experimental data matches well with the model, then we know that the postulation is correct.

And then, we can actually verify the postulate. And we can say that, that is the isotherm. So, such kind of an isotherm is what is called as Langmuir isotherm. So, what we have just derived for 2 cases of dissociated adsorption versus non-dissociated adsorption is essentially,

we have derived the Langmuir isotherm which essentially quantifies the amount of gas that is actually adsorbed onto the active sites at different pressures and at a fixed temperature.

It gives you what is the, what is the relationship between the concentration of adsorbed species and the partial pressure of the gas. That is what is called as a Langmuir isotherm. And such an isotherm is actually very useful in order to understand how the adsorption process happen and how to quantify the adsorption process.

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So next, let us look at the fourth step which is essentially the surface reaction term. And note that in the previous case where we derived the Langmuir isotherm what we have actually implicitly assumed is that the active sites are uniformly distributed. So, we have implicitly assumed during the derivation that the active sites are actually uniformly distributed. So, let us now move onto the fourth step in the catalytic reaction process where it is a surface reaction.

So now, the question is if, what happens, how do you find the rate at which the surface reaction happens. And if I understand the rate, if I am able to relate the rate to the concentration of the adsorbed species or concentration of the measurables, then I can actually, I have found a way by which I can actually quantify the surface reaction process. So, let us look at how to do that. So, essentially, there are many many ways to quantify surface reaction.

So, we will look at how to find the rate at which the surface reaction happens for a few cases. So, we will specifically look at single site case. We will look at dual site case. Then we will also look at what is called as the Eley-Rideal case. And even in the dual site case, there are actually 3 different cases we will look at, where you have, 1 adsorbed species, we have multiple adsorbed species and then we have dual catalyst case.

We will look at each of these cases where we will try to find out what is the rate at which the reaction happens, the surface reaction happens for a single site case. We will look at it for a dual site case. And we will look at it for a Eley-Rideal case where in dual site case we will look at 3 different possibilities. So, what we have essentially covered in this lecture is we attempted to quantify the adsorption process.

We attempted to find out what is the rate at which the adsorption process happens and how to relate the concentration of the species which is adsorbed onto the active sites versus the partial pressure of the species in the gas phase. So next, in the next class we will start looking at what, how to quantify the surface reaction. Thank you.