Chemical Reaction Engineering - II
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Module - 1
Lecture - 4
Steps in Catalysis

Hi. In the last lecture, we looked at the properties of the catalyst. We looked at how catalysts work. Particularly we looked at adsorption process. And we observed that the adsorption is actually a function of temperature. We also observed that the heat of adsorption, particularly for the chemical adsorption case is the same order of magnitude as that of the heat of reaction. And therefore, the temperature at which the reaction is actually conducted should be in the same range as that of the temperature that facilitates the adsorption process.

Otherwise the yield of the reaction actually is going to be lower. There will be very minimal productivity otherwise. In this lecture we will start looking at the steps that are involved in catalytic reaction.

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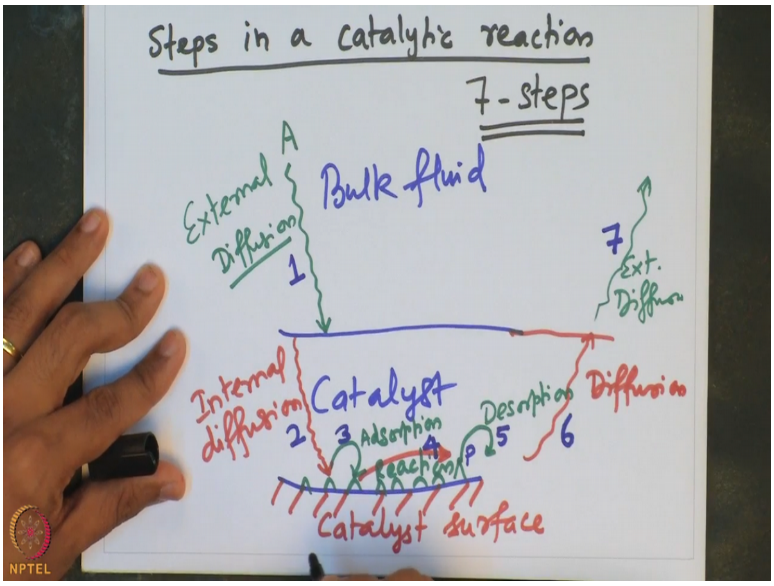

So, the catalytic reaction actually involves 7 particular steps. Suppose we depict the surface of a catalyst, let us say that this is the surface of the catalyst. That is the surface of the catalyst. And suppose this is the boundary or the interface between the bulk fluid outside and the exterior surface of the catalyst. This is the catalyst surface where the active sites are present. So, let us mark the active sites here. These are the active sites.

And if this is the exterior surface of the catalyst which is in contact with the bulk fluid. And let us say that the bulk fluid is present here. And this is the catalyst. Now, the species which is present in the bulk fluid, let us say species A, has to first diffuse to the exterior surface of the catalyst. So, there is a diffusion process where the species has to diffuse to the exterior surface of the catalyst, following which the species has to actually have an internal diffusion, where it diffuses to the surface of the catalyst, to the active surface or active sites.

So, this is the internal diffusion. One may term the diffusion in the bulk fluid as actually external diffusion. And then, there has to be adsorption of the species onto the surface. So, there will be adsorption of species onto the surface. So, that could be an adsorption step, adsorption of species onto the surface, following which the species which is adsorbed actually has to undergo a reaction. So, that is the reaction step.

And let us assume that because of this reaction a certain product is actually formed at this location. Now, the product which is formed, now has to desorb from the active surface. There is a desorption that has to happen. And after the desorption of the product species, then the species, product species have to undergo an diffusion process to reach the surface. So, this is the again a diffusion process, internal diffusion.

And then, following which the species which has actually reached the surface, has to now diffuse back into the bulk fluid. So, the products which is actually formed; so, let us name, label the product here. So, let us call that P is the product and A is the reactant. So, let us say that the external diffusion is step number 1, where the species actually diffuses from the bulk to the surface of the catalyst pellet, through external diffusion.

And then, the species which has now reached the surface of the catalyst pellet through internal diffusion reaches the active surface of the catalyst. Let us say that, that is step number 2. And then, once the species reaches the active surface the species has to adsorb onto the catalyst site, which let us say we call it step 3. And then, once the species is adsorbed, the reaction has to happen to form the product. Let us say that is step 4.

And the product that is formed have to desorb from the active sites. Let us say that is step 5. And then, the product which is formed has to diffuse back to the surface of the catalyst pellet, which is, let us say is step 6. And then, step 7, the product species from the surface of the catalyst pellet has to diffuse into the bulk fluid. So the, essentially 7 steps which are involved in the catalytic reaction for the species from the bulk fluid to react on the catalyst surface and the product species to actually come out of the catalyst pellet.

There are essentially 7 steps that are involved. And each of these steps is actually very crucial and each of these steps are actually governed by different principles. Now, what is the overall reaction rate. All we are interested in, is actually the overall reaction rate, because that is going to directly affect the productivity of that particular reaction. If I want to look at how much, how much of that particular product species is actually formed, that strongly depends upon the productivity and that strongly depends upon the rate at which the reaction is actually happening.

So, what is of interest to quantify the catalytic reaction is essentially to find out what is the rate at which the species is actually being or the reactant species is being converted to products. Because there are 7 steps that are actually involved, the question arises as to which of these 7 steps actually controls the reaction rate. So, let us look at what is called as rate controlling step.

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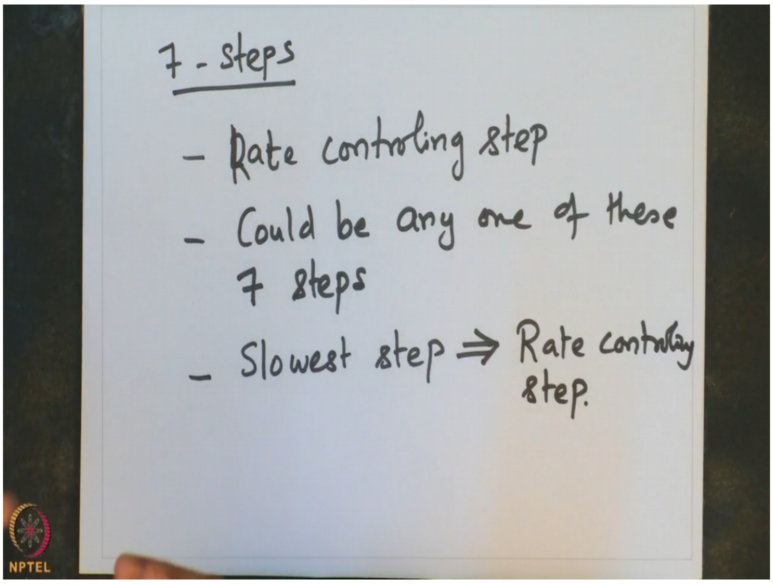

7 - steps

- Rate controlling step
- Could be any one of these 7 steps
- Slowest step ⇒ Rate controlling step.

Because there are 7 steps, there must be a rate controlling step. Could be any 1 of these 7 steps. So, whichever step is actually the slowest step; the slowest step actually, the rate at which the slowest step happens actually decides the rate at which the overall reaction is actually occurring, rate at which the overall reaction actually occurs. So, this slowest step is actually the rate controlling step.

Now, the reason is that, this slowest step, whichever step which actually is the slowest to happen, that actually dictates what is the rate, what is the overall reaction rate. This is because, relative to the speed at which that step happens, all the other steps are actually faster. So therefore, the overall rate at which the species is converted to products is essentially controlled by that particular step which actually occurs in the slowest fashion.

So, let us look at each one of these cases as to which one is likely to be the slowest step. And we will characterise and try to understand how to find out the rate of each of these step. And if that turns out to be the slowest step, what will be the overall reaction rate.

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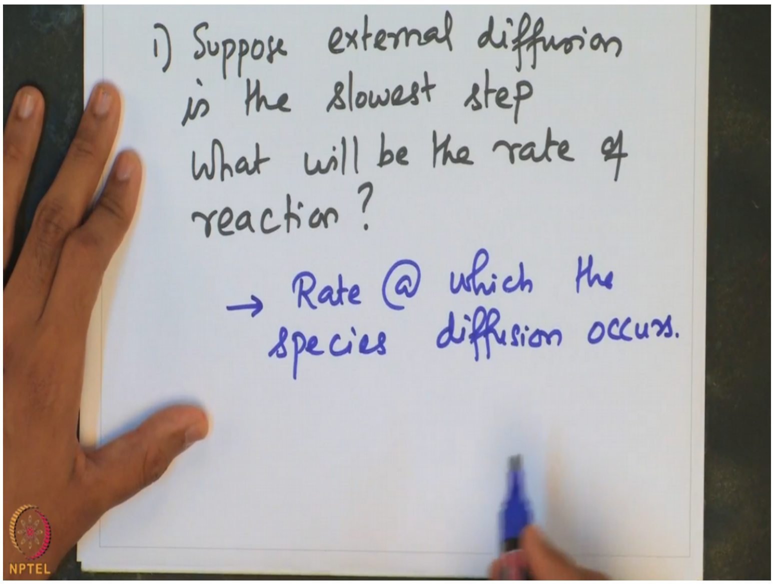

i) Suppose external diffusion is the slowest step
What will be the rate of reaction?
→ Rate @ which the species diffusion occurs.

So, suppose if external diffusion, suppose external diffusion is the slowest step, then what will be the; the question is, what will be the rate of reaction. Now, we can answer this question if we can find out what is the rate at which the species diffusion; so, if we know what is the rate at which the species diffusion occurs, then we will know what is the rate at which the overall reaction is happening.

Because the mass transport is actually controlling or the slowest step that actually; it is the relatively slowest step compared to all the remaining steps. And so, that will decide what is the rate at which the reaction actually happens. So now, let us characterise what will be the rate at which the species diffusion occurs or what will be the rate at which the mass transport occurs due to external diffusion.

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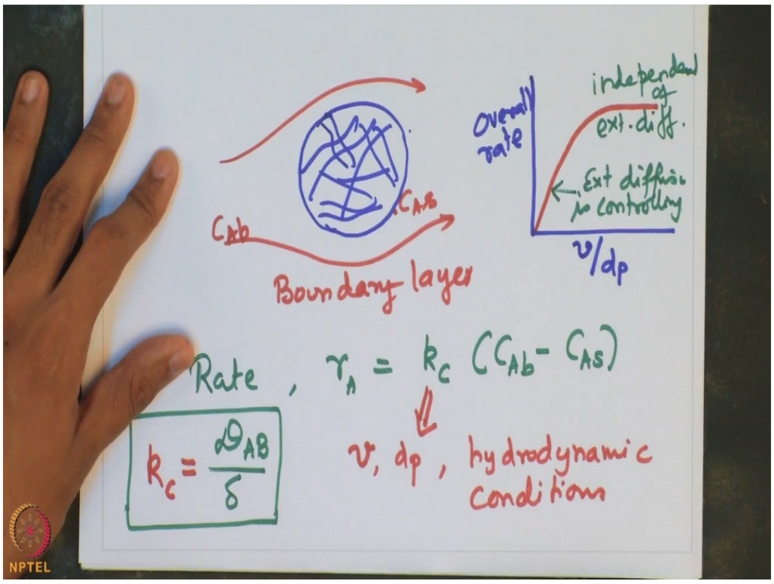

So, let us consider a spherical pellet. And if the species which is in the fluid stream, let us say is actually flowing past to this pellet. Then, there will be a boundary layer which will be present. There will be a boundary layer which will be present around this pellet, because the fluid is actually flowing past this object. Now, suppose the concentration of the species is C A bulk in the bulk fluid. And suppose we assume that the concentration of the species at the surface is given by C A S.

Then, the rate at which mass transport happens is essentially given by k c which is a corresponding mass transport coefficient into C A bulk – C A S. Now, this mass transport coefficient will clearly be a function of the velocity with which the fluid is moving, the diameter of the particle and other hydrodynamic conditions. In fact, we know from mass transport course that the mass transport coefficient for such a case would essentially be given by the diffusivity, counter diffusivity between A and B.

Here, we have assumed that A is the reactant species and B is the product species and if D A B is the equimolar counter diffusivity, then D A B divided by delta would essentially give the mass transport coefficient for that particular species between the bulk fluid and the particles. Note that the particles will be, will have lot of pores inside.

But in this case the diffusion of the species or what happens inside these pores, whether the reaction is happening, whatever rate at which it happens, it does not matter, because we have assumed that the external diffusion by which the species actually reaches the surface of the catalyst pellet, is actually the slowest step. So therefore, whatever happens inside the catalyst pellet is irrelevant for estimating what is the overall rate at which the reaction is happening.

So, as long, as far as we know what is the mass transport coefficient, if the external diffusion is actually the slowest step, that means that it controls the overall reaction rate. Then, we should be able to estimate what is the rate at which the reaction is happening if we know what is the mass transport coefficient. And if the boundary layer is present, then one could relate the mass transport coefficient to the equimolar counter diffusivity and the boundary layer thickness.

Clearly it is a function of the velocity. So, let us look at that. Suppose, I look at the dependence of v by d p which is the velocity with which the fluid is actually flowing divided by the particle diameter and the overall rate. The typical behaviour would be that, in slow velocities the species is actually diffusing; and in fact, that is what is controlling the overall reaction. And when we increase the velocity, then the species is much more available and it is actually diffusing much faster to the surface.

So, which means that, in the region where the velocity is small, v by d p is small, it is most likely the external diffusion is controlling. And in the region where the v by d p is sufficiently larger, then it is independent, the rate is independent of the external diffusion process. So clearly, depending upon the velocity or the hydrodynamic conditions, the overall rate actually is going to be either dependent on the external diffusion or it is going to not be dependent on the external diffusion.

In other words, if the hydrodynamic conditions are such that the diffusion is actually faster, then external diffusion is no more controlling the overall rate of the reaction. On the other hand, if the external definition slower because of the certain hydrodynamic conditions, such as low flow rates, then the external diffusion actually controls the overall rate of the reaction.
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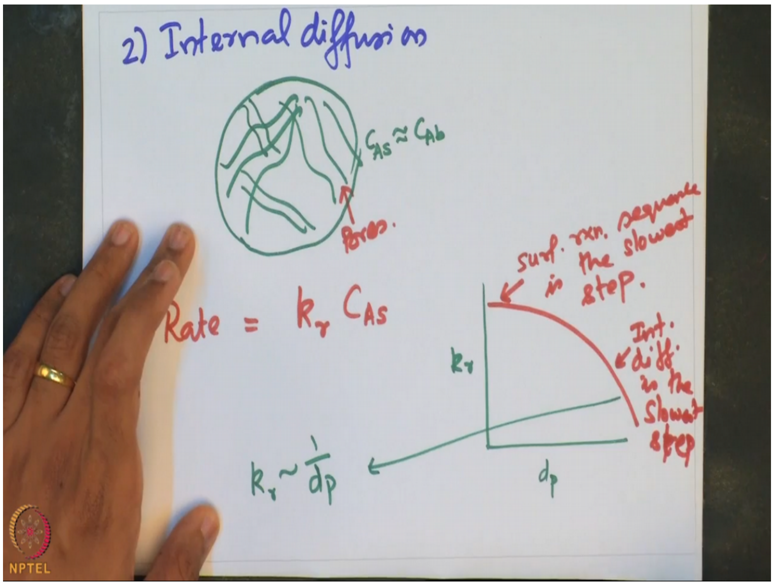

So, let us now look at the next case of internal diffusion. So, if we now sketch the catalyst; there are pores that are actually present. These are the pores. So, when we say that the internal diffusion is actually the slowest step, then we implicitly assume that the external diffusion is not the slowest step. Which means that the concentration of the species at the surface is = that of the bulk concentration.

So, we can assume that the surface concentration is approximately = the bulk concentration, because the slowest step is the internal diffusion. And by the time the internal diffusion happens, the external diffusion has already happened and the species actually has sufficiently reached the surface of the catalyst pellet. And therefore, the surface concentration which is at the edge of the catalyst pellet is almost = that of the bulk concentration.

So, the diffusion which actually happens through this pores, that depends upon the diffusivity and that might be controlling the internal diffusion process. And so, the rate at which, the overall observed rate of reaction would essentially be some rate constant multiplied by C A S. So, this rate constant takes into account all the internal diffusion processes, everything that is happening inside.

And this k r is actually a function of the diameter of the particle. Clearly, it is a function of the diameter of the particle. Because if the particle is smaller in size, then, whatever species which is actually present at the surface of the catalyst pellet; that will be readily available and it will immediately penetrate into the catalyst pores. And it will be available for reaction at, for adsorption at the surface of the catalyst pellet.

But, on the other hand if the catalyst size is slightly larger, then, even before the species actually enters sufficiently inside, the reaction would immediately happen because, we have assumed that the internal diffusion is the slowest step and the reaction is actually happening faster, adsorption in the reaction steps are actually happening. So, which means that if the particle is actually larger, the catalyst particle is actually of larger diameter, then the species, as soon as it reaches the immediate layer which is close to the periphery of the pellet, the reaction would happen.

And the catalyst which is actually present inside would actually essentially remain unused. So, there is a trade-off between the size of the catalyst and the rate at which the reaction actually happens. So, if I attempt to capture the dependency of k r on d p, then the typical behaviour would be that, it will be the surface reaction, if the d p is very small, then the internal diffusion is very very fast because it is immediately available.

And so, it is likely that the surface reaction sequence is actually the slowest step. On the other hand, if I have a larger d p, then it is most likely that the internal diffusion is the slowest step. In fact, it has been observed that in this region, k r actually scales as 1 by d p. And so, if, as the particle diameter goes much much larger, then the rate actually falls very quickly. And so, therefore, clearly the rate at which the reaction is going to happen is a strong function of d p, because k r which is the rate constant in this case is actually a function of the particle diameter. Let us look at the third step where the adsorption process may be rate controlling.

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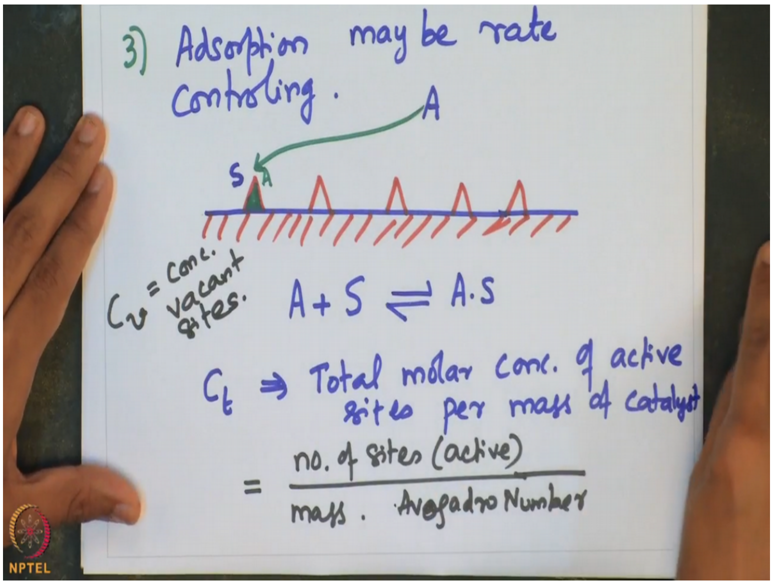

3) Adsorption may be rate controling.

C_v = conc. vacant sites.

$A + S \rightleftharpoons A.S$

$C_t \Rightarrow$ Total molar conc. of active sites per mass of catalyst

$= \dfrac{\text{no. of sites (active)}}{\text{mass . Avogadro Number}}$

So, let us look at step 3 where the adsorption may be rate controlling. So, let us try to understand or quantify the adsorption process. Suppose we have this catalyst surface, and let us say that these are the active sites which are actually present on the catalyst surface. So, if S, let us say that S is a vacant site. Let us assume that S is a vacant site. And A is the species which is actually undergoing a reaction, A is the reactant species.

Then the species A actually has to adsorb onto a vacant site. Remember that we have assumed that the internal and external diffusion are no more rate controlling. It is the adsorption which is rate controlling. Which means that the species A is actually readily available for it to get adsorbed onto the vacant site, if it is available. So, what happens is that when the species is present close to the surface, then the species will actually go and adsorb onto the vacant site.

And suppose, let us say that we shade it with green to say the species A has occupied this particular site. So, the empty cones are essentially the vacant site and the filled cones are the sites where the species is actually adsorbed onto that particular surface. Remember that the external diffusion and the internal diffusion are no more the slowest steps. And therefore, the species is readily available at the surface for it to get adsorbed onto the empty or the vacant sites.

Now, we can postulate this or we can sort of, we can actually model this as a simple reaction step. And let us say that A is the species which is actually is getting adsorbed onto the vacant site and S is the vacant site. Then typically it is a reversible step. So, it gets adsorbed. And we can represent this site which is actually having the species say adsorbed onto it, is as some sort of a adsorbed species A dot S, which is actually, represents A which is having been adsorbed onto the vacant site S.

Now, we can define a quantity called C t which is the total molar concentration of active sites per mass of the catalyst. This can actually be written as the number of sites, active sites, divided by the mass of the catalyst multiplied by the Avogadro number. You should note that, although there are several sites which are actually present, not all sites may be active. Because, the support which is present, where there are different sites where the catalyst can be present, but during the impregnation of the catalyst material onto the support, it is possible that not all sites actually uniformly have the catalyst particle.

So, there may be sites which may not have the catalyst particles. So, those sites are not active sites. So, what is important for adsorption is only the actual number of the active sites which are actually present. So, one can define a total concentration or the total molar concentration of active sites as the number of active sites which is present per mass of the catalyst divided by the Avogadro number.

There is one more definition that we need to look at, which is called the concentration of the vacant sites. So, suppose we define C v as the concentration of the vacant sites, we can define C v as the concentration of the vacant sites. And so, these 2 quantities together would actually enable us to quantify the adsorption process. So, what we have seen in today's lecture, in this lecture is essentially the different steps; there are 7 different steps that are actually involved in a catalytic reaction.

Starting from the species from the bulk fluid all the way up to the surface where the reaction happens and the product that actually is taken back into the bulk. Now, the overall rate of reaction which is typically of the interest because that is what is going to control the eventual productivity of the product species is actually controlled by what is called as the slowest step, whatever is the, whichever is the slowest step out of these 7 essentially is going to decide what is going to be the overall rate at which the reaction is going to happen. Thank you.