

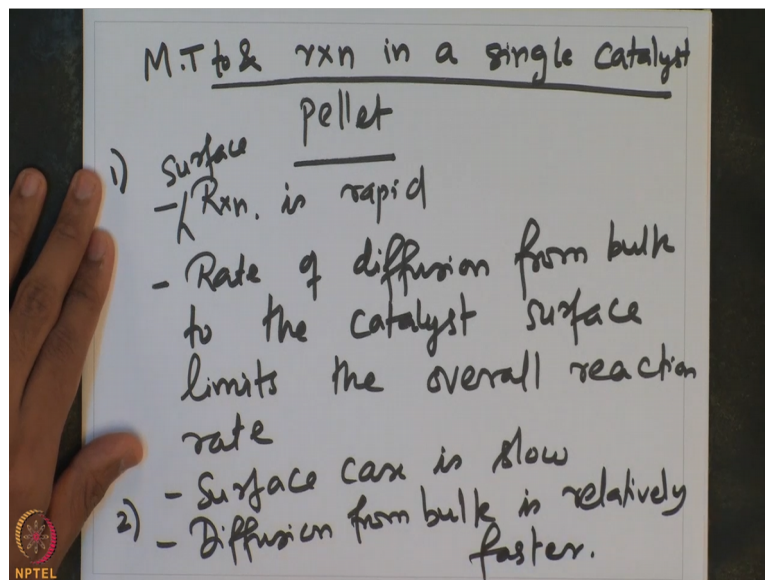
Chemical Reaction Engineering - II
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Module - 6
Lecture - 27
Mass Transfer to a Single Particle with Reaction

In the last lecture, we looked at how to estimate mass transport coefficient for flow past a single particle. We specifically observed that, in a packed bed reactor let us say, that there are, that is filled with catalyst particles. And the fluid is actually flowing through the packed bed where the reaction is happening at the surface on the catalyst. We zoomed up the location of a catalyst. We observed that there may be a boundary layer and we assume that the curvature is negligible.

We assumed a planar boundary layer. And then we found out what is the way to estimate the heat mass transport coefficient, based on the boundary layer analogy. In today's class we will look at how to combine the mass transport process that is happening and simultaneously with the reaction in a single catalyst pellet.

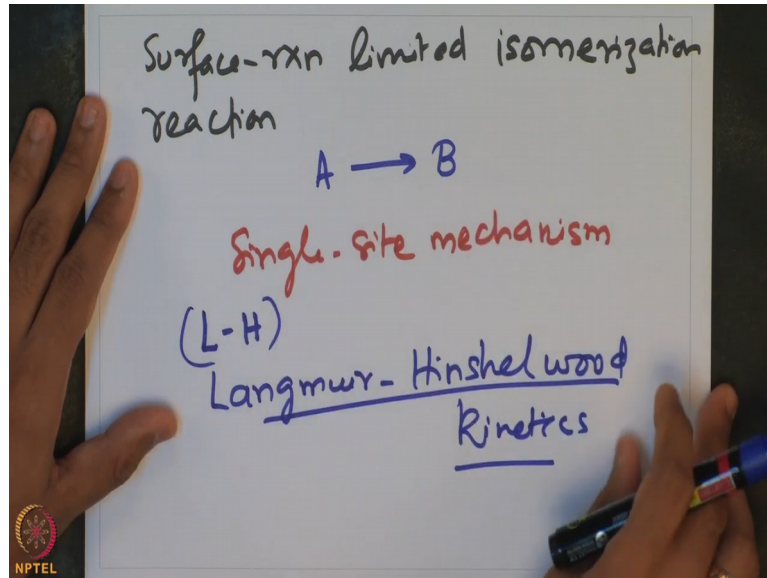
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Mass transport to and reaction in a single catalyst pellet. Now, for a, let us assume that the reaction, the surface reaction is actually rapid, because we want to characterise the mass transport limitations or the external diffusion limitations. And so, for a moment let us assume that the surface reaction is actually rapid. And then, we also assume that the rate of diffusion from bulk to the catalyst surface limits the overall reaction rate.

So, in the second case; so, this will be the first case we will look at. And the second case, we will consider the case where the surface reaction is slow and the diffusion from bulk is relatively faster. So, let us consider the specific example of isomerization reaction that we have looked at a several lectures go.

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So, let us take the specific surface reaction limited isomerization reaction. Let us say that the stoichiometric expression for this, or stoichiometric equation is, let us say species A actually goes to products. Let us further assume that the reaction, surface reaction is actually controlled or surface reaction is governed by a single-site mechanism.

Recall that there are multiple mechanisms which may be, which could be employed for actually looking at or understanding what is happening at the catalyst surface while the reaction is happening or how to actually quantify the surface reaction process. Now, we will look at the single-site mechanism for this particular case. But, in principle, one can actually employ any different mechanism for different kinds of reactions. And the systematic procedure which you will develop is actually, will remain the same.

So, let us assume that the surface reaction is actually captured by Langmuir-Hinshelwood kinetics. Let us assume that it is captured by the Langmuir-Hinshelwood kinetics which we actually looked at using this. What will be the Langmuir-Hinshelwood kinetics for a single-site mechanism, we looked at a several lectures ago. And let us employ the rate expression based on the Langmuir-Hinshelwood single-site mechanism.

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Assume external mass transport limitations

$A \rightarrow B$

$C_A > C_{A,S}$

$$-r_{A,S}'' = \frac{k_r C_{A,S}}{1 + K_A C_{A,S} + K_B C_{B,S}}$$

High T

$$K_A C_{A,S} + K_B C_{B,S} \ll 1$$

$$\Rightarrow -r_{A,S}'' = k_r C_{A,S}$$

So, suppose we have a catalyst where, let us say species A is diffusing from the bulk to the catalyst surface and species B is actually, let us say the product which is diffusing out. And suppose the surface concentration of the species is $C_{A,S}$. Bulk concentration C_A , C_A is actually is greater than $C_{A,S}$, which means that the species is actually diffusing from bulk to the surface of the catalyst.

And of course, there are pores which are present inside the catalyst. What is the single-site Langmuir-Hinshelwood kinetics? The surface reaction based on the surface area of the reaction, let us say in this case, because this is, we assume mass transport limitation. Let us say the surface area, external surface area. And that will be = some constant into surface concentration $C_{A,S}$ divided by $1 +$ some other constant capital K_A into $C_{A,S} + K_B$ into $C_{B,S}$.

So, let us also assume that the reaction A going to be, both A and B are actually affecting the rate at which the surface reaction is actually happening. Suppose, let us say that the reaction is conducted at high temperatures, suppose we assume that the reaction is conducted at high temperature. And it is not a bad assumption because typically these reactions, there will be several side reactions that may be, actually have occur simultaneously along with the primary reaction that is actually targeted or that is desirable.

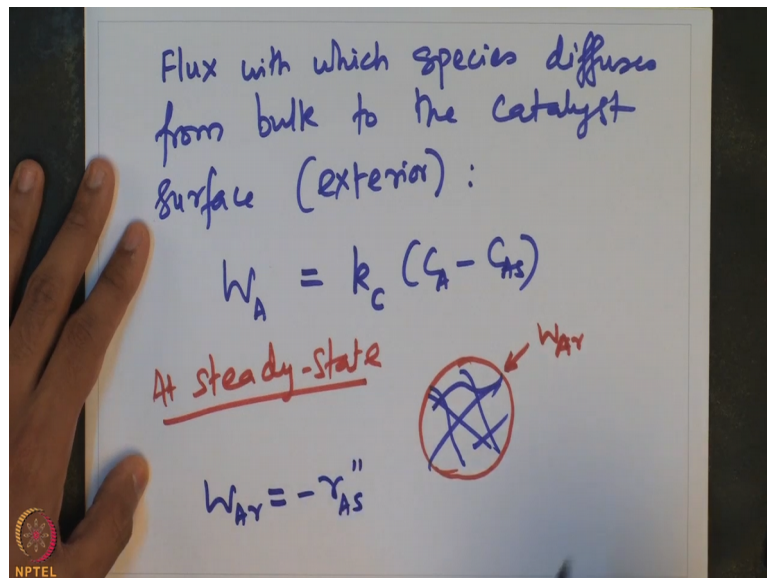
So, 1 simple trick to avoid the side reactions to occur simultaneously with the desired reaction is, 1 trick to avoid side reactions to happen is essentially to operate the reactor at a high temperature. And this is a very common practice in the industry where the reactor is

actually operated at high temperature, so as to avoid the undesired products that may be forming during the reaction that is happening, during the, because of the side reactions.

And as a result, the product stream that comes actually has contamination or the species that is produced because of the product species. Now, because of the side reactions. Now, if these product species that are formed because of the side reactions are present then there is an extra separation step which is required. And in order to avoid the extra cost that may be involved in such a separation step, it is a common practice to operate the reactor at a high temperature.

So, let us assume that it is actually operated at a high temperature. And typically, at high temperatures K_A into $C_A S$ which we have already seen in one of the previous lectures is typically much smaller than 1. So therefore, in such a condition, we can assume that the surface reaction based on the surface area is essentially given by k_r into $C_A S$ where k_r is the in, is the rate constant, intrinsic rate constant and $C_A S$ is the concentration of the species close to the surface.

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So now, the flux with which the, flux with which species diffuses from bulk to the catalyst surface, that is exterior surface, is essentially given by W_A is = some mass transport coefficient k_c multiplied by $C_A - C_{As}$. Now, we observed in the last lecture that the flux with which the species actually diffuses onto the catalyst surface. So, here is a catalyst. So, the flux with which the species diffuses onto the catalyst surface, let us say W_{Ar} which is there radially inward flux with which the species diffuses.

And at steady-state this flux $W_A r$ should essentially be = the rate at which the reaction is happening per unit surface area of the catalyst pellet, the exterior surface area of the catalyst pellet. Now, this is an incorrect assumption because we have a situation where the surface reaction may be very fast. And therefore, the reaction would essentially happen at the exterior catalyst surface pellet, catalyst surface.

And therefore, the flux with which the species comes to the catalyst surface is essentially = the rate at which the reaction happens per unit area of the catalyst surface. Now, we know that, we assume that the reaction is happening at high temperatures and under that condition, we know that W_A ;

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The image shows a whiteboard with the following handwritten equations:

$$W_A r = k_c (C_A - C_{As})$$

$$= -r''_{As}$$

$$= k_r C_{As} \quad (\text{At high } T)$$

An arrow points to a boxed equation:

$$\Rightarrow k_c (C_A - C_{As}) = k_r C_{As}$$

Below this, the text "Eliminate C_{As} " is written in red, followed by:

$$\Rightarrow k_c C_A = (k_r + k_c) C_{As}$$

W_A which is $= k_c (C_A - C_{As})$ is essentially $= -r''_{As}$, which is $= k_r C_{As}$ at high temperatures. So therefore, from here we can deduce that the mass transport flux which is given by $k_c (C_A - C_{As})$ is essentially $= k_r C_{As}$. Now, if one performs an experiment, what are the measurable quantities? So, the bulk concentration is something that can be measured.

But measuring the surface concentration or concentration of the reacting species at the catalyst surface is actually a very difficult task. And in fact, it is not possible in most of the cases to measure what is the concentration of the species at the catalyst surface, catalyst exterior surface. So therefore, we can use this expression to eliminate the concentration of the species at the surface of the exterior surface of the catalyst pellet.

Now, how do we do that? So, from here we can say that $k_c C_A = k_r + k_c C_A$. So, from here we can easily deduce that the surface concentration $C_{A,S}$;

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The image shows a whiteboard with the following handwritten equations and notes:

$$C_{A,S} = \frac{k_c C_A}{k_r + k_c}$$

$$W_A = -r_{A,S}'' = k_r C_{A,S}$$

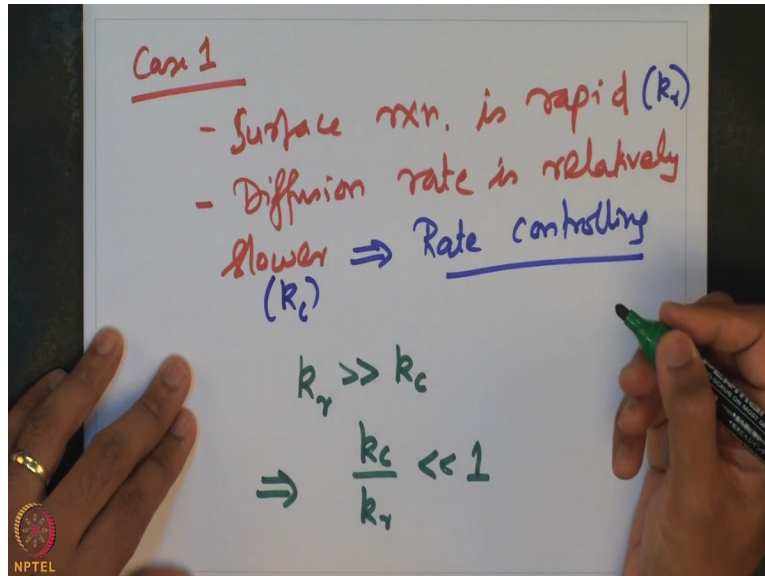
$$-r_{A,S}'' = \frac{k_r k_c C_A}{k_r + k_c}$$

⇒ Gives the overall rate @ which rxn. occurs in terms of observables

Can easily deduce that the surface concentration $C_{A,S} = k_c C_A / (k_r + k_c)$. So now, the flux with which the reaction happens, which is, flux with which the species diffuses onto the catalyst surface, which is W_A , which is also $= r_{A,S}''$, is $= k_r C_{A,S}$. So now, we can substitute this expression for $C_{A,S}$ here. And so, we, by which we can actually get the rate at which the reaction happens in terms of the observable quantities.

So, that will be $= k_r k_c C_A / (k_r + k_c)$. So, here this is the rate at which, this expression gives the overall rate at which reaction occurs in terms of the measurable quantities, in terms of the observables. What can be measured experimentally is essentially the concentration C_A . And so, from this expression we can contrast the overall rate at which the reaction happens. And we can relate that to the concentration of the species that can be measured. So, let us now consider the 2 cases that we actually described we will look into at the start of this lecture.

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We said that we will look at case 1, where the surface reaction is rapid and the diffusion rate is relatively slower. This means that the diffusion rate is the rate controlling process. So, how can we express or quantify this assumption in terms of the rate that we saw. We saw that the overall rate at which the reaction happens is essentially given by this expression. So, how can we capture these 2 observations.

So, the surface reaction is essentially quantified by the rate constant k_r surface reaction rate constant k_r and the diffusion rate is quantified by the mass transport coefficient. So, if the surface reaction is rapid and the diffusion reaction, diffusion rate is relatively slower, then it automatically implies that k_r is actually much larger than k_c , which means that k_c by k_r is actually much smaller than 1. Now, how do we incorporate this in the rate expression? So, the rate expression is given by;

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The whiteboard shows the following derivation:

$$-r_{As}'' = \frac{k_c k_r C_A}{k_c + k_r} = k_{eff} C_A$$

\downarrow
 $\frac{k_c k_r}{k_c + k_r}$

$$= \frac{k_c C_A}{\frac{k_c}{k_r} + 1}$$

$$\frac{k_c}{k_r} \ll 1 \Rightarrow -r_{As}'' \sim k_c C_A$$

NPTEL

The rate expression is essentially given by $k_c k_r C_A$ divided by $k_c + k_r$. So now, if I divide this expression by k_r , numerator and denominator. So, I will see that $k_c C_A$ divided by k_c by $k_r + 1$. So, if k_c by k_r is much smaller than 1, then this means that the overall rate at which the reaction happens is essentially approximately $k_c C_A$. Now, which means that the mass transport, external mass transport is essentially controlling the overall rate at which the reaction happens.

Now, we can look at it in a slightly different manner. So, suppose let us say, I express the overall rate at which the reaction happens, if there is no, if we do not know which one is limiting, then one can actually write this as what is called as the effective rate constant multiplied by C_A , where effective rate constant is $k_c k_r$ by $k_c + k_r$. Now, if I slightly rewrite this effective rate constant, suppose let us say I slightly rewrite the effective rate constant.

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$$k_{\text{eff}} = \frac{k_c k_r}{k_c + k_r}$$

$$= \frac{1}{\frac{1}{k_r} + \frac{1}{k_c}}$$

$k_r \gg k_c$

resistance offered due to surface rxn

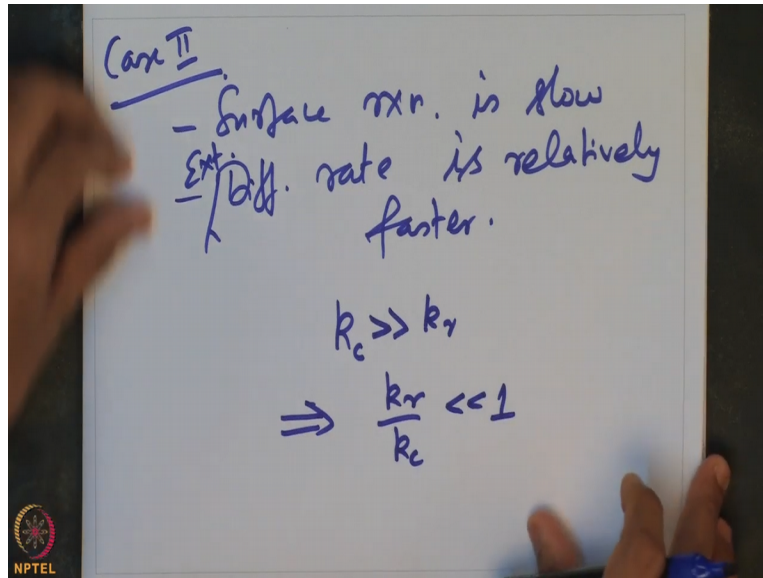
resistance offered due to M.T (ext)

So, k effective is $= k_c k_r / (k_c + k_r)$. Divide the numerator and denominator with k_c and k_r . So essentially, I will have 1 divided by $1/k_r + 1/k_c$. So, what I essentially see is that, I see that there are 2 resistances that are actually present here. So, this is the resistance offered due to surface reaction. And this is the resistance offered due to the mass transport, external mass transport.

Now, when we assume that the surface reaction is fast. We assume that k_r is much larger than k_c , what we essentially mean is that, this resistance offered by, due to surface reaction is actually extremely small compared to the resistance that is offered due to the mass transport. So therefore, which means from here we can clearly see that the effective rate constant which essentially determines or quantifies the overall rate at which the reaction happens will depend only on $1/k_c$ or the resistance offered due to the mass transport.

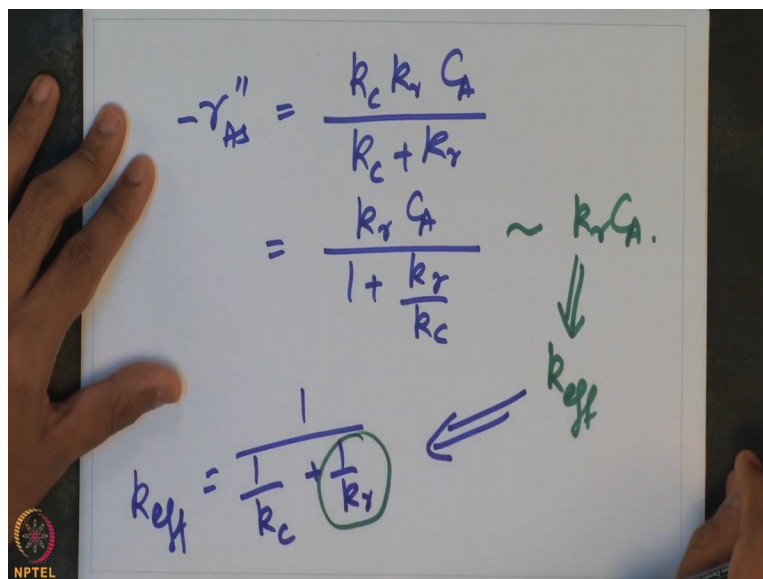
There is another way to look at it. And 1 way to look at it is what we saw just a few moments ago by directly comparing or knocking off the terms in the rate expression, overall rate expression. Or we can actually look at it from the rate constant perspective as well. So, let us consider the second case now.

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So, the second case is where we said that the surface reaction is slow. And the diffusion, external diffusion rate is relatively faster. So, in this case, what does it mean? k_c is actually much larger than k_r . And so thus, k_r by k_c is actually much smaller than 1. So, once again we can plug in this into the overall rate expression.

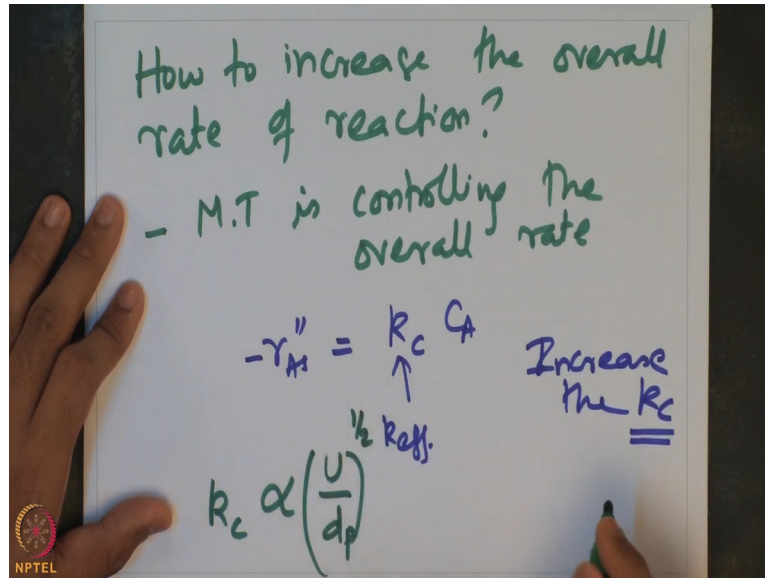
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So, the overall rate expression is $= k_c k_r$ into C_A , divided by $k_c + k_r$. So, I now divide by k_c . So, I will see that this is $= k_r C_A$ divided by $1 + k_r$ by k_c . Now, we said that k_r by k_c is actually much smaller than 1. So therefore, we can, this is essentially $= k_r$ into C_A . So, which means that the surface reaction is slower and the diffusion rate is actually relatively faster. Then the overall rate is essentially captured by the rate at which the surface reaction is happening or the rate constant corresponding rate constant is essentially the intrinsic rate constant.

So, the k effective is essentially $= k_r$ and this can be deduced from the resistances as well. So, k effective can be written as $1/k_c + 1/k_r$. And if k_c is actually relatively faster, then this is a small number. And the resistance is essentially because of the surface reaction. So, that can be deduced from the resistance concept as well.

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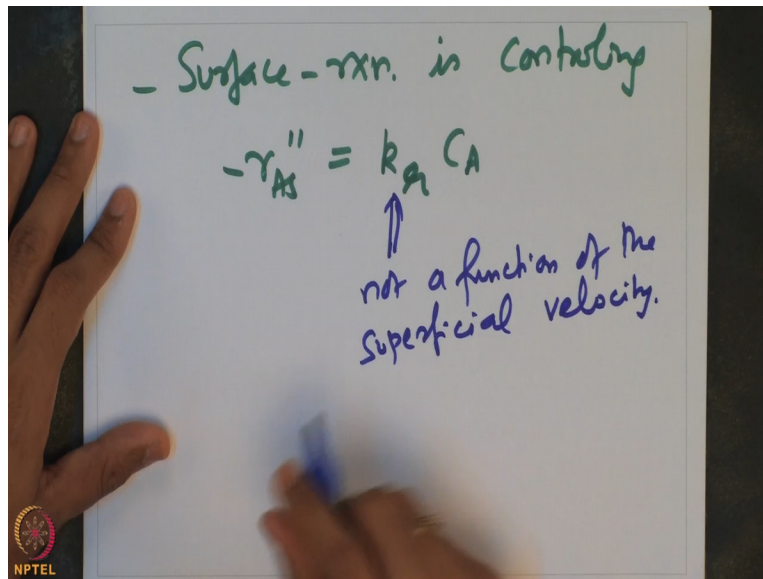


So now, the question is, how do we increase the, how to increase the overall rate of reaction? How do we increase the overall rate of reaction? So, let us look at the first case where we said that the mass transport is controlling the overall rate. So, what does the overall rate depend upon when mass transport is controlling? Let us look at the rate expression for that. We say we derive that the overall rate is essentially given by $k_c C_A$, where this is nothing but the effective rate constant.

And if effective rate constant is controlled only by the mass transport coefficient, then the way to increase the overall rate of reaction is by increasing the, increase the mass transport coefficient k_c . Now, how do we increase mass transport coefficient? We saw in the last lecture, how to actually modulate mass transport coefficient. We said that the mass transport coefficient k_c is actually proportional to the superficial velocity divided by the particle diameter to the power of half.

So, by changing U or d_p we should be able to achieve a situation where we can actually increase the mass transport coefficient, by modulating the superficial velocity or the particle diameter. On the other hand, if I look at the second case where the surface reaction is actually controlling.

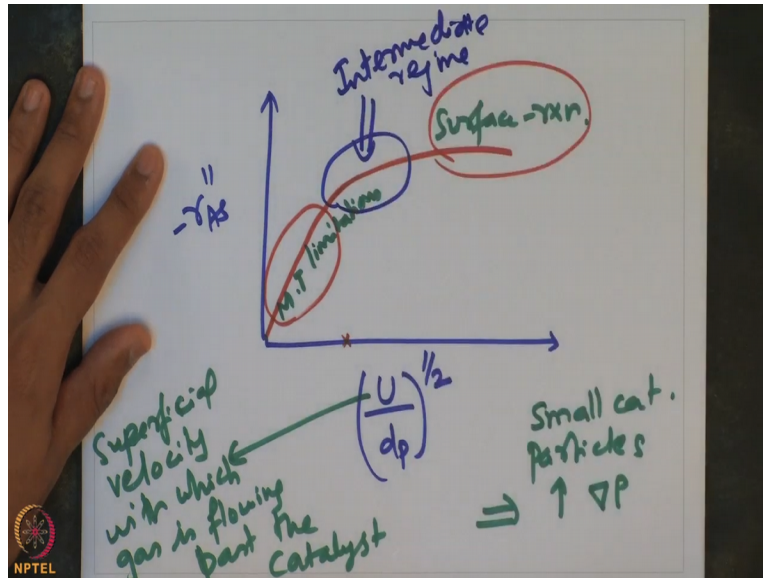
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If I look at the second case where the surface reaction is controlling, then the rate at which the reaction happens is essentially given by k_r which is the intrinsic surface reaction rate constant multiplied by C_A . Now clearly, this k_r is actually not a function of the superficial velocity. But of course, the diameter of the particle could affect the overall rate at which the reaction is happening, if there are some internal diffusional limitations.

Of course, we have assumed that there is no internal limitations, internal diffusional limitations. If there is no internal diffusion limitations, then the particle diameter is not going to directly affect the rate at which the surface reaction happens. And therefore, if the surface reaction is controlling and there is no internal diffusion or external diffusion, then essentially the overall rate is going to be controlled by the intrinsic kinetics of that particular reaction. So, let us now sketch the rate at which the reaction happens as a function of the superficial velocity.

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So now, if the velocity is very small, let us say that the U by d_p is very small. Let us say we fix the diameter of the particle for a moment. And we are now going to change the superficial velocity. What is this U ? This is the velocity, superficial velocity with which gas is flowing past the catalyst. So, if this superficial velocity is very small, then clearly that region must be having a mass transport limitations.

Because, if the velocity is very small, then the corresponding mass transport coefficient is going to be small. And as a result, the superficial velocity is going to control the mass transport rate. And so, if the velocity is small then the external diffusion rate is going to be smaller. And so, in that situation, the external diffusion is actually going to control the overall rate at which the reaction can happen.

So clearly the, at the initial phase, as you increase the velocity, we will see that the rate is going to increase because we are going to actually operating under the mass transport control regime and increasing the superficial velocity. As we saw in the last lecture that, at keeping the diameter of the particle constant, we will see that the, it is going to increase the mass transport rate. And that is going to lead to increase in the overall rate at which the reaction is actually happening.

Now, what happens after the superficial velocity is increase sufficiently larger. The mass transport is so fast that the mass transport is no more controlling. And the rate at which the mass transport happens to because of the external diffusion, would actually overtake the rate

at which the surface reaction might happen at a certain superficial velocity for a fixed value of the particle diameter.

So, at that stage, it is the surface reaction which will actually take over. And so, at that stage the surface reaction is going to control the overall rate at which the reaction can happen. So, suppose if the transition happens, let us say at this velocity U . Then the, after this point it essentially, the surface reaction which is going to take over. So, if we now mark on this graph, what is the, what are the regimes where different limitations are present, then at this low velocity U , it will be mass transport limitations.

And for high value of U , it will essentially be surface reaction. Now, if I, I can also change the particle diameter. So, if I now change the particle diameter then I actually require a very small particle diameter. Note that the d_p is appearing in the denominator here. So, if I now reduce the particle diameter sufficiently smaller, then what it means is that I have very tiny particle and the, whatever surface which is available is directly available for reaction.

So, essentially it is the surface reaction which is going to control the overall rate at which the reaction can happen. But, having a very tiny particle is actually not a desirable situation. So, small particles, small catalyst particle is actually not desirable because this is going to lead to an increase in the pressure drop, increase in the pressure drop through the reactor.

Flowing a fluid through the bed is actually an important aspect, because pumping actually involves some cost. And so, we want to design the reactor in such a way that the pressure drop for pumping the fluid is as minimum as possible. So, having a very small tiny catalyst particle is not always a desirable situation unless it is absolutely required to have a tiny size particles.

Where, because that the pressure drop is going to be increased, will increase if the particle size is small and that will increase the pumping cost and it is an undesirable situation. So, what we have seen in this lecture is, we looked at mass transport through single catalyst particle, while the reaction is actually happening simultaneously. We looked at 2 specific cases where the reaction might be, surface reaction might be rate controlling or the external mass transport, that is the diffusion rate might be rate controlling or controlling the overall rate at which the reaction is happening.

We also defined what is called the overall or the effective rate constant, which captures the intrinsic rate constant that describes the surface reaction and the mass transport coefficient that actually quantitatively captures the rate at which the species diffuses from bulk to the catalyst surface. So, such an effective rate constant which captures both the intrinsic properties of surface reaction and the diffusion rate can be used to quantify the regimes where the overall rate is neither mass transport controlling or a surface reaction controlling.

For example, if you look at this curve here, in the initial small velocity ranges, small U ranges, it will be mass transport limiting and for very high U for a fixed particle diameter, it will be surface reaction controlling. But in the intermediate regime where the, neither the mass transport nor the surface reaction might be controlling. In these cases, it is the effective rate constant which actually considers both the effects of surface reaction and the mass transport of the species from the bulk to the catalyst surface has to be used.

In the next lecture we will see how to actually take it forward to design the actual packed bed reactor. In this lecture what we saw is the quantification of mass transport and simultaneous reaction around a single catalyst pellet. But packed bed reactor is actually having multiple catalyst pellet. And let us see how to extend this to designing the packed beds which contains several catalyst particles inside. Thank you.