Chemical Reaction Engineering - II
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Module - 7
Lecture - 32
Overall Effectiveness Factor II

In the last lecture we started by assuming that the external resistance to mass transport and the internal resistance to mass transport are actually comparable. And we want to understand how to quantify this particular situation where both the resistances are comparable. We also observed that, at steady-state the rate of transport of the species from the bulk to the surface should be = the rate of the reaction in the surface area inside the catalyst pellet and also on the external surface of the catalyst pellet.

And this is because the reaction can happen both at the external surface and also in the internal surface where the active material is actually coated. Now, we also compared what is the typical surface area which is available for the reaction inside the catalyst pellet and also compared that with the total area which is available in the exterior of the catalyst pellet. And let us look at that numbers again.

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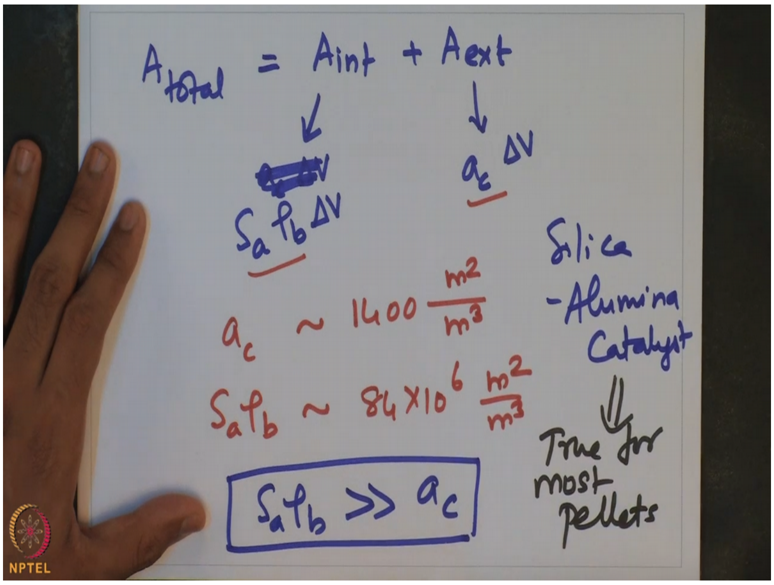

$$A_{total} = A_{int} + A_{ext}$$

$$\downarrow \qquad \downarrow$$

$$\cancel{a_c \Delta V} \qquad a_c \Delta V$$

$$S_a \rho_b \Delta V$$

$$a_c \sim 1400 \frac{m^2}{m^3}$$

$$S_a \rho_b \sim 84 \times 10^6 \frac{m^2}{m^3}$$

$$\boxed{S_a \rho_b >> a_c}$$

Silica -Alumina Catalyst

$\Downarrow$

True for most pellets

So, we said that the total area for the reaction is essentially = the internal area + the external area. And the internal area is essentially given by a c into delta V and the internal area is essentially given by S a which is the active surface area per gram of catalyst multiplied by the bulk density into delta V. And the external surface area is given by a c into delta V. We looked at the numbers for these 2 for typical catalyst.

And we saw that a c is typically of the order of magnitude of 1400 metre square per metre cube of the catalyst, metre cube of the reactor volume. And S a rho b is of the order of magnitude of 84 into 10 to the power of 6 metre square per metre cube of the reactor volume. So, from here, we can clearly see that S a rho b which is the internal surface area which is available per unit volume of the reactor is significantly higher than the external surface area of the catalyst pellet that is available for reaction.

So clearly, this is typically larger, much larger than the external surface area. Now this we specifically saw for the silica alumina catalyst. And in fact, this is true for most of the catalyst pellets, most of the pellets that are actually being used in the industry these days. So, how do we incorporate that in the balance. So, let us see what the balance is in the first place. So, the balance was that;

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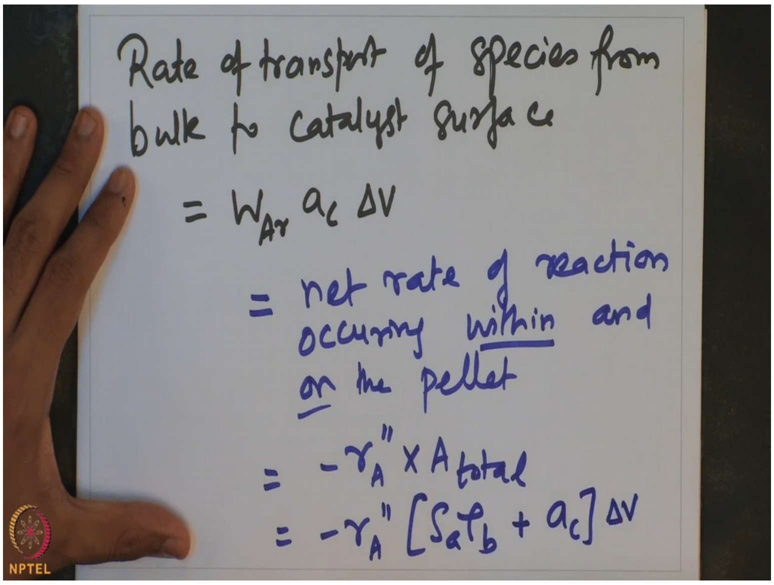

Rate of transport of species from bulk to catalyst surface

$= W_{Ar} a_c \Delta V$

= net rate of reaction occurring within and on the pellet

$= -r_A'' \times A_{total}$

$= -r_A'' [S_a \rho_b + a_c] \Delta V$

We said that the rate of transport of species from bulk to catalyst surface, which is = the flux with which the species comes from the bulk to the catalyst surface, that multiplied by the area per unit volume of the reactor into delta V. And we said that, that should be = the net rate of reaction occurring within and on the pellet. We also observed that, this should be = – r A double prime which is the rate defined per unit area of the surface which is available for reaction.

And that multiplied by the total area. So, that multiplied by the A total which is = – r A double prime into S a into rho b which is the area correspond to, corresponding to the available surface inside the catalyst pellet + the external surface area into delta V which is the volume of the reactor. So, now we can cancel out the volume terms and we can actually reduce this equation. And so;

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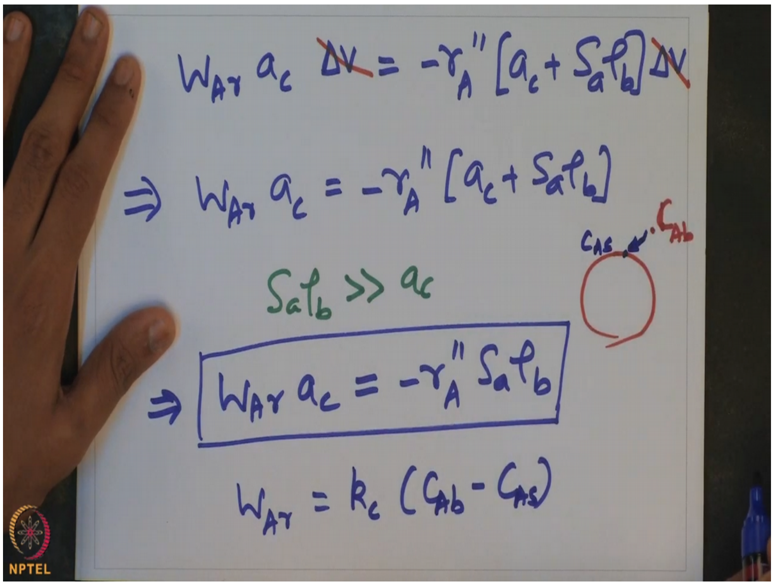

$$W_{Ar}\, a_c \cancel{\Delta V} = -r_A''\,[a_c + S_a\rho_b]\cancel{\Delta V}$$

$$\Rightarrow W_{Ar}\, a_c = -r_A''\,[a_c + S_a\rho_b]$$

$$S_a\rho_b >> a_c$$

$$\Rightarrow \boxed{W_{Ar}\, a_c = -r_A''\, S_a\rho_b}$$

$$W_{Ar} = k_c\,(C_{Ab} - C_{AS})$$

So, W A r into a c into delta V is = – r A double prime into a c + S a rho b into delta V. And we can cancel out the volume term here. And so, from here it reduces to, into a c = S a into rho b. Now we also observed that the at S a into rho b is typically much larger than a c. So, if we ignore this small term inside the area total, we can further reduce this equation to W A r into a c is = – r A double prime into S a into rho b.

Now, what is the flux with which the species actually diffuses from the bulk to the surface. We already characterised that when we looked at the external resistance to mass transport part, when we quantified the external resistance to mass transport. So, what is the flux? The flux W A r is essentially = some whatever mass transport coefficient, that multiplied by C A b – C A S where C A b is the concentration of the species in bulk.

So, this is the bulk concentration. And C A S is essentially the concentration of the species at the surface where the diffusion is actually happening from bulk to the surface of the catalyst pellet. So, we can plug that into the balance. And what do we get when you plug that in.

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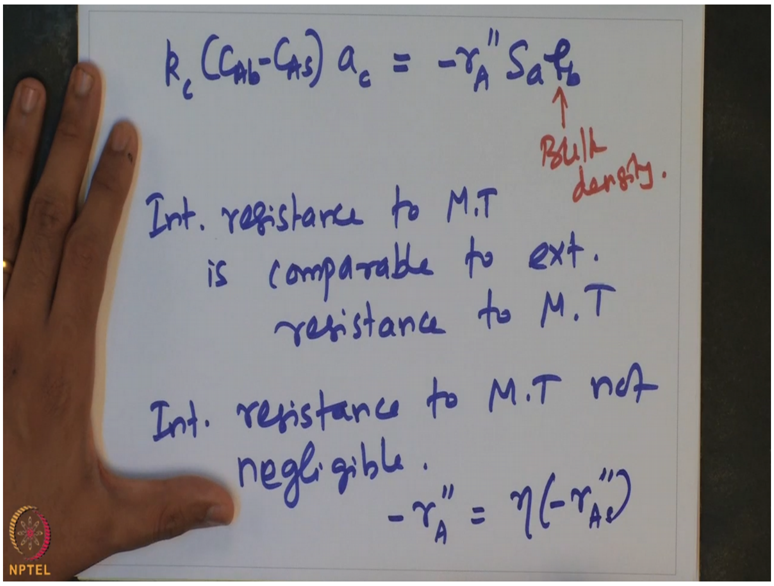

$k_c(C_{Ab}-C_{As})\,a_c = -r_A'' S_a \rho_b$

↑ Bulk density.

Int. resistance to M.T is comparable to ext. resistance to M.T

Int. resistance to M.T not negligible.

$-r_A'' = \eta(-r_{As}'')$

So, that will be k c into C A b – C A S, that multiplied by a c is essentially = – r A double prime into S a into rho b. So, this is the bulk density. So, now we know this expression. What do we do next? We said that we want to assume a first order reaction. So, we can now use the property of first order reaction to actually find out what is this r A double prime. Now, how do we substitute that here?

Now, suppose if the, we also said that the internal diffusional limitations or internal resistance to mass transport is comparable to external resistance to mass transport. Which immediately suggests that the internal resistance to mass transport is not negligible. So, if internal resistance to mass transport is not negligible, we saw in the internal diffusional limitations case. We saw that the overall rate at which the reaction happens can be related to the rate at which the reaction happens if the species is actually at the surface concentration.

Or we can relate it to the intrinsic kinetics by using the internal effectiveness factor. How do we do that. So, we can now say that the r A double prime is essentially = the internal effectiveness factor eta multiplied by r A at the surface conditions, r A S at the surface conditions. Now, we said that we want to do this for a first order reaction. What happens when we actually plug in the kinetics of a first order reaction?

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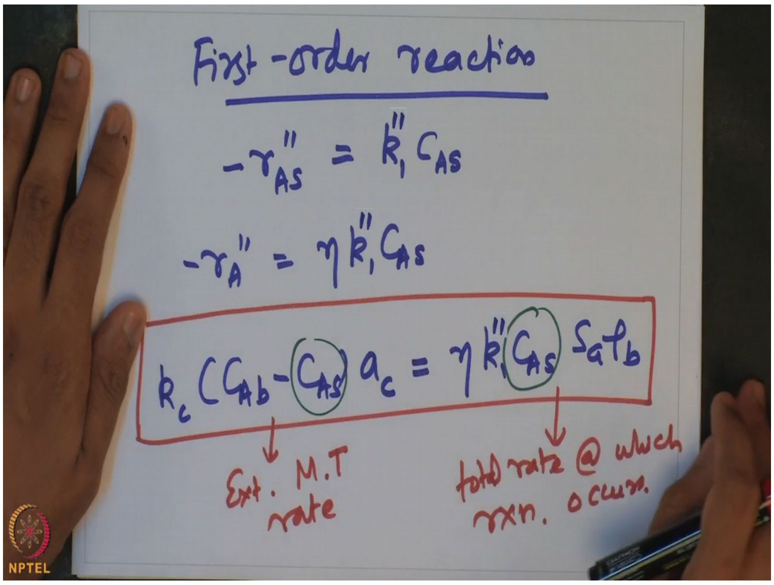

First-order reaction

$$-r''_{AS} = k''_1 C_{AS}$$

$$-r''_A = \eta k''_1 C_{AS}$$

$$\boxed{k_c (C_{Ab} - C_{AS}) a_c = \eta k''_1 C_{AS} S_a \rho_b}$$

Ext. M.T rate

total rate @ which rxn. occurs.

For a first order reaction, what is the intrinsic kinetics? We know the kinetic expression for the intrinsic kinetics, which is essentially r A S double prime is essentially = some rate constant k 1 corresponding to the first order reaction multiplied by the concentration of the species which is basically that, it is actually at the surface conditions. So, plugging that into the balance, we will see that the – r A double prime is = eta into k 1 into C A S.

And plugging this into the balance, we will see that k c into C A b – C A S which is the rate at which the transport happens multiplied by the external surface area per unit volume of the catalyst. And that should be = eta k 1 C A S S a into rho b. So, this is the balance which relates the external mass transport rate to the rate, total rate at which the reaction happens. So, what are the measurable quantities?

So, the measurable quantities are essentially the bulk concentration. We will not be able to measure what is the concentration of the species at the catalyst surface. So therefore, we can use the balance to eliminate the concentration of the species at the catalyst surface. So, we essentially want to eliminate this quantity. We want to eliminate the concentration of the species at the surface. How do we do that? We can use this expression, we can do a little algebra.

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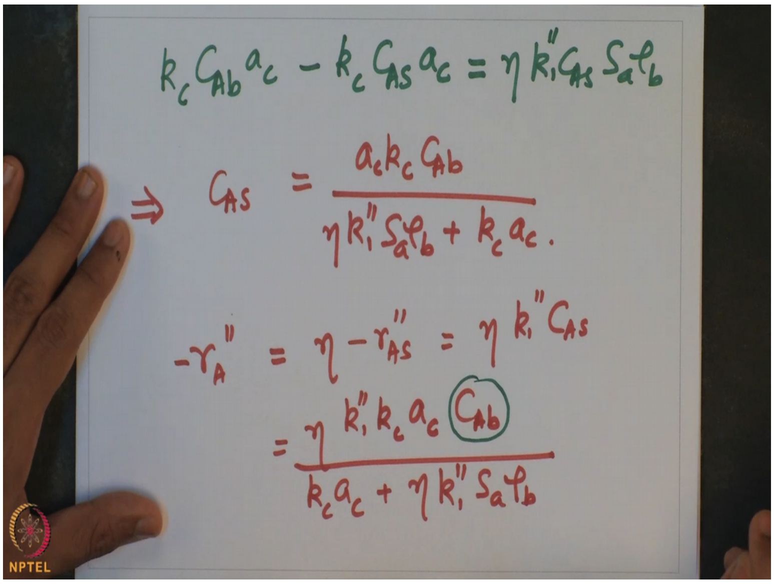

$$k_c C_{Ab} a_c - k_c C_{AS} a_c = \eta k_1'' C_{AS} S_a \rho_b$$

$$\Rightarrow C_{AS} = \frac{a_c k_c C_{Ab}}{\eta k_1'' S_a \rho_b + k_c a_c}.$$

$$-r_A'' = \eta - r_{AS}'' = \eta k_1'' C_{AS}$$

$$= \eta \frac{k_1'' k_c a_c \boxed{C_{Ab}}}{k_c a_c + \eta k_1'' S_a \rho_b}$$

So, the algebra suggests that k c into C A b into a c – k c C A S into a c. That should be = eta k 1 C A S into S a into rho b. So now, from this we can find out that C A S is essentially = k c into C A b multiplied by a c divided by eta k 1 double prime S a rho b + k c into a c. So, the concentration of the species at the surface is essentially given by this expression here. Now, how do we further use this expression?

We know what is the overall rate at which the reaction happens in terms of the effectiveness factor and the rate at the surface conditions. We can substitute this into that expression. So, from here – r A double prime is essentially = eta into – r A S double prime. And that should be = eta into k 1 double prime into C A S. And we know what is the expression for C A S. We can substitute that here.

Eta k 1 double prime k c a c C a b divided by k c a c + eta k 1 double prime S a into rho b. So, what we have found is the overall rate at which the reaction happens per unit area of the catalyst in terms of the bulk concentration of the species, which is actually a measurable quantity. And all the, recall that, if you look at this expression, all the other quantities are actually a known quantity if the effectiveness factor of the catalyst is known.

k 1 double prime is the intrinsic kinetics. k c is the mass transport coefficient. a c is the external surface area per unit volume of the catalyst. And S a rho b is the, they are the surface area, internal surface area per gram of the catalyst. And rho b is the bulk density of the bed. So, once we know these quantities, we can actually find out what is the overall rate at which the reaction happens in terms of the bulk concentration which is typically a measurable quantity or an observable quantity which can be measured when the reactor is actually run.

Now earlier, so earlier we defined a quantity called the internal effectiveness factor when the internal resistance to mass transport is actually present. Now, in this case, the resistance to external mass transport and the internal mass transport actually are comparable. So, let us first look at what is the definition of the effectiveness factor when only the internal resistance to mass transport is present. And we can extend that to the situation where the external and internal resistance to mass transport are actually comparable.

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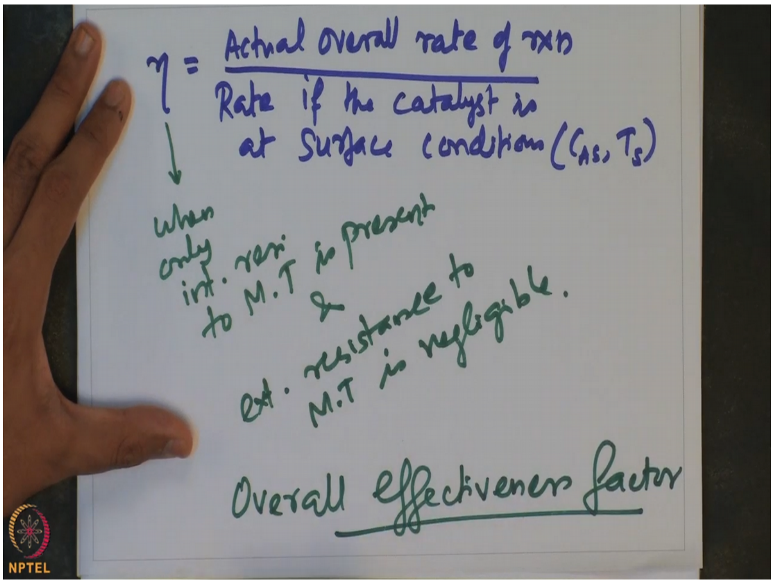

$$\eta = \frac{\text{Actual overall rate of rxn}}{\text{Rate if the catalyst is at surface conditions } (C_{AS}, T_S)}$$

↓

when only int. resi to M.T is present & ext. resistance to M.T is negligible.

Overall effectiveness factor

So, the effectiveness factor when only the internal resistance to mass transport is present is essentially given by, the actual overall rate of reaction divided by the rate if the catalyst is at surface conditions. That is, concentration C A S and the temperature T S. Now in a similar fashion, this is true only for; so, this definition is when only internal resistance to mass transport is present. And the external resistance is, to mass transport is negligible.

Now we can, because bulk concentration is an observable property, we can now introduce a new definition where the effectiveness factor will now be defined based on the bulk concentration or bulk conditions, which is what is called as the overall effectiveness factor. So, let us see how to define that now.

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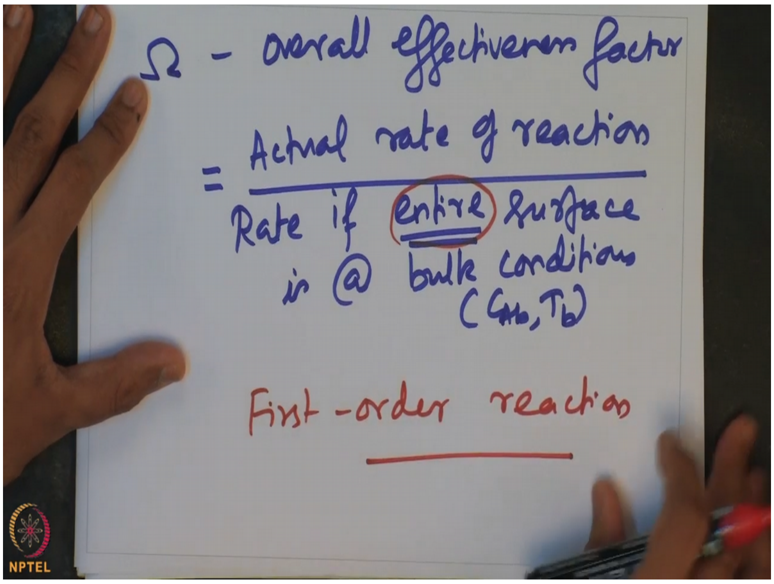

Ω - overall effectiveness factor

$$= \frac{\text{Actual rate of reaction}}{\text{Rate if entire surface is @ bulk conditions } (C_{Ab}, T_b)}$$

First-order reaction

So, the overall effectiveness factor, typically, the symbol that is used is this capital omega, which is the overall effectiveness factor. And the definition for this is, it is the ratio of actual rate of reaction divided by rate if entire surface is at bulk conditions. That is C A b and the temperature in bulk. Note that we said it should be the entire surface which is the external and the internal surface of the catalyst pellet where the reaction is actually happening.

So, the definition of overall effectiveness factor is essentially based on the observable properties which is the bulk concentration and the temperature of the bulk fluid stream when the external resistance and the internal resistance for mass transport are actually comparable. Let us see how to find this for a first order reaction. So, we want to now do it for a; So, the balance that we wrote earlier and found out what is the overall rate at which the reaction happens, that rate is essentially given by;

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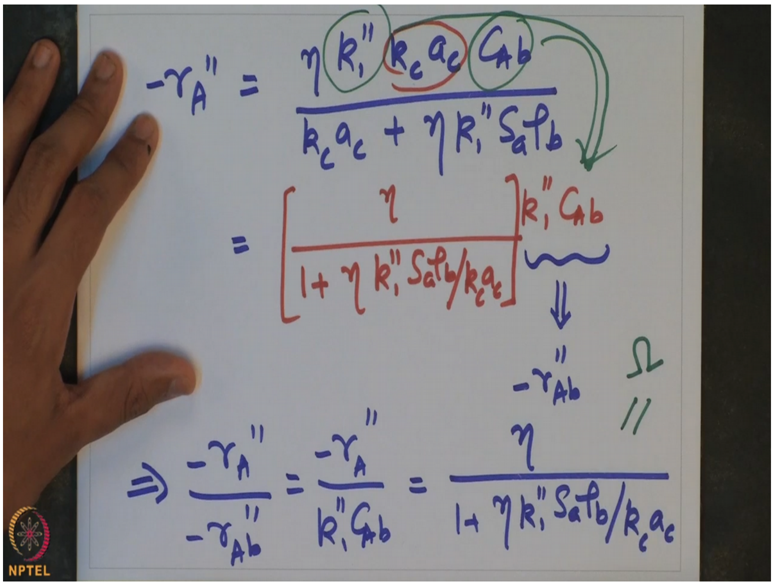

$$-r_A'' = \frac{\eta k_1'' k_c a_c C_{Ab}}{k_c a_c + \eta k_1'' S_a \rho_b}$$

$$= \left[\frac{\eta}{1+\eta k_1'' S_a \rho_b / k_c a_c}\right] \underbrace{k_1'' C_{Ab}}_{\Downarrow \; -r_{Ab}''}$$

$$\Rightarrow \frac{-r_A''}{-r_{Ab}''} = \frac{-r_A''}{k_1'' C_{Ab}} = \overset{\overset{\Omega}{/\!/}}{\frac{\eta}{1+\eta k_1'' S_a \rho_b / k_c a_c}}$$

Is = eta into the intrinsic kinetics rate constant divided by k c into a c + eta k 1 double prime S a into rho b. Now we can rewrite this in a slightly different manner. We can rewrite this as, if I pull out k1 double prime into C A b outside and I divide the expression in the numerator and the denominator with k c a c. So, this can be rewritten as eta divided by 1 + eta k 1 double prime S a rho b divided by k c into a c.

So, all I have done is I have essentially pulled this 2 term outside, pull these 2 terms here outside and then we can divide the numerator and the denominator with this k c a c term divide the numerator and denominator with k c a c. We will get this expression. What is there on this, what is these 2 term correspond to? This is essentially the intrinsic rate if I now define a rate based on bulk conditions and because it is a first order reaction.

So, this is nothing but r A based on the bulk conditions which is nothing, which is basically the intrinsic rate constant multiplied by the concentration of the species in the bulk conditions. So, from here, I can now write – r A double prime divided by – r A b double prime is essentially = – r A double prime divided by k 1 double prime into C A b for a first order reaction.

And that is = eta divided by 1 + eta k 1 double prime into S a into rho b divided by k c into a c. So, what we saw here, what we see here in the right-hand side is what is called as the overall effectiveness factor. Recall the definition of the overall effectiveness factor. It is the actual rate at which the reaction happens divided by the rate if the entire surface of all the catalyst pellet and inside the pores all the surface each at the bulk condition.

And now if you stare at this expression on the left-hand side, what we essentially have is exactly that ratio. So, what we have on the right-hand side of this expression is essentially the overall effectiveness factor. So, let us write down the overall effectiveness factor.

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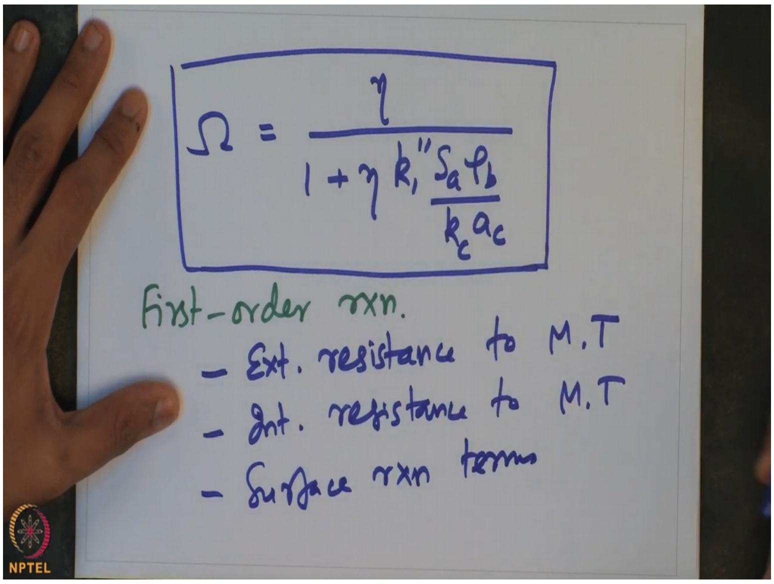

$$\boxed{\Omega = \frac{\eta}{1 + \eta k_1'' \frac{S_a \rho_b}{k_c a_c}}}$$

First-order rxn.

- Ext. resistance to M.T
- Int. resistance to M.T
- Surface rxn terms

The overall effectiveness factor omega is essentially given by eta divided by 1 + eta k 1 double prime S a rho b divided by k c into a c. So, this overall effectiveness factor now accounts for the internal diffusional resistances. It also accounts for the external resistance for mass transport. How do we see that in the expression? We can now stare the expression here. Eta essentially corresponds to the resistance of mass transport inside the catalyst pellet compared to that if the reaction is happening at the surface conditions.

So, that takes care of the resistance to mass transport inside the catalyst pellet. And if I now look at the denominator here, the k c a c essentially quantifies the resistance to mass transport outside the catalyst pellet. That is resistance offered for transport of species from the bulk to the surface of the catalyst pellet. What is 1 by k c a c? Essentially tells me, what quantifies the resistance of the external resistance for mass transport outside the catalyst pellet. So therefore, the overall effectiveness factor for a first order reaction; this is for a first order reaction.

It essentially accounts for the external resistance to mass transport. It accounts for internal resistance to mass transport and of course it also has the surface reaction terms. Note that the intrinsic rate constant is actually present in the denominator. So, all 3 processes which are actually occurring or which may be controlling the overall rate at which the reaction happens.

All these 3 are actually simultaneously captured in this important quantity called the overall effectiveness factor.

Now, how is the overall effectiveness factor for the definition of rate at different conditions? Let us see how to look at that. So, how is the rate, how is the overall effectiveness factor related to the other definitions of rates? Let us see.

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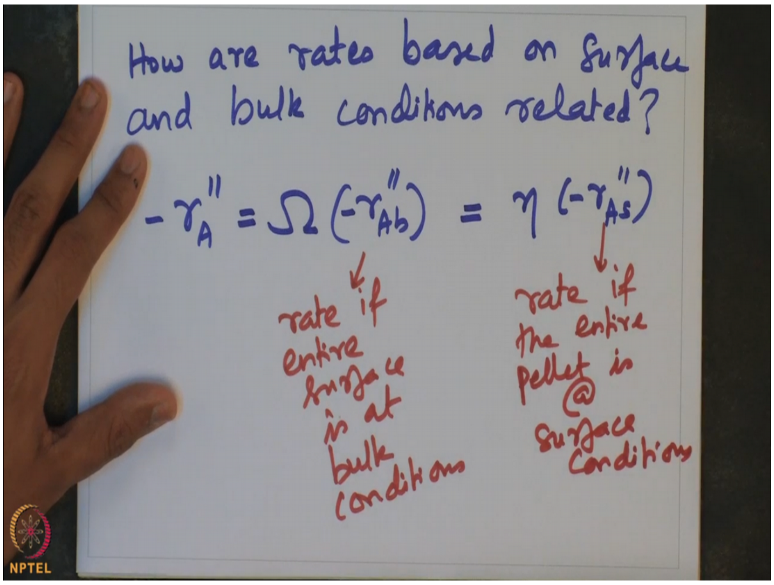

How are rates based on surface and bulk conditions related?

$$-r_A'' = \Omega(-r_{Ab}'') = \eta(-r_{As}'')$$

rate if entire surface is at bulk conditions

rate if the entire pellet is @ surface conditions

How are they related? We know that, by definition of the overall effectiveness factor, – r A double prime is essentially = the overall effectiveness factor, that multiplied by the rate as so if it was bulk conditions at every location or entire surface in the reactor. This is the rate if entire surface is at bulk conditions. But we also know that the internal mass transport resistance is actually finite. And if eta is the internal effectiveness factor, we can also define the overall rate in terms of the rate of the species under the surface conditions.

How do we do that? So, this is essentially = eta into the rate at the surface condition. So, this is the, we set surface conditions. Now we know that the actual rate at which the reaction happens is actually rate per surface area which is available for reaction multiplied by the surface area per unit volume, which tells me what is the rate per unit volume of the reactor. So, let us use the definition and see how to relate the overall rate of the reactor.

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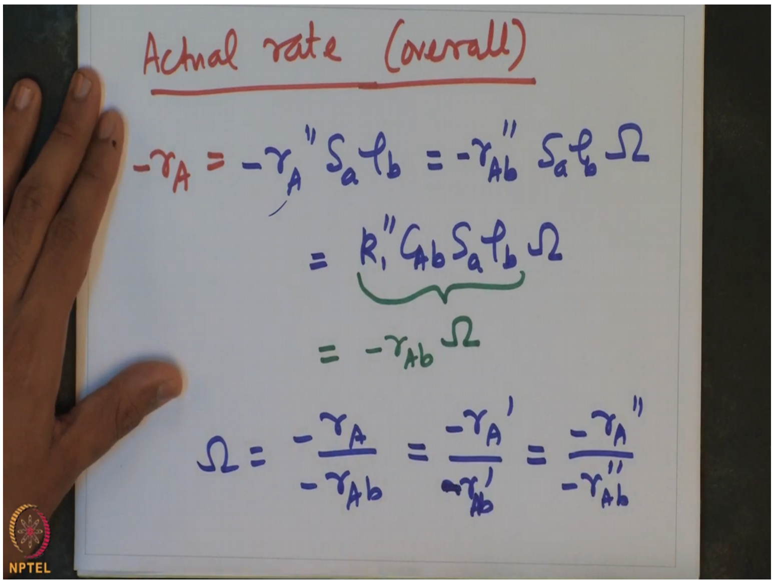

Actual rate (overall)

$$-r_A = -r_A'' S_a \rho_b = -r_{Ab}'' S_a \rho_b \Omega$$

$$= \underbrace{k_1'' C_{Ab} S_a \rho_b} \Omega$$

$$= -r_{Ab} \Omega$$

$$\Omega = \frac{-r_A}{-r_{Ab}} = \frac{-r_A'}{-r_{Ab}'} = \frac{-r_A''}{-r_{Ab}''}$$

So, the actual overall rate or total rate is essentially given by – r A which is = – r A double prime into S a into rho b which is the bulk density. Note that the area, external area of the catalyst is actually very small compared to the internal area which is available for reaction. But is principal one could also consider that area which is available for the reaction. But typically, it is a very small contribution.

So, therefore the overall rate, actual rate can be related to the rate per unit area multiplied by S a into rho b which is essentially = – r A b double prime into S a into rho b into the overall effectiveness factor. And that is = k 1 double prime C A b S a rho b into omega. Now, what is this term here? What is this term? This is nothing but, the overall actual rate at which the reaction happens if the conditions of the entire surface is actually at the bulk condition.

So, from here, clearly we can deduce that omega is also = – r A by – r b. So, what does it immediately suggest is that, this is also should be = – r A prime by – r b prime, – r A b prime. And that is also = – r A double prime by – r A b double prime. Where this is the rate defined based on surface area, this is the rate defined based on the weight of the catalyst. So, this is – r A b which is the rate defined based on the weight of the catalyst.

So therefore, the overall effectiveness factor is uniformly applicable whether the rate is available as per volume of the reactor or it is available as the per unit weight of the catalyst or it is available as the per unit surface area of the catalyst. So, to summarise what we have seen is that we have defined a quantity called overall effectiveness factor for a first order reaction which essentially simultaneously captures the resistance which is available for or resistance offered for mass transport outside the catalyst for transport of the species from bulk to the surface of the catalyst pellet.

And also the resistance offered for transport of species from the surface of the pellet to the inside of the catalyst where the actual reaction happens in the pores of the catalyst in which location the catalyst material is actually impregnated. So, the overall effectiveness factor which accounts simultaneously for all the resistances is actually widely used for these kind of systems to quantify the rate at which the reaction happens and what is the observed rate and to use, and to correlate that with the observable which is basically the bulk concentration and bulk temperature.

Starting from the next lecture we will start looking at how to diagnose whether the resistances are actually present in an observed system if the data of the overall rate at which the reaction happens actually is measured. So, can we identify if the internal diffusional limitations or the external mass transport resistances are actually present in the system that is actually being considered. Thank you.