Chemical Reaction Engineering II
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Lecture - 15
Implications to Rate Data Interpretation and Design – I

Friends, in this lecture we going to look at how to estimate or how to identify. Whether a particular catalytic reaction, particular heterogeneous reaction is diffusion limited or reaction limited. Often in industry, several experiments can be perform. But, it is important to understand, under what situations, under what conditions the heterogeneous reaction will be diffusion limited or reaction limited.

And it is very useful to have a certain tools, which can be used to identify these regimes. So, what we are going to see today is to look at how to detect from the experimental data? That is the observed reaction rates under different situations and different conditions. How to identify what is the under what situation the heterogeneous reactions diffusion limited and under what situation, it is a surface reaction limited.

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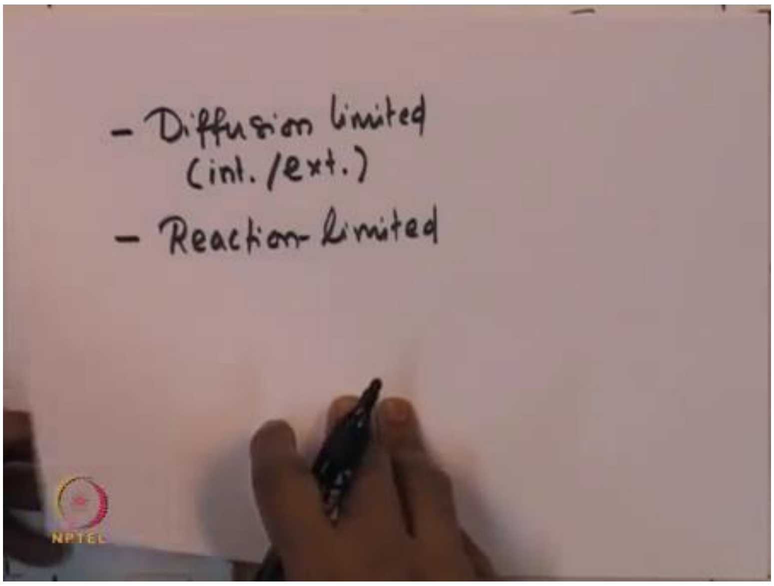

- Diffusion limited
  (int./ext.)
- Reaction limited

So, the diffusion limited situation can actually be of two types. One can be the external diffusion. So, a diffusion limited reaction conditions can be either internal diffusion controlled or the external diffusion controlled. The other possibilities are where it is the reaction limited. The conditions are reaction limited. So, as a first step we will look at the

Weisz Prater criterion, which is often used in industry. In order to identify whether the reaction is internal diffusion limiting.

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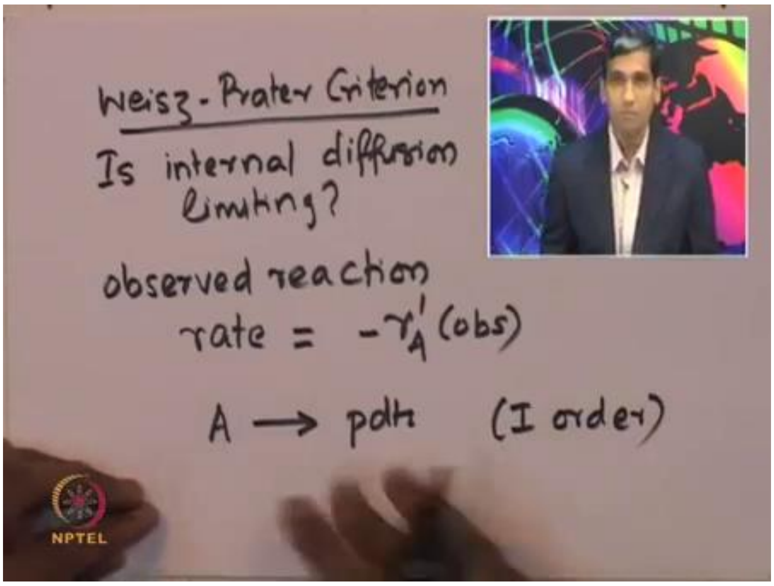

Weisz - Prater Criterion

Is internal diffusion limiting?

observed reaction rate = $-r_A'$ (obs)

A → pdt (I order)

So, start with Weisz Prater criterion. And so the Weisz Prater criterion is actually used to answer this question. Is the, is internal diffusion controlling is internal diffusion limiting the current conditions. Are such that, it is internal diffusion limiting the actual performance of the heterogeneous catalytic reaction. So, suppose if from experimental data we are able to obtain what is the observed reaction rate. So, if the observed reaction rate is given by let us say, minus r A prime o b s is a, let us it stands for the observed reaction rate.

And we will use this nomenclature for the rest of the lecture. And let us consider a first order reaction, where A which is a reactant which undergoes a certain heterogeneous catalytic reaction and the results in forming a product. And let us assume that, it is a first order reaction. So, now for a first order reaction in the last few lectures, you would have noticed that there is a relationship between the effectiveness factor and the Thiele modulus.

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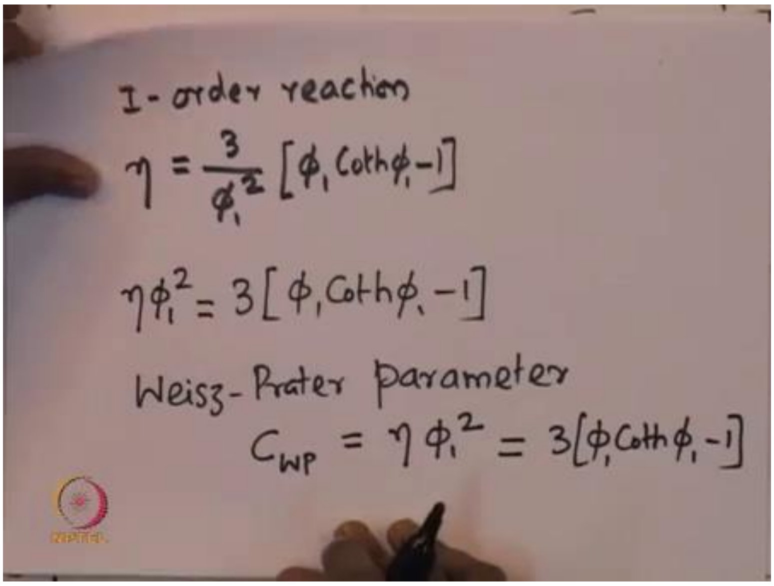

I- order reaction

$$\eta = \frac{3}{\phi_1^2}\left[\phi_1 \text{Coth}\,\phi_1 - 1\right]$$

$$\eta \phi_1^2 = 3\left[\phi_1 \text{Coth}\,\phi_1 - 1\right]$$

Weisz- Prater parameter

$$C_{WP} = \eta \phi_1^2 = 3\left[\phi_1 \text{Coth}\,\phi_1 - 1\right]$$

So, for a first order reaction the relationship between the effectiveness and Thiele modulus is given by eta, which is the effectiveness factor. That is given by 3 divided by phi 1 square. 1 stands for the, 1 here refers to the first order reaction. 3 by phi 1 square multiplied by phi 1 cot hyperbolic phi 1 minus 1. So, that is the relationship between the effectiveness factor and Thiele modulus, for a first order reaction.

Now, this is equation can actually be modified as eta into phi 1 square. That is equal to 3 into phi 1 cot hyperbolic phi 1 minus 1. So, all I have done is, just multiply the whole equation with phi 1 square. So, once we do this we can now define a new parameter call the Weisz Prater parameter. So, we define a parameter call the Weisz Prater parameter. And this parameter is, you see C WP subscripts w p represents Weisz Prater parameter and that is equal to eta into phi 1 square.

So, we define a new parameter call C WP which is equal to eta into phi 1 square. And that would be equal to 3 into phi 1 cot hyperbolic phi 1 minus 1. So, now what is this parameter? So, let us look at what is the meaning of this parameter C WP. So, let us look at the meaning of this parameter.

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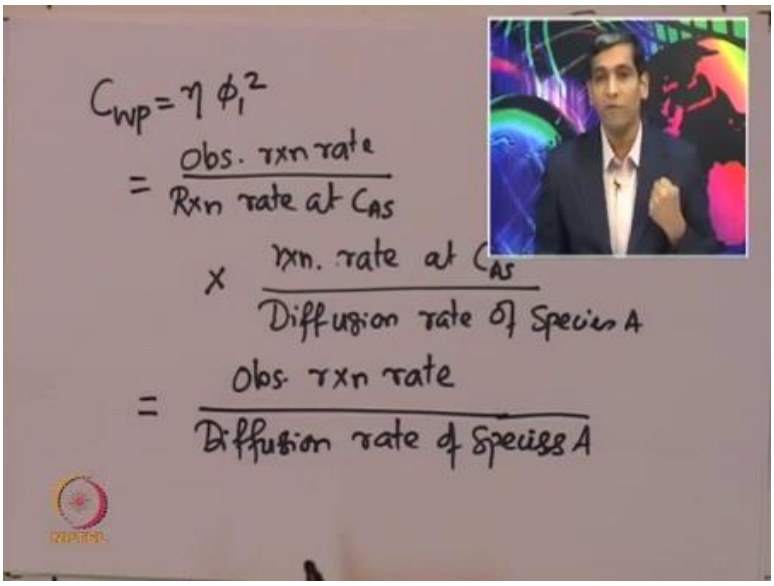

$$C_{WP} = \eta \phi_1^2$$

$$= \frac{\text{Obs. rxn rate}}{\text{Rxn rate at } C_{AS}} \times \frac{\text{rxn. rate at } C_{AS}}{\text{Diffusion rate of Species A}}$$

$$= \frac{\text{Obs. rxn rate}}{\text{Diffusion rate of Species A}}$$

So, C WP is eta into phi 1 square. The effectiveness factor is essentially, the ratio of the observed reaction rate to the reaction rate evaluator at the bulk concentration C AS. So, if the, so that will be bulk observed reaction rate divided by the reaction rate at the bulk concentration. If we assume that there is no mass transfer limitations, that will be equal to the concentration at the surface of the catalyst.

And that multiplied by the Thiele modulus. So, phi 1 square is nothing but the reaction rate evaluated at the surface concentration. If there is no mass transfer limitations, divided by the diffusion rate of the species that is actually undergoing the reaction. So, that will be reaction rate at C AS divided by the diffusion rate of species A. So, now from here we can actually rewrite this expression. So, you can see that we can cancel of the denominator in the first expression and the numerator in the second expression.

And we can rewrite this Weisz Prater parameter, as observed as a ratio of observed reaction rate divided by the diffusion rate of species A. So, this parameter Weisz Prater parameter provides or it provides a mechanism to compare the observed reaction rate divided by the diffusion rate of the species A. So, let us look at what we can do with this Weisz Prater parameter. Remember, that the objective is find out whether the reaction is being conducted under inter diffusion limitations.

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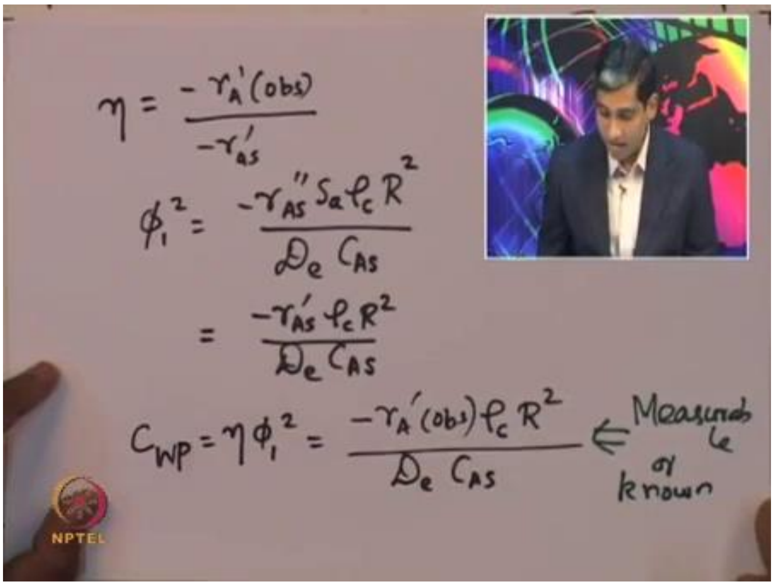

$$\eta = \frac{-r_A'(obs)}{-r_{AS}'}$$

$$\phi_1^2 = \frac{-r_{AS}'' S_a \rho_c R^2}{\mathcal{D}_e C_{AS}}$$

$$= \frac{-r_{AS}' \rho_c R^2}{\mathcal{D}_e C_{AS}}$$

$$C_{WP} = \eta \phi_1^2 = \frac{-r_A'(obs) \rho_c R^2}{\mathcal{D}_e C_{AS}} \Leftarrow \text{Measurable or known}$$

So, now effectiveness factor eta. If we put the expressions corresponding to the effectiveness factor on the Thiele modulus into the Weisz Prater parameter, what we see that effectiveness factors, the observed rate divided by the reaction rate at the surface concentration and phi 1 square which is the Thiele modulus. It is given by the reaction rate per unit surface area of the catalyst, multiplied by the surface area of the catalyst per gram of the catalyst.

Multiplied by the density of the catalyst into r square, where r is the radius of the catalyst pellet in which the reaction is being conducted, divided by the diffusivity of the species multiplied by the concentration of the species at the surface. And so that is equal to minus r AS into rho c into r square divided by C AS. So, now plugging in these two expressions into the Weisz Prater parameter, we will find that C WP is equal to eta phi 1 square.

And that is equal to minus r A, observed rate multiplied by the density of the catalyst rho c multiplied by r square, which is the square of the diameter of the pellet that is used, in which the reaction is occurring, hydrogenous reaction is occurring divided by the diffusivity divided by concentrations of the species at the surface at the catalyst. So, now if we observe this carefully, if we observe this expression carefully we find that all the quantities which is represented here. They are either measurable quantity or a known quantity.

For example, they are all measurable or known quantities. All information present in this particular expression, they are all measurable or known quantities. So, the measurable quantity here is the reaction rates. So, reaction rate is the measurable quantity in this expression here. And the density, radius and diffusivity are again known quantities. And the reaction rate and the concentration of the surface are all measurable quantities. So, once we know these quantities, we know what the Weisz Prater parameter is.

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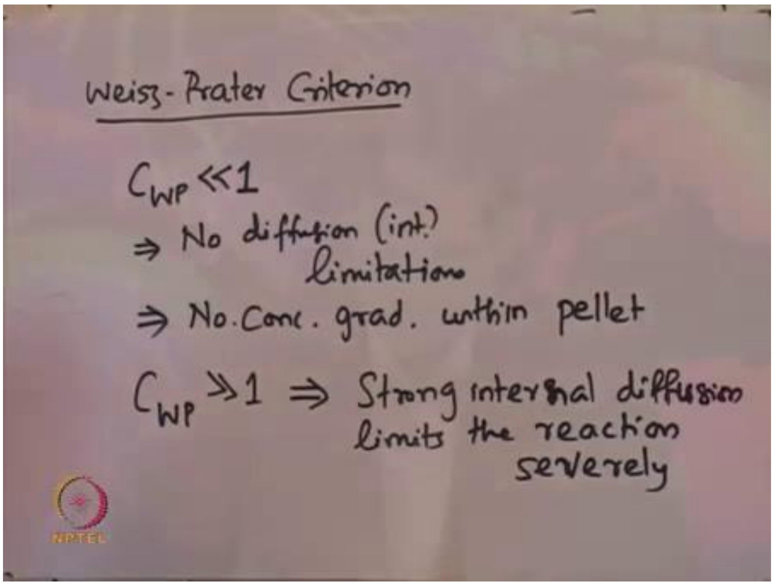

Weisz-Prater Criterion

$C_{WP} \ll 1$

$\Rightarrow$ No diffusion (int.) limitation

$\Rightarrow$ No. Conc. grad. within pellet

$C_{WP} \gg 1$ $\Rightarrow$ Strong internal diffusion limits the reaction severely

So, the Weisz Prater condition or the Weisz Prater criterion is that, Weisz Prater criterion is when the parameter C WP which is the Weisz Prater parameter. If that is significantly smaller than 1, which means that the ratio of the observed reaction rate to the rate of diffusion of the species into the catalyst, in the catalyst if that is much smaller than 1, then it means that there are no diffusion limitation, internal diffusion limitation.

Now, this also means that there is no concentration gradient within the catalyst prater, because the diffusion is very fast. And so even before the reaction occurs, all of the catalyst is now repletion with the reactant species. So, therefore there is no concentration gradient within the pellet, within the catalyst pellet. So, that is an important parameter. So, once we know these parameters, which can be estimated from the measurable and the known quantities, one can actually decipher whether reaction is being conducted as the diffusion limitations or not.

So, when Weisz Prater criterion, see parameter C WP if that is significantly larger than 1, then this implies that there is a strong internal diffusion limitations. And in fact, it means that the strong internal diffusion limits the reactions severely. So, simply by using the observed quantities, that is measurable quantities and some of the unknown properties of the system, one can actually decipher using the Weisz Prater criterion, whether the internal diffusion is limiting the reaction or not.

And that is an important aspect, when it comes in practice. It is also important to note that, why the Weisz Prater criteria can be used for non first order reactions. The effectiveness factor in Thiele modulus for such reactions, cannot be obtained using the method illustrated in this lecture. So, let us look at a specific example.

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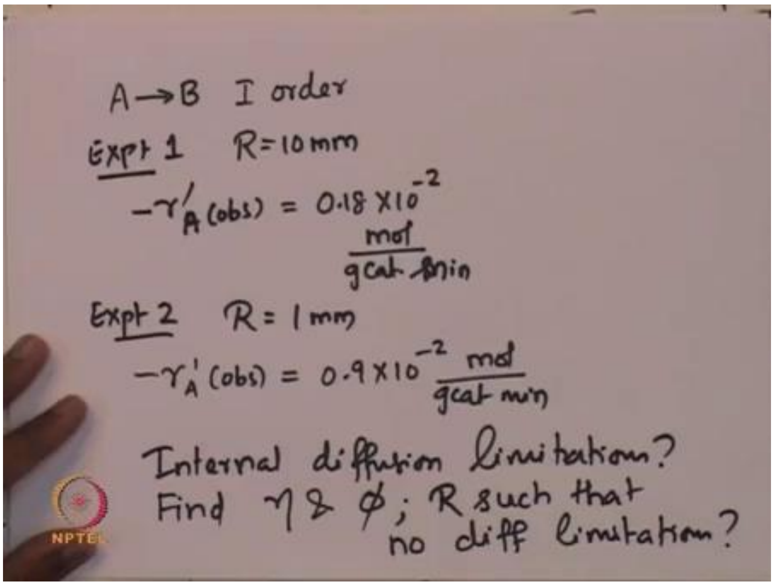

$A \rightarrow B$ I order

Expt 1 $R = 10\,mm$

$$-r'_{A}(obs) = 0.18 \times 10^{-2} \frac{mol}{gcat.min}$$

Expt 2 $R = 1\,mm$

$$-r'_{A}(obs) = 0.9 \times 10^{-2} \frac{mol}{gcat\ min}$$

Internal diffusion limitation?

Find η & ϕ; R such that no diff limitation?

So, let us consider a first order reaction. A going to B, let consider a first order reaction. Now, an experiment has been performed with different catalyst. And let say that, there is experiment 1, in which the catalyst of 10 Millimeter diameter was used to conduct the hydrogenous catalyst reaction. And let us assume that it was performed in an appropriate reactors such that, there is no external mass transfer diffusion limitations.

And so which means that the surface is the concentration of the species at the surface is equal to the concentration of the species and bulk. And the reaction rate that was observed is about .18 into 10 power minus 2 moles per gram catalyst per second per minute. That is the observed reaction rate for, when the reaction was conducted using a catalyst pellet of 10 Millimeter of diameter.

Now, suppose the same reaction was conducted under same conditions, except that a smaller pellet was used. So, there is another experiment, where the pellet that was used is 1 Millimeter in diameter, 1 Millimeter spherical particles. And the observed reaction rate is .9 into 10 power minus 2 moles per gram catalyst per minute. So, now because the experiments were conducted such that, with the under appropriate conditions.

So, there is no mass transfer assistance. So, here we need to estimate, whether it is internal diffusion controlled or not, whether the internal diffusion or there any internal diffusion limitations. So, that is the first question. Then, the next question is find the effectiveness factor eta and the effectiveness factor and the Thiele modulus for both these cases. And what should be radius of the pellet, such that there is no diffusion limitations.

So, the question is find the effectiveness factor and Thiele modulus and what should be the radius of the catalyst such that, there is no diffusion limitations. So, how do we handle this question? So, we have just now leant the Weisz Prater parameter. So, Weisz Prater parameter is basically based on the observe quantity, is such as the reaction rate etcetera. So, we can attempt to use the Weisz Prater criteria, in order to find out the effectiveness factor and Thiele modulus, from the observed reaction rate.

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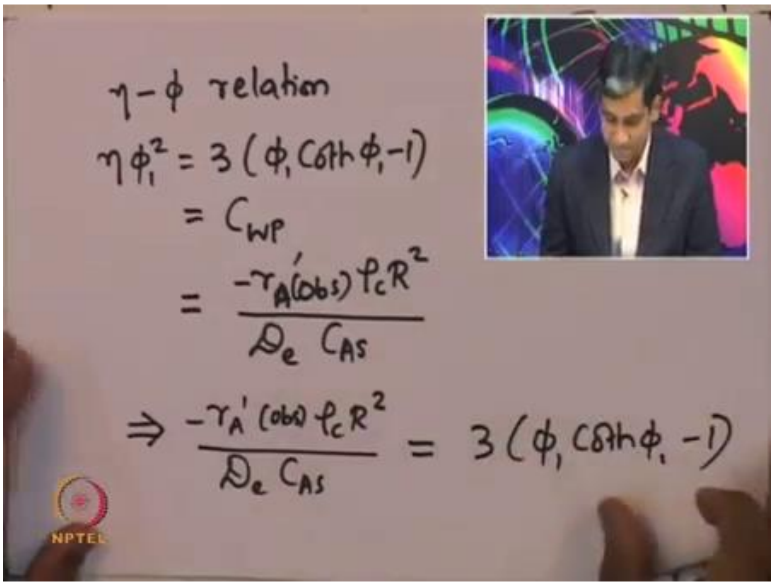

$\eta - \phi$ relation

$$\eta \phi_1^2 = 3(\phi_1 \coth\phi_1 - 1)$$

$$= C_{WP}$$

$$= \frac{-r_A'(obs)\rho_c R^2}{D_e C_{AS}}$$

$$\Rightarrow \frac{-r_A'(obs)\rho_c R^2}{D_e C_{AS}} = 3(\phi_1 \coth\phi_1 - 1)$$

So, the Thiele modulus effectiveness factor relationship suggests that, eta into phi 1 square which is the Weisz Prater parameter. That is equal to 3 times phi 1 cot hyperbolic phi 1 minus 1. Now, so this is which is equal to the Weisz Prater parameter C WP. And that is also equal to the observed reaction rate multiplied by the density of the catalyst multiplied by the square of the radius of the particle that is used, divided by the diffusivity into the concentration at the surface.

Because, the mass transport limitations are not there. So, the let us say that the surface of the catalyst, concentration of species in the surface is equal to the concentration of the species in bulk. So, from here by looking at this relationship, we find that minus r A into rho c into R square divided by diffusivity into C AS. That should be equal to 3 times phi 1 cot hyperbolic phi 1 minus 1. So, that is bring a relationship between the observed reaction rate and the Thiele modulus.

Now, for each of these runs each of these experimental runs, we could actually find out what this relationship is. That is, how the reaction rate at a given particular particle given particular radius of the pellet. How is that related to the corresponding Thiele modulus?

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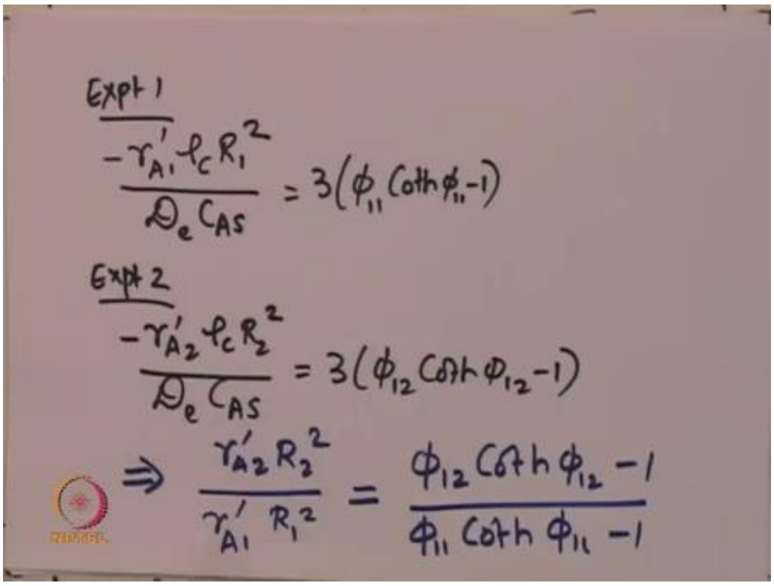

Expt 1

$$\frac{-r'_{A1}\rho_c R_1^2}{\mathcal{D}_e C_{AS}} = 3(\phi_{11}\coth\phi_{11}-1)$$

Expt 2

$$\frac{-r'_{A2}\rho_c R_2^2}{\mathcal{D}_e C_{AS}} = 3(\phi_{12}\coth\phi_{12}-1)$$

$$\Rightarrow \frac{r'_{A2}R_2^2}{r'_{A1}R_1^2} = \frac{\phi_{12}\coth\phi_{12}-1}{\phi_{11}\coth\phi_{11}-1}$$

So, for experiment 1 this is given by minus r A 1, which is the observed reaction rate when the catalyst pellet is, let us say 10 Millimeters multiplied by rho c into R 1 square divided by D e into C AS. That should be equal to 3 into phi 1 1. Now, phi 1 1 corresponds to the Thiele modulus of the first order reaction for the first experimental run and multiplied by cot hyperbolic phi 1 1 minus 1.

And similarly for experiment 2, for the other particle other radius of the pellet, for which experimental data is available. So, that will be minus A 2 into rho c into R 2 square divided by diffusivity multiplied by the corresponding surface concentration. Remember, that the experiment was conducted exactly under same conditions. So, therefore the concentration of the species at the surface of the reactor is same for both R 1 and R 2.

So, that is equal to 3 times phi 1 2 cot hyperbolic phi 1 2 minus 1. So, now taking the ratio of these two expressions here, we can now find a relationship between the observed reaction rates for both runs and the corresponding Thiele modulus. So, by taking a ratio we find that r A 2 into R 2 square divided by 1 into R 1 square. So, that should be equal to phi 1 2 cot hyperbolic minus 1 divided by minus 1.

So, this relates the information that has been observed experimentally and the corresponding Thiele modulus. So, the left hand side of this expression is essentially the one, which actually contains all the information that have been estimated experimentally and the parameters or the properties of the system, that is being used. And the right hand side is basically the Thiele module, line ratio of the Thiele module, line ratio of the function of Thiele module line. So, now let us look at the expression for the Thiele modulus.

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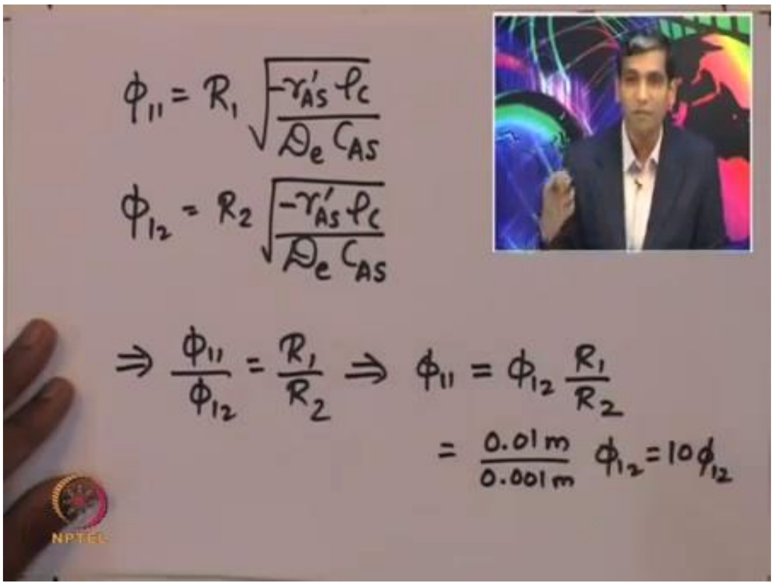

$$\phi_{11} = R_1 \sqrt{\frac{-r'_{AS}\rho_c}{\mathcal{D}_e C_{AS}}}$$

$$\phi_{12} = R_2 \sqrt{\frac{-r'_{AS}\rho_c}{\mathcal{D}_e C_{AS}}}$$

$$\Rightarrow \frac{\phi_{11}}{\phi_{12}} = \frac{R_1}{R_2} \Rightarrow \phi_{11} = \phi_{12}\frac{R_1}{R_2}$$

$$= \frac{0.01\,m}{0.001\,m}\phi_{12} = 10\phi_{12}$$

So, phi 1 1 which is the Thiele modulus for the first order reaction for the first experiment. That is given by 1, which is the radius of the pellet multiplied by square root of minus r AS, which is the reaction as if it were conducted on the surface concentration, multiplied by rho c divided by the diffusivity into the concentration of the species at the surface. And similarly phi 1 2 will be r 2 into square root of minus r AS into rho c divided by D e into C AS.

Now, from here taking the ratio take dividing these two equations, we will find that phi 1 1 by phi 1 2. That should be equal to R 1 by R 2. So, the ratio of the Thiele model is given by the ratio of the radius of the pellet itself. And there from here, one can find out the relationship between the Thiele modulus, under different experimental conditions. So, that will be phi 1 2 into R 1 by R 2. So, now plugging in the numbers we will see that, phi 1 1is equal to .01 Meter by .001 Meter of into phi 1 2.

So, that is equal to 10 times the phi 1 2. So, the Thiele modulus under one experimental condition is about 10 times the Thiele modulus of the second experimental condition. So, that is the relationship that we get from the Thiele modulus of these two experimental conditions. So, now earlier we looked, we derive the relationship between the ratio of the reaction rates with the corresponding Thiele modulus.

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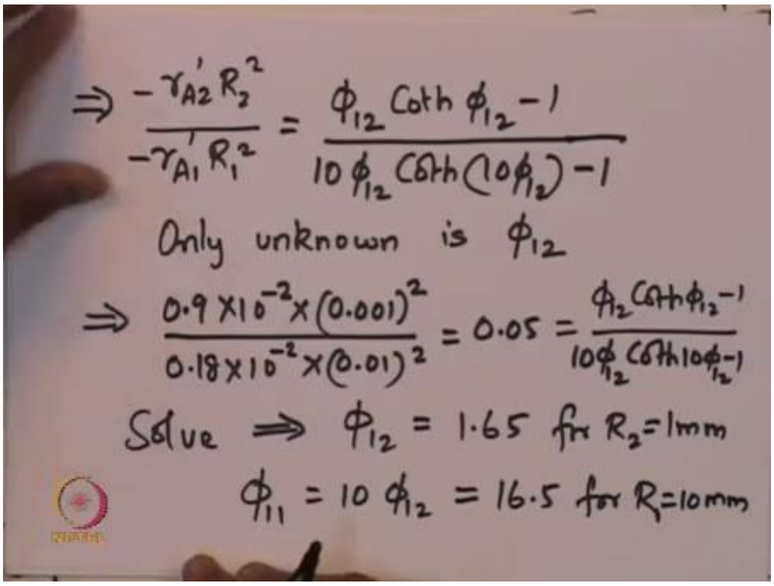

$$\Rightarrow \frac{-r'_{A2} R_2^2}{-r'_{A1} R_1^2} = \frac{\phi_{12} \coth \phi_{12} - 1}{10 \phi_{12} \coth(10\phi_{12}) - 1}$$

Only unknown is ϕ_{12}

$$\Rightarrow \frac{0.9 \times 10^{-2} \times (0.001)^2}{0.18 \times 10^{-2} \times (0.01)^2} = 0.05 = \frac{\phi_{12} \coth \phi_{12} - 1}{10\phi_{12} \coth 10\phi_{12} - 1}$$

Solve $\Rightarrow$ $\phi_{12} = 1.65$ for $R_2 = 1\text{mm}$

$\phi_{11} = 10\,\phi_{12} = 16.5$ for $R_1 = 10\text{mm}$

So, now we have to we can plug in the relationship between the Thiele modulus under these two experimental conditions into that expression. And that will be minus r A 2 into

R 2 square divided by minus r A 1 into R 1 square. And that should be equal to phi 1 2, which is the Thiele modulus for the second experimental run, into cot hyperbolic phi 1 2 minus 1 divided by 10 times phi 1 2 into cot hyperbolic, 10 times phi 1 2 minus 1.

So, all the information here is known. The only variable is, only unknown is phi 1 2. So, we need to estimate phi 1 2 using all the other information, that we already know. So, from here we can plug in the numbers. So, the reaction rate for the second condition will be .9 into 10 power minus 2, multiplied by the square of the corresponding radius divided by .18 into 10 power minus 2 into .01 the whole square.

And that is equal to .05 and that will be equal to phi 1 2 cot hyperbolic, phi 1 2 minus 1 divided by 10 times phi 1 2 into cot hyperbolic 10 times phi 1 2 minus 1. So, now by solving this expression we can find out, what is the Thiele modulus for this second experimental runs. So, solving we can find that phi 1 2 is about 1.65. This is for R 2 equal to 1 Millimeter. We all know the, we also know the relationship between the Thiele modulus of these two experimental conditions.

So, from there we can find out phi 1 1, which is 10 times phi 1 2. That is equal to 16.5 for R 1 equal to 10 Millimeters. So, we have now found the Thiele modulus. Now, once we know the Thiele modulus, we can actually estimate what is the effectiveness factor, because effectiveness factor and the Thiele modulus under given experimental conditions, are actually related.

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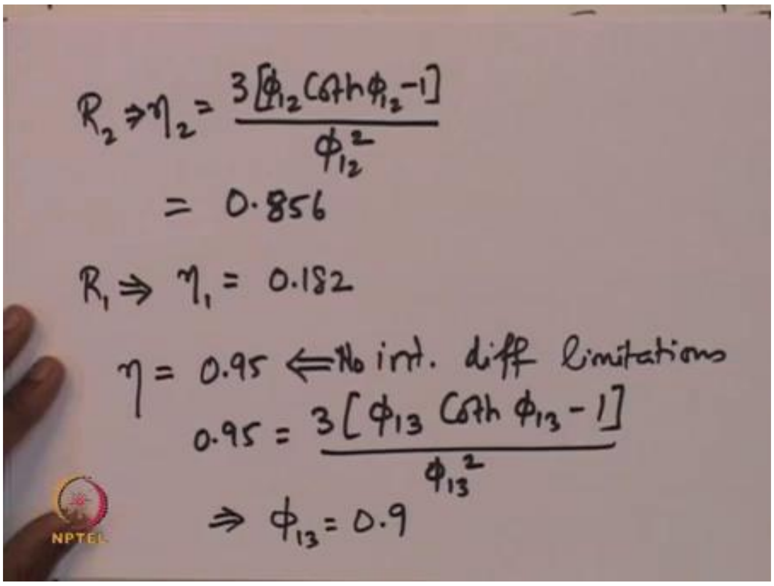

$$R_2 \Rightarrow \eta_2 = \frac{3[\phi_{12}\coth\phi_{12}-1]}{\phi_{12}^2}$$

$$= 0.856$$

$$R_1 \Rightarrow \eta_1 = 0.182$$

$\eta = 0.95 \Leftarrow$ No int. diff limitations

$$0.95 = \frac{3[\phi_{13}\coth\phi_{13}-1]}{\phi_{13}^2}$$

$$\Rightarrow \phi_{13} = 0.9$$

So, for R 2 which is the second experimental run eta 2 equal to 3 times phi 1 2 into cot hyperbolic phi 1 2 minus 1 divided by phi 1 2 square. And so once we plug in the Thiele modulus data. So, we will find out that this effectiveness factor is about .856. And then similarly for the first experimental run the effectiveness factor eta 1 will be .182. Now, the next question is, can we find out what is the smallest radius at which the internal diffusion limitations does not exist?

That is, there is no internal diffusion limitation that is, limiting the reaction. So, suppose if we assume that the effectiveness factor should be .95. Suppose, if the effectiveness factor should be .95 at which there is no internal diffusion limitations. Then, we can actually use the relationship between the effectiveness factor and the Thiele modulus, in order to find out what is the corresponding Thiele modulus. So, we know that .95 that is equal to 3 times phi 1 3 cot hyperbolic phi 1 3 minus 1 divided by phi 1 3 square.

So, by solving this we can find out that phi 1 3 is about .9. So, that is the Thiele modulus. That should be the Thiele modulus, if the reaction has to be conducted under no internal diffusion limitations. So, once we know the Thiele modulus we also know, what is the relationship between the Thiele modulus ratio and the corresponding radius? So, we can use that expression in order to find out, what should be the particle radius in order for the internal diffusion limitations, do not exists.

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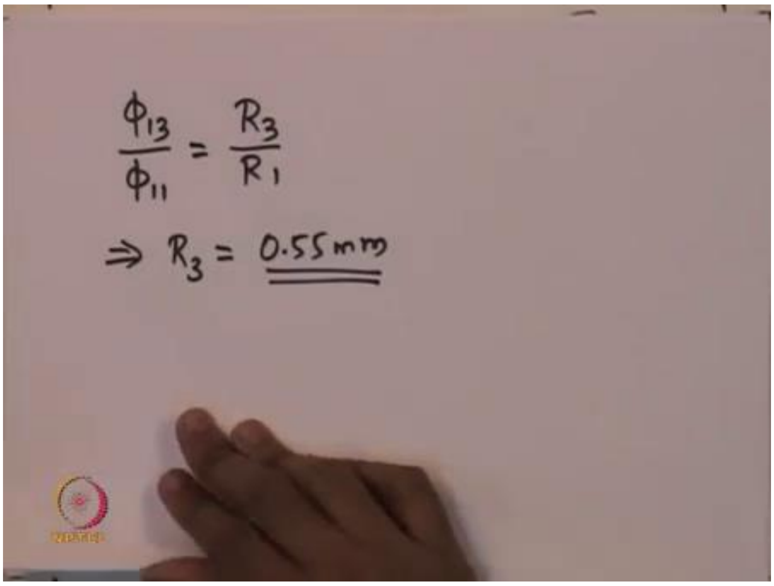

$$\frac{\phi_{13}}{\phi_{11}} = \frac{R_3}{R_1}$$

$$\Rightarrow R_3 = \underline{\underline{0.55\,mm}}$$

So, phi 1 3 divided by phi 1 1. So, this is phi 1 1 is the Thiele modulus corresponding to one of the already conducted experiments. And so that will be R 3 by R 1. So, from here we can find out that R 3 should be equal to about .55 Millimeters. The smallest pellet, at which the internal diffusion will not limit the reaction, is about .55 for the given set of experimental conditions. So, in this way we using some trial experiments.

One can actually find out, what should be the pellets size under which the reaction has to be conducted in order for the internal diffusion, to not be present and not affect the reaction severely. Now, let us let us move on to the external diffusion. We looked at the internal diffusion. What is the method to use the experimental observable data, in order to find out whether the reaction is being conducted under internal diffusion limitations?

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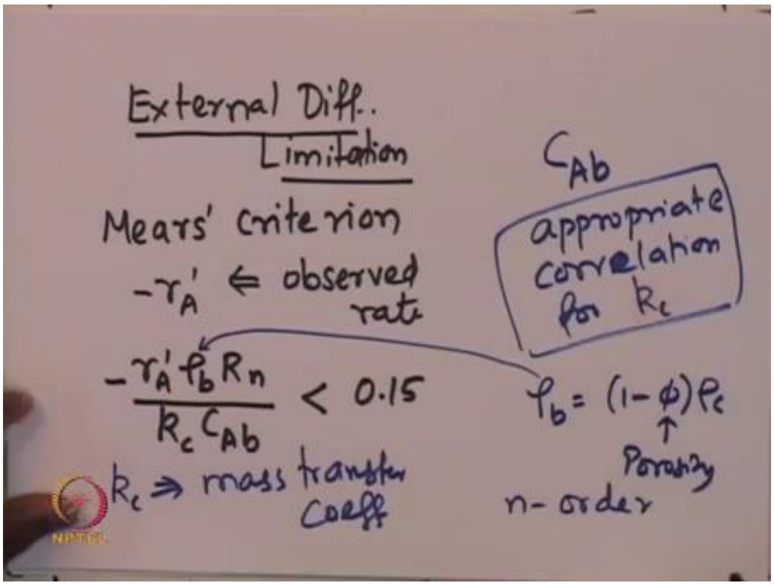

External Diff. Limitation

Mears' criterion

$-r'_A$ ⇐ observed rate

$$\frac{-r'_A \rho_b R_n}{k_c C_{Ab}} < 0.15$$

k_c ⇒ mass transfer coeff

C_{Ab}

appropriate correlation for k_c

$\rho_b = (1-\phi)\rho_c$

↑ Porosity

n- order

So, next let us look at the external diffusion limitations. So, one has to use a criteria developed by Mears is called the Mears criterion. So, Mears criterion can be used to find out, whether the catalytic reaction being conducted under external diffusion limitations. That is mass transfer diffusion limitations, is the transport of species from the bulk to the surface of the catalyst, is that limiting the reaction severely.

So, the expression is, suppose if minus r A is the observed reaction rate. It is the observed rate. Then, the criterion is that if minus r A into rho b into R into n divided by k c into C a bulk, if that is smaller than .15. So, if the ratio of, if this expression of the left hand side that is basically contains, the observed reaction rate. So, the observed reaction rate is multiplied by the corresponding density, bulk density of the catalyst.

So, the bulk density of the catalyst rho b is given by 1 minus phi into rho c, where phi is the porosity of the bed, that is used and rho c is the solid density of the catalyst. So, if we know what is the bulk density? Then, we can plug it in here. And then we can find this expression. And n is the order of reaction, n stands for the order of reaction and the reaction order. And k c is the corresponding mass transfer coefficient.

So, one needs to estimate what is the mass transfer coefficient, for transporting the species from bulk to the surface of the catalyst. And then one needs to know, what is the concentration of this species in bulk, which is again a measurable quantity? And one can, one may also use different appropriate correlation. There are several correlations, which are available to estimate the mass transfer coefficient.

One may use the appropriate correlation, in order to estimate what is the value of this mass transport coefficient for the given conditions. That is for flow through packed beds. So, once we know these numbers, we will be able to estimate what is this quantity of the left hand side? And if this is smaller than .15, then the external diffusion limitations are not playing any role. And that can be ignored. If it is greater than .15, then certainly external diffusion limitations have to be taken into account.

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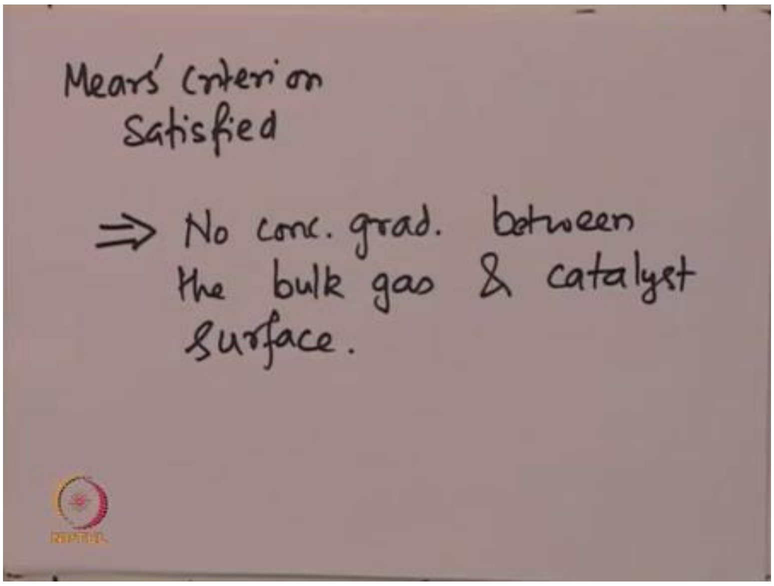

Mears' Criterion
Satisfied

$\Rightarrow$ No conc. grad. between the bulk gas & catalyst surface.

So, now if the Mears criterion is satisfied, then this means that there is no concentration gradient between the bulk gas, on the external surface of the catalyst pellet. So, there is no concentration gradient between the bulk gas and the catalyst surface, if the Mears criteria is satisfied. Now, we looked at the concentration gradient, one may ask what is the, what about the temperature gradient.

So, can we get an estimate, can we find a criteria in order to know whether the temperature gradient, external temperature gradient does it play role. That is the gradient of the temperature between the temperature at the surface of the catalyst and the temperature of the bulk stem. Does it play any role in limiting the reaction?

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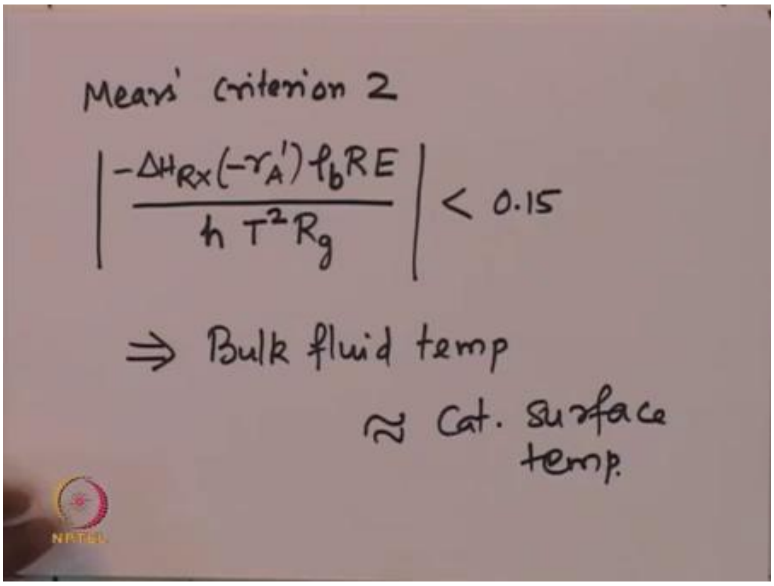

Mears' criterion 2

$$\left| \frac{-\Delta H_{Rx}(-r_A')\rho_b R E}{h T^2 R_g} \right| < 0.15$$

$\Rightarrow$ Bulk fluid temp

$\approx$ Cat. surface temp.

So, Mears has come up with another criteria. So, it is Mears criterion 2. Now, this suggest that if the modulus of this expression, where delta h is the heat of reaction into minus r A prime, which is the observed reaction rate multiplied by rho b, which is the bulk density of the catalyst into the radius of the pellet that is used, multiplied by the activation energy e divided by a corresponding heat transport coefficient.

There are several correlation, which are available in order to estimate the heat transport coefficient, multiplied by the square of the bulk temperature of the fluid stream, multiplied by the corresponding gas constants. So, if this absolute value of this ratio if that is less than .15, then it means that the temperature gradient does not play any role, which means that the bulk fluid temperature is approximately equal to the catalyst surface temperature. Note, that inter particle gradient need not necessarily be negligible. However, Weisz Prater criteria can be used to indentify when these gradients may be neglected.

So, this is an important criterion. So, these two criterions can actually be used. These two criteria can actually be used in order to decipher, whether the particular reaction is being conducted under diffusion limitations or not. So, now let us summarize what we have learnt so far.

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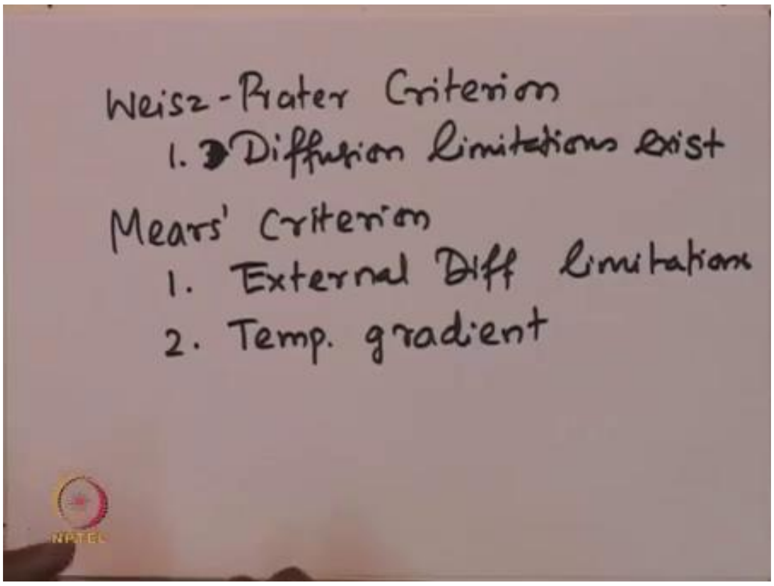

Weisz-Prater Criterion
1. Diffusion limitations exist

Mears' Criterion
1. External Diff limitations
2. Temp. gradient

So, we have look at the Weisz Prater criterion. And the first one is to decipher whether it is the Weisz Prater criterion. Basically, decipher if the diffusion limitations exist. And then we looked at the Mears criterion. So, the first criterion basically to see the external diffusion limitations exist, to check whether the external diffusion limitations exist. And then the second one is to check whether the temperature gradient is important, external temperature gradient is important.

So, these three criteria Weisz Prater criterion and the Mears criterion, they play a very, very important role in real situations, because if the experimental data is available then this information can actually be used in order to decipher, whether the reaction the reaction is being conducted under diffusion limitations or not. So, next let us look at design of a packed bed reactor. As to how we can incorporate the concept of effectiveness factor, in order into the packed bed reactor design.

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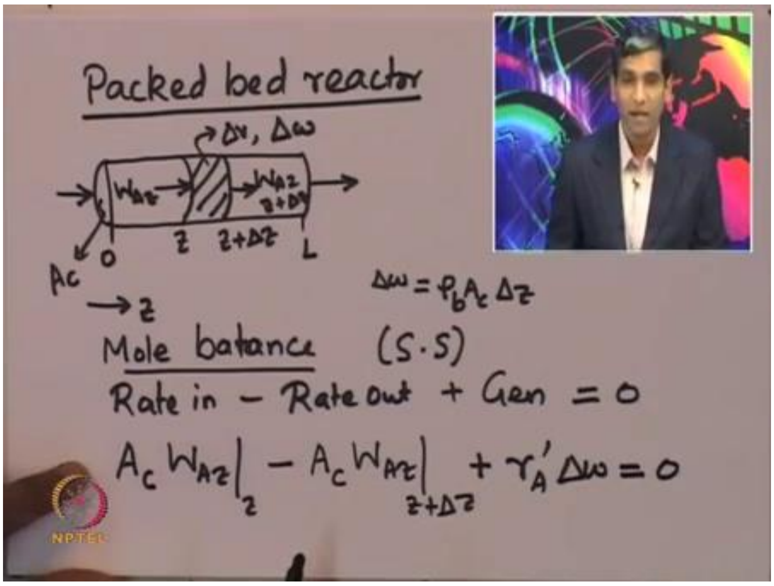

Packed bed reactor

$\Delta w = \rho_b A_c \Delta z$

Mole balance (S.S)

Rate in − Rate out + Gen = 0

$$A_c W_{Az}\big|_{z} - A_c W_{Az}\big|_{z+\Delta z} + r_A' \Delta w = 0$$

Now, let us consider a packed bed reactor. Packed bed reactor is essentially a tube, and filled with the catalyst. And the fluid stream goes from one end of the tube into the other end of the tube. So, let us consider a tube. And there is a fluid stream, which goes into this tube and it leaves the tube from this end. So, if I mark this as z equal to 0, z is my coordinate system, so 0 to l. So, l is the length of the reactor and if A c is the cross sectional area of the tube.

And now, I can write a mole balance in order to capture the dynamics or the behavior or the relationship of the conversion, with all the other parameters. So, now if I write a shell balance, I now identify a small shell which is filled with catalyst. And let us assume that, the volume of the shell is delta v. And the amount of catalyst we just packed inside is delta small w. And if this is the location, where this elements starts is z and the location where it ends is z plus delta z.

So, this immediately means that delta w which is the differential amount of catalyst, which is present in that location should be equal to the bulk density of the catalyst. Multiplied by the cross sectional area, multiplied by the delta z which is the thickness of that particular element, that we have chosen. So, now we can write a mole balance for this small element. And we can find out, what is the model equation which captures the relationship between the concentrating of these species, which is undergoing the catalytic reaction with respect to other parameters.

So, suppose if the flux of species that enters this small element is W A z, that the flux that enters at that location. And the flux that leaves is W A z , evaluated as z plus delta z. So, that is the flux that leaves that location. Then, we can write a mole balance. The mole balance is essentially the rate at molar rate, at which the species enter that element, minus the molar rate at which the species leaves the element plus whatever is generated, that should be equal to zero 0 under steady state condition.

So, if we assume steady state conditions, then this is the balance that captures the process that is happening in the small element. So, what is the rate at which the species is getting into the element? That is given by the cross sectional area A c multiplied by the flux, with which the species is actually entering into that element, which is W A z evaluated at that particular location minus the rate at which the species leaves is given by, the cross sectional area multiplied by the flux at which the species leaves that element.

That is W A z at z plus delta z. And the generation is given by, the reaction rate per unit weight of the catalyst multiplied by the amount of catalyst, which is packed inside by that small element delta z.

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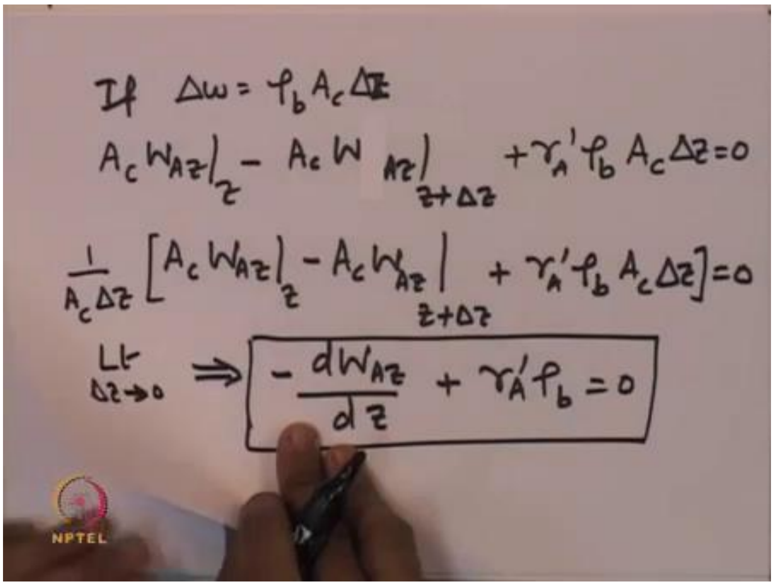

If $\Delta w = \rho_b A_c \Delta z$

$$A_c W_{Az}\big|_z - A_c W_{Az}\big|_{z+\Delta z} + r_A' \rho_b A_c \Delta z = 0$$

$$\frac{1}{A_c \Delta z}\left[A_c W_{Az}\big|_z - A_c W_{Az}\big|_{z+\Delta z} + r_A' \rho_b A_c \Delta z\right] = 0$$

$$\underset{\Delta z \to 0}{Lt} \Rightarrow \boxed{-\frac{dW_{Az}}{dz} + r_A' \rho_b = 0}$$

So, now we know that the if the reactor volume is constant, we know that we can actually rewrite this expression as delta w is equal to rho b A c into delta v delta z. That is the differential amount of catalyst, that is packed inside that element. And so now we can incorporate this into the model. And therefore, the model will be A c into W A z minus A c A z at z plus delta z, plus the rate multiplied by the bulk density into the cross sectional area into delta z is equal to 0. So, that is the modeled.

Now, we can divide this whole equation by cross sectional area into delta z. So, that will be 1 by A c into delta z. That is multiplied by A c minus z plus delta z plus r A prime into rho b into A c into delta z that is equal to 0. So, now if we take limit, delta z is going to 0. That, if the element is very very small infinite is small then the modeled equation becomes minus d W A z by d z plus r A prime rho b equal to 0.

So, this is the mole balance for species A, which is undergoing heterogeneous reaction in a packed bed reactor, where W A z is essentially the flux with which the species is actually entering the flux of this species at a particular location z.

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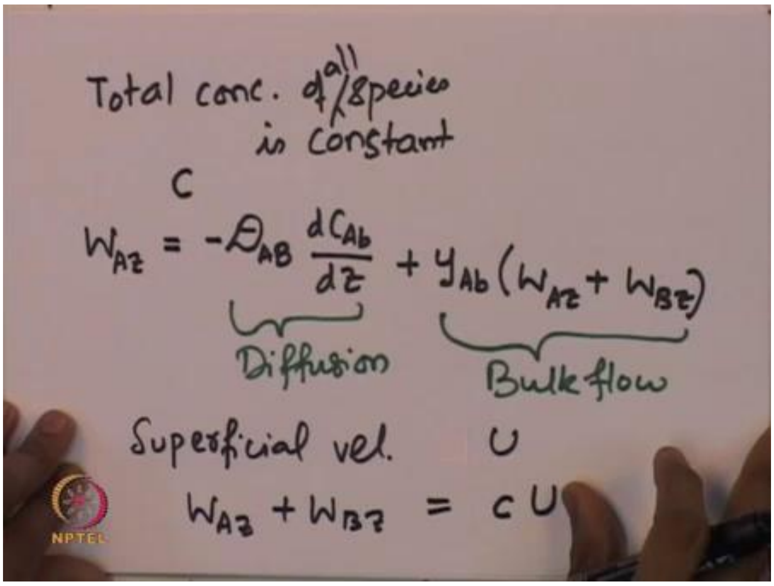

Total conc. of all species is constant

C

$$W_{Az} = \underbrace{-\mathcal{D}_{AB}\frac{dC_{Ab}}{dz}}_{\text{Diffusion}} + \underbrace{y_{Ab}(W_{Az} + W_{Bz})}_{\text{Bulk flow}}$$

Superficial vel. U

$$W_{Az} + W_{Bz} = cU$$

Now, if I assume that the total concentration is constant. So, if you assume that the total concentration of species, all species is constant. So, total concentration of all species put together, if it remains constant, and if that value, let say is c. Now, the flux with which the species crosses a particular location, that can be written as minus D AB which is the diffusivity of the species, equimolar counter diffusivity of that species A multiplied by the concentration gradient D AB divided by d z plus y a b, which is the mole fraction of the species, multiplied by the W A z which is the flux of the species at that location, plus the flux of species b at that location.

So, now if we stair at this equation, the first term here corresponds to the diffusion term, corresponds to the species diffusion. And the second term corresponds to the bulk flow. Second term corresponds to the bulk flow, which is like a convective transport and the first term corresponds to the diffusion mode of transport. So, now if we know what is the superficial velocity? So, suppose the superficial velocity is U, then the total flux that is crossing a particular location W A z plus W B z, that should be equal to the total concentration c, multiplied by superficial velocity U.

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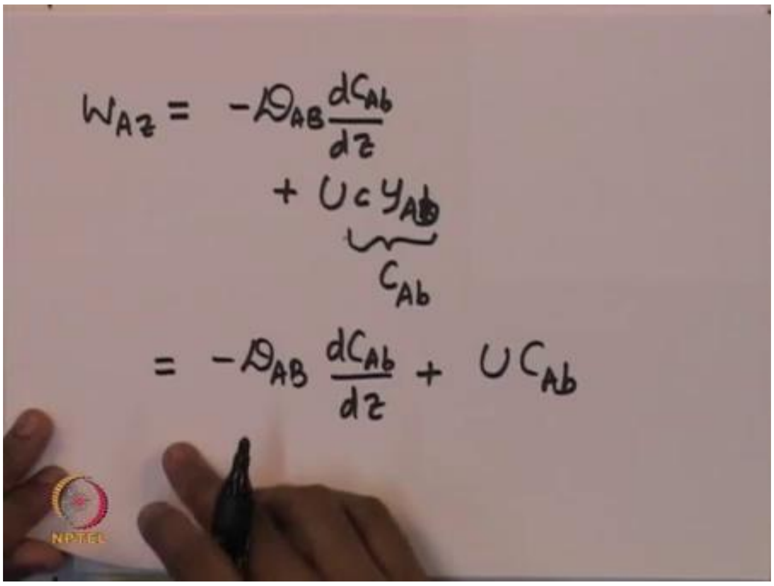

$$W_{Az} = -\mathcal{D}_{AB}\frac{dC_{Ab}}{dz} + U\,\underbrace{c\,y_{Ab}}_{C_{Ab}}$$

$$= -\mathcal{D}_{AB}\frac{dC_{Ab}}{dz} + U\,C_{Ab}$$

So, now plugging in this expression, we can rewrite the expression for the a flux of species that is W A z. And that should be equal to minus D AB into d C A b by d z. So, that is the bulk concentration of the species, at that particular location plus U into C into y A b, y a bulk small b. So, now if we look c into y a, c into y a bulk is nothing but the concentration of the species at that location.

And therefore, it will be minus D AB into d C A b by d z plus U into C A b. So, that is the expression for the flux of species that is crossing, any particular location z inside the reactor. So, now plugging in the expression for the flux in the mole balance, we can rewrite the mole balance as.

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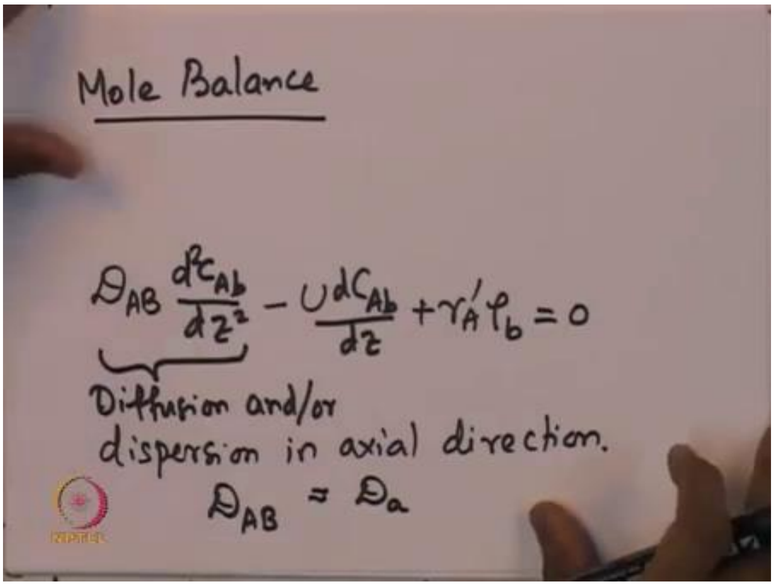

Mole Balance

$$\underbrace{\mathcal{D}_{AB}\frac{d^2C_{Ab}}{dz^2}}_{\text{Diffusion and/or dispersion in axial direction.}} - U\frac{dC_{Ab}}{dz} + r_A'\rho_b = 0$$

$$\mathcal{D}_{AB} \approx \mathcal{D}_a$$

Now, the mole balance can be rewritten as D AB, which is the dispersion coefficient of the species, t into d squarer C A b by d z square. So, that is the second differential of this concentration of this species, minus U which is the superficial velocity multiplied by d C A bulk by d z plus r A prime, which is the rate at which species is being consumed. Rate at which species is being generated, multiplied by the bulk density that should be equal to 0.

So, now this first term here, which is the diffusion into the second derivative of the bulk concentration of the species. So, that is because that is due to diffusion and or it could be either because of diffusion. The transport of species that is captured by this term, could be either because of pure diffusion or because of axial dispersion, because of dispersion in the axial direction.

So, therefore for rest of the design equation, mole balances we would consider D AB which is the equimolar counter diffusivity, should be approximately equal to D a, which is basically the quantity that captures the extent of diffusion or the extent of the dispersion or diffusion and dispersion together. So, here after we will refer to as D a in this lecture.

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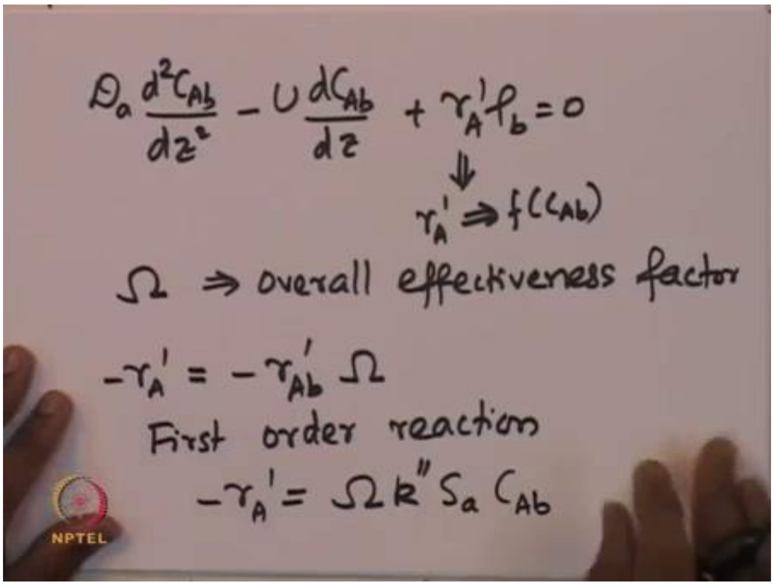

$$D_a \frac{d^2 C_{Ab}}{dz^2} - U \frac{dC_{Ab}}{dz} + r_A' \rho_b = 0$$

$$\Downarrow$$

$$r_A' \Rightarrow f(C_{Ab})$$

$\Omega \Rightarrow$ overall effectiveness factor

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

First order reaction

$$-r_A' = \Omega k'' S_a C_{Ab}$$

So, the modified mole balance using this representation is D a into d square C A b by d z square minus U into d C A b by d z plus r A prime into rho b equal to 0. So, now using this expression now the next step we need to relate, r A to concentration. We need to find out, what is this relationship with the concentration of the species. So, if suppose if omega is the overall effectiveness factor, if this is the overall effectiveness factor.

So, it is the overall effectiveness factor then the rate of reaction r A prime can actually be given by minus r A bulk. So, this is the reaction rate in the catalyst. Now, that should be equal to the reaction rate, if all the catalyst surface is now exposed. And it is present at the concentration of the species on the surface. Then, that concentration of species in bulk then multiplied by the overall effectiveness factor. We will actually be the actual reaction rate, inside the catalyst.

So, now if we assume that is, it is a first order reaction. If it is a first order reaction then minus r A prime is given by the effectiveness factor multiplied by the specific reaction constant into the surface area of the catalyst per gram, per unit weight of the catalyst multiplied by the bulk concentration C A b. So, now plugging in this expression into the mole balance.

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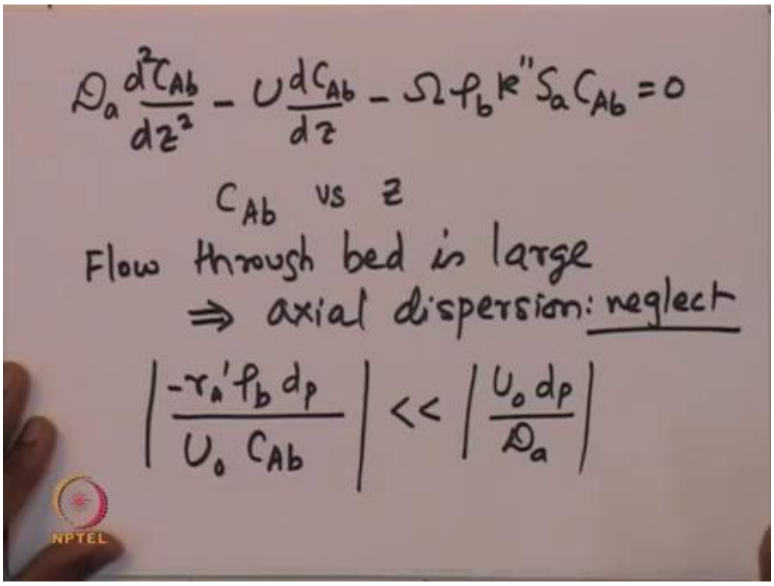

$$\mathcal{D}_a \frac{d^2 C_{Ab}}{dz^2} - U\frac{dC_{Ab}}{dz} - \Omega \rho_b k'' S_a C_{Ab} = 0$$

C_{Ab} vs z

Flow through bed is large

$\Rightarrow$ axial dispersion: <u>neglect</u>

$$\left|\frac{-r_A' \rho_b d_p}{U_0 C_{Ab}}\right| << \left|\frac{U_0 d_p}{\mathcal{D}_a}\right|$$

We can find that the mole balance is D a, which is dispersion coefficient multiplied by d square C A b by d z square minus U, which is a superficial velocity into d C A b bulk by d z minus omega, into the bulk density rho b into k prime, which is the specific reaction constant, multiplied by the surface area per gram catalyst into C A b equal to 0. So, now if the flow through beds, so we need to solve this equation. In order to find out the relationship between C A b, and the how C A b or the bulk concentration, changes with location inside the reactor.

So, now suppose if the flow through the bed is large, suppose if the flow through the bed is significantly large then one can actually neglect the axial dispersion. And that is not true always. Only when this flow through bed is large, and in fact one can actually quantify, what is the situation under which the axial dispersion can be neglected. So, the condition that has to be satisfied in order to assume that, the axial dispersion is can be neglected is given by minus r A prime into rho b, which is the bulk density multiplied by the diameter of the particle, divided by the superficial velocity. If that is much smaller than this quantity, U naught d p by D a then it is acceptable to neglect the axial dispersion from the mole balance. So, this also suggest that the.

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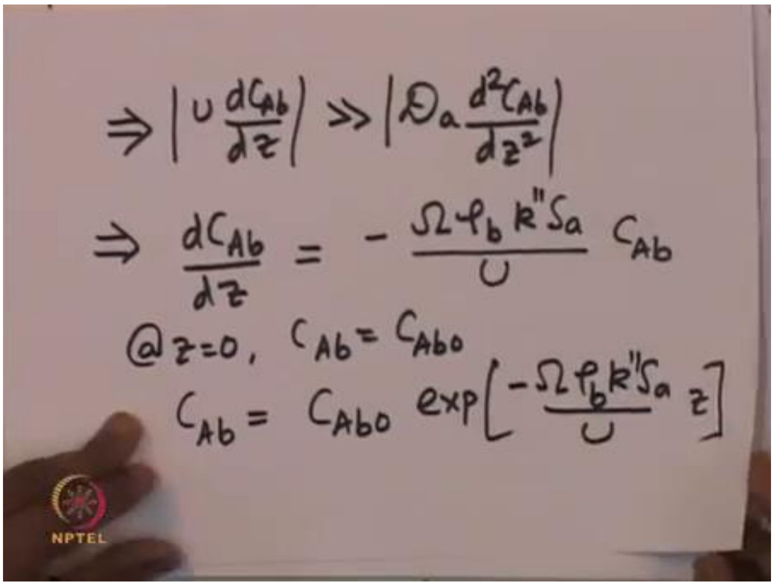

$$\Rightarrow \left| u \frac{dC_{Ab}}{dz} \right| >> \left| \mathcal{D}_a \frac{d^2C_{Ab}}{dz^2} \right|$$

$$\Rightarrow \frac{dC_{Ab}}{dz} = - \frac{\Omega \rho_b k'' S_a}{U} C_{Ab}$$

$@ z=0, \; C_{Ab} = C_{Ab0}$

$$C_{Ab} = C_{Ab0} \exp\left[- \frac{\Omega \rho_b k'' S_a}{U} z \right]$$

So, when axial dispersion can neglected it also suggest that the, u into d C A by d z which is the term that corresponds to the convective transport. That is significantly larger than the diffusive transport, inside the packed bed reactor. So, it suggest that the convective transport is large than the diffusive transport. And under these conditions, one can actually neglect the dispersion inside the reactor. And so the modified mole balance which accounts for these assumptions is d C A b by d z.

That is equal to minus m omega is the effectiveness factor into rho b into k, k is the reaction rate constant. And S a is the area of the catalyst per gram of the catalyst, surface area of the catalyst which is available divided by the superficial velocity into C A b. So, if suppose at the entry of the reactor z is equal to 0, if C A b is equal to some constant value, C A naught which is the concentration with which the species enters the reactor.

Then, we can integrate this expression and find that C A b is equal to C A b naught into exponential of minus omega rho b S a by superficial velocity U into z. And or we can use this expression in order to find out, what is the conversion of the species in the reactor.

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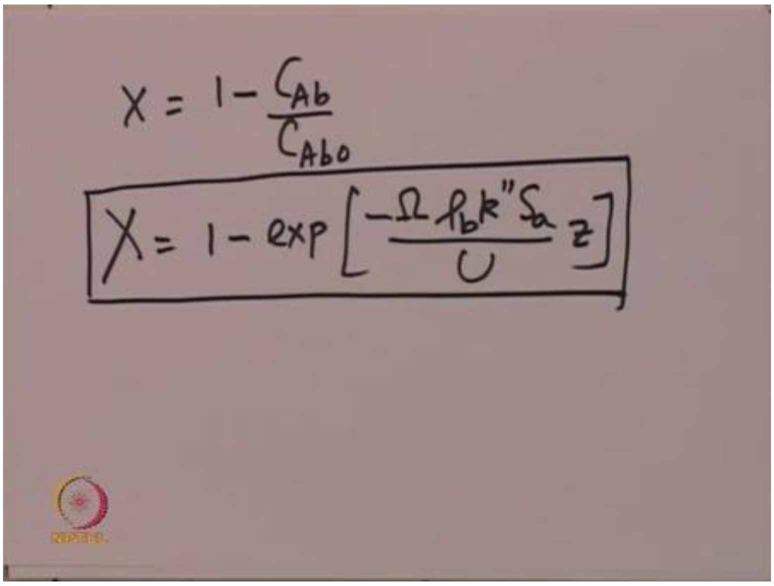

$$X = 1 - \frac{C_{Ab}}{C_{Ab0}}$$

$$\boxed{X = 1 - \exp\left[\frac{-\Omega \rho_b k'' S_a}{U} z\right]}$$

And the conversion is given by this expression here, where x is equal to 1minus C A b by C A b naught, which is equal to 1 minus exponential of minus omega into rho b into k into S a by U, which is the superficial velocity into z. So, this expression captures the relationship between the conversion, as a function of the location inside the reactor. And so this is very useful in terms of estimating, what is the reaction what is the conversion, given the overall effectiveness factor and the system parameter and configuration of the reactor.

That is, what is the particle diameter, etcetera. So, what we have seen in today's lecture is, we have looked at the criterion for when the internal diffusion is important and when the external diffusion limitations are important. And that is simply based on the experimental data, that has been obtained from the real reactors system. And also we had attempted to see, how to incorporate the effectiveness factor into the mole balance of the packed bed reactor. In order to find out, how the conversion changes as a function of position, in the packed bed reactor?

Thank you.