Chemical Reaction Engineering - II
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Lecture – 33
Identification of Internal Diffusion - and Reaction-Limited Regimes

Friends, in this lecture, we are 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 performed 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 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 reaction is diffusion limited and under what situation, it is surface reaction limited. So the diffusion limited situation can actually be of 2 types. One can be the external diffusion.

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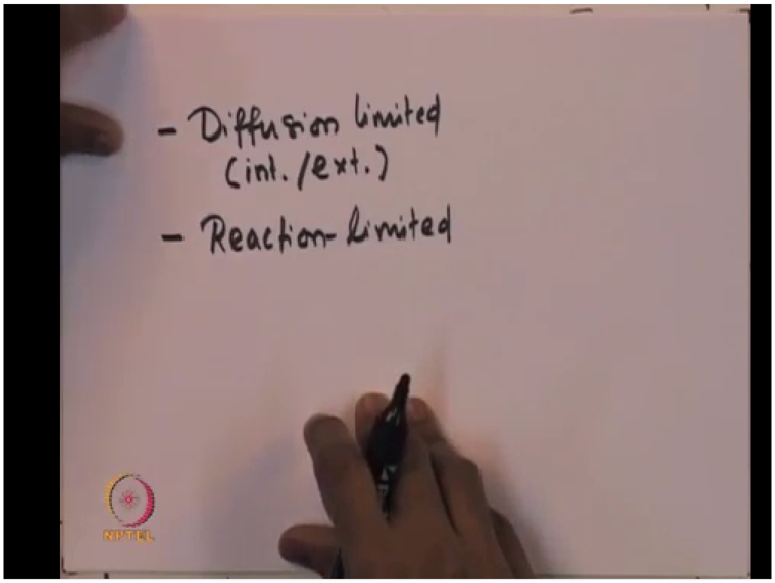

- Diffusion limited
  (int./ext.)
- Reaction-limited

The diffusion limited experimental conditions can actually be diffusion limited, reaction conditions can be either internal diffusion controlled or the external diffusion controlled. The other possibility is 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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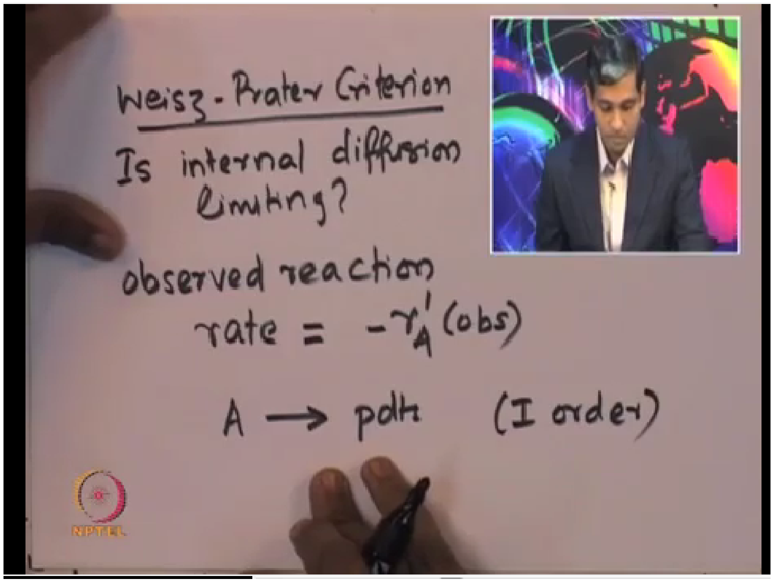

Weisz - Prater Criterion

Is internal diffusion limiting?

observed reaction rate = $-r'_A$ (obs)

A $\longrightarrow$ pdt (I order)

So we will start with Weisz-Prater criterion. So the Weisz-Prater criterion is actually used to answer this question, is internal diffusion controlling the, is internal diffusion limiting, the current conditions, 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, -rA prime obs is the, let us say, 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 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 relationship between the effectiveness factor and Thiele modulus.

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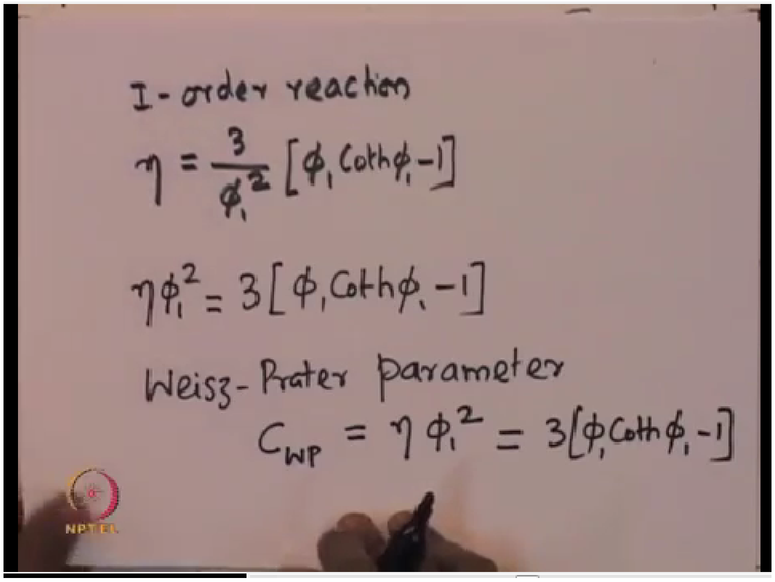

I-order reaction

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

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

Weisz-Prater parameter

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

So for a first order reaction, the relationship between the effective and Thiele modulus was given by eta which is the effectiveness factor, that is given by 3/phi 1 square, 1 stands for the, 1 here refers to the first order reaction, 3/phi and square*phi1 Cot hyperbolic phi1-1. So that is the relationship between the effectiveness factor and Thiele modulus for a first order reaction. Now this equation can actually be modified as eta*phi1 square=3*phi1 Cot hyperbolic phi1-1.

So all I have done is just multiplied the whole equation with phi1 square. So once we do this, we can now define a new parameter called the Weisz-Prater parameter. So we define a parameter called the Weisz-Prater parameter. And this parameter is CWP, C subscript WP represents the Weisz-Prater parameter and that is=eta*phi1 square. So we define a new parameter called CWP=eta*phi1 square and that would be =3*phi1 Cot hyperbolic phi1-1.

So now that is this parameter? So let us look at what is the meaning of this parameter CWP? So we can look at the meaning of this parameter.

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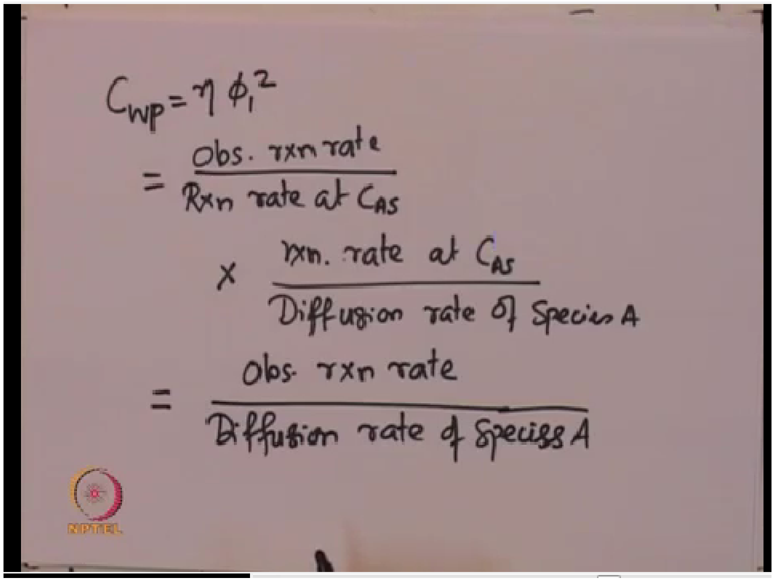

$$C_{WP} = \eta \phi_1^2$$

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

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

So CWP=eta*phi1 square. The effectiveness factor is essentially the ratio of the observed reaction rate to the reaction rate evaluated at the bulk concentration, CAS. So that will be bulk observed reaction rate/reaction rate at the bulk concentration. If you assume that there is no mass transfer limitations, that will be equal to the concentration at the surface of the catalyst and that, *Thiele modulus.

So phi1 square is nothing but the reaction rate evaluated at the surface concentration if there is no mass transfer limitations/the diffusion rate of the species that is actually undergoing the reaction. So that will be reaction rate at CAS/the diffusion rate of species A. So now from here, we can actually rewrite this expression. So we can see that we can cancel off the denominator in the first expression and the numerator in the second expression.

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

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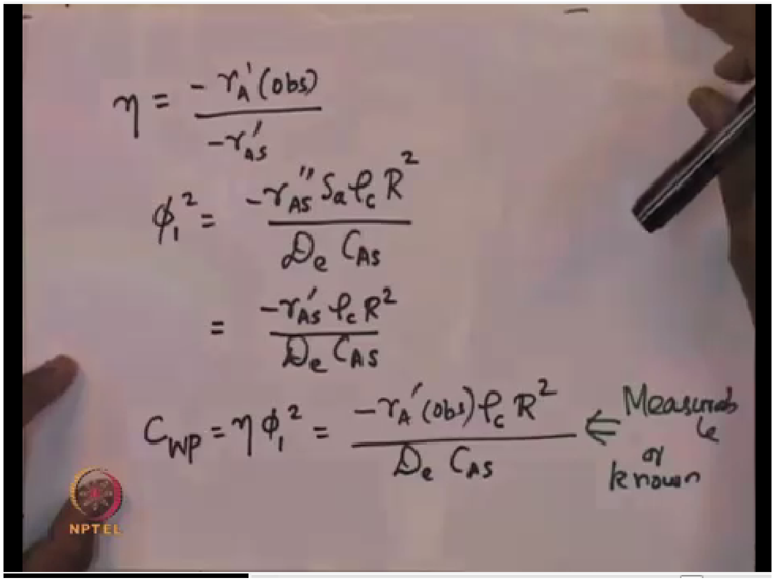

$$\eta = \frac{-r_A'(obs)}{-r_{AS}'}$$

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

$$= \frac{-r_{AS}' \rho_c R^2}{D_e C_{AS}}$$

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

So now effectiveness factor, eta, if we put the expressions corresponding to the effectiveness factor in the Thiele modulus into the Weisz-Prater parameter, what we see is that effectiveness factor is the observed rate/reaction rate at the surface concentration and phi1 square which is the Thiele modulus is, it is given by the reaction rate per unit surface area of the catalyst*the surface area of the catalyst program of the catalyst*the density of the catalyst*R square, where R is the radius of the catalyst pallet in which the reaction is being conducted/the diffusivity of the species*the concentration of the species at the surface.

And so that is equal to -rAS*rho C*R square/CAS. So now plugging in these 2 expressions into the Weisz-Prater parameter, we will find that CWP*eta phi1 square and that is equal to -rA observed rate*density of the catalyst rho C*R square which is the square of the diameter of the pallet that is used in which the reaction is occurring, heterogeneous reaction is occurring/diffusivity/concentration of the species at the surface of the catalyst.

So now if we observe this carefully, if you 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 measurable quantity here is the reaction rate.

So the reaction rate is the measurable quantity in this expression here and the density, radius, diffusivity are again known quantities. And the reaction rate and the concentration on the surface are all measurable quantities. So once we know these quantities, we know what the Weisz-Prater parameter is.

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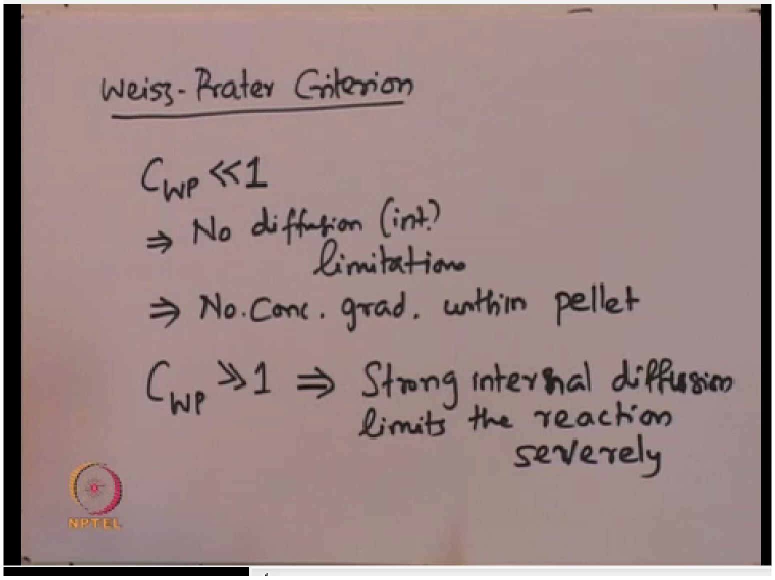

Weisz-Prater Criterion

$C_{WP} \ll 1$

⇒ No diffusion (int.) limitation

⇒ No. Conc. grad. within pellet

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

So the Weisz-Prater condition or the Weisz-Prater criterion is when the parameter CWP 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 is no diffusional limitations, internal diffusion limitations.

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

So when Weisz-Prater criterion C, parameter CWP, 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 known 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 criterion 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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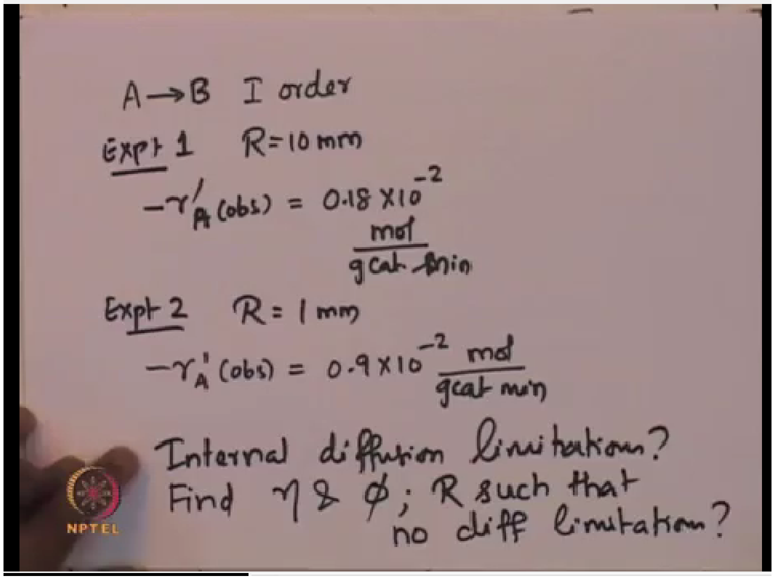

$A \rightarrow B$ I order

Expt 1 $R = 10\ mm$

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

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 us consider a first order reaction. Now an experiment has been performed with different catalysts and let us say that there is experiment 1 in which the catalyst of 10 mm diameter was used to conduct the heterogeneous catalytic reaction and let us assume that it was performed in an appropriate reactor such that there is no external mass transport diffusion limitations and so which means that the surfaces, the concentration of the species at the surface is equal to the concentration of the species in bulk.

And the reaction rate that was observed is about 0.18*10 power -2 mol/gram catalyst per minute, that is the observed reaction rate for when the reaction was conducted using a catalyst pallet of 10 mm diameter. Now suppose the same reaction was conducted under same conditions except that a much smaller pallet was used. So there is another experiment where the pallet that was used is 1 mm in diameter, 1 mm spherical particles.

And the observed reaction rate is 0.9*10 power -2 moles/gram catalyst per minute. So now because the experiments were conducted such that, under appropriate conditions that there is no mass transfer resistance, so here we need to estimate whether it is internal diffusionally controlled or not, whether the internal diffusion, are 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 the radius of the pallet 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, okay. So how do we handle this question? So we have just now learnt the Weisz-Prater parameter.

So Weisz-Prater parameter is basically based on the observed quantities such as the reaction rate, etc. So we can attempt to use the Weisz-Prater criterion in order to find out the effectiveness factor and the Thiele modulus from the observed reaction rate.

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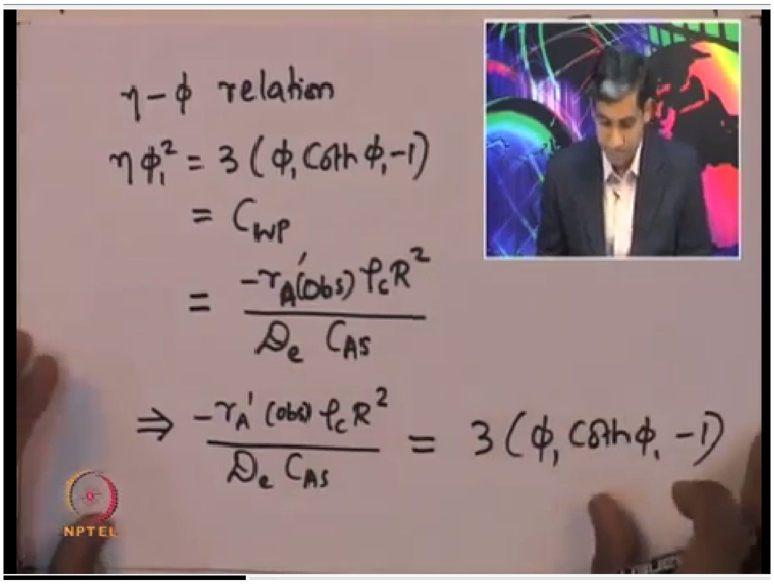

$\eta - \phi$ relation

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

$$= C_{WP}$$

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

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

So the Thiele modulus or effectiveness factor relationship suggests that eta*phi1 square which is the Weisz-Prater parameter, that is equal to 3*phi1 Cot hyperbolic phi1-1. Now, which is equal to the Weisz-Prater parameter CWP and that is also equal to the observed reaction rate*the density of the catalyst*the square of the radius of the particle that is used/the diffusivity*the concentration at the surface because the mass transport limitations are not there.

So let us say that the surface of the catalyst, concentration of the 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 -rA*rho C*R square/diffusivity*CAS, that should be equal to 3*phi1 Cot hyperbolic phi1-1. So that brings relationship between the observed reaction rate at 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 pallet, how is that related to the corresponding Thiele modulus.

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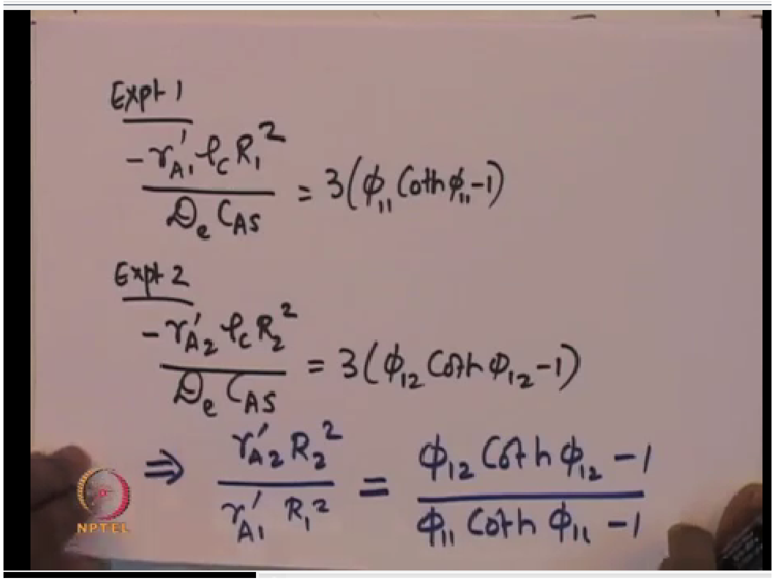

Expt 1

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

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 -rA1 which is the observed reaction rate when the catalyst pallet is, let us say 10 mm, *rho C*R1 square/De*CAS, that should be equal to 3*phi11. Now phi11 corresponds to the Thiele modulus of the first order reaction for the first experimental run and, *Cot hyperbolic phi11-1. And similarly for experiment 2 for the other particle, other radius of the pallet for which the experimental data is available.

So that will be -A2*rho C*R2 square/the diffusivity*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 reactant is same for both R1 and R2. So that is equal to 3*phi12 Cot hyperbolic phi12-1.

So now taking the ratio of these 2 expressions here, we can now find relationship between the observed reaction rate for both runs and the corresponding Thiele modulus. So by taking the ratio, we find that rA2*R2 square/1*R1 square, so that should be equal to phi12 Cot hyperbolic -1/-1. So this relates the information that has been observed experimentally and the corresponding Thiele moduli.

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 ratio of the Thiele moduli, ratio of the function of Thiele moduli. So now let us look at the expression for the Thiele modulus.

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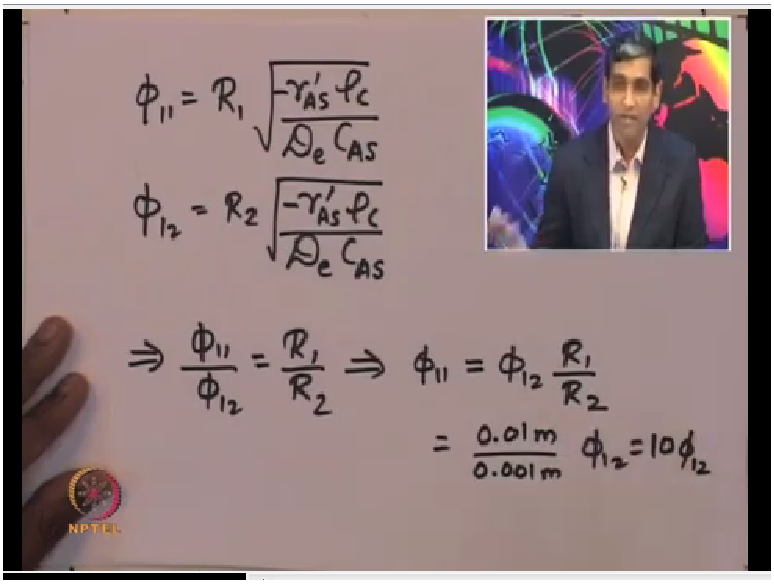

$$\phi_{11} = R_1 \sqrt{\frac{-r'_{AS}\rho_c}{\mathcal{D}_e C_{AS}}}$$

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

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

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

So phi11, which is the Thiele modulus for first order reaction for the first experiment that is given by R1 which is the radius of the pallet*square root of -rAS, which is the reaction as if it were conducted on the surface concentration, *rho C/the diffusivity*the concentration of the species at the surface. And similarly, phi12 will be R2*square root of -rAS*rho C/De*CAS. Now from here, taking the ratio, dividing these 2 equations.

We find that phi11/phi12, that should be equal to R1/R2. So the ratio of the Thiele modulus is given by the ratio of the radius of the pallet itself and from here, one can find out the relationship between the Thiele modulus under different experimental conditions. So that will be phi12*R1/R2. So now plugging in the numbers, we will see that phi11=0.01 m/; *phi12, so that is equal to 10*phi12.

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 2 experimental conditions. So earlier we derived the relationship between the ratio of the reaction rates with the corresponding Thiele modulus. So now we have to, we can plug in the relationship between the Thiele modulus under these 2 experimental conditions into that expression.

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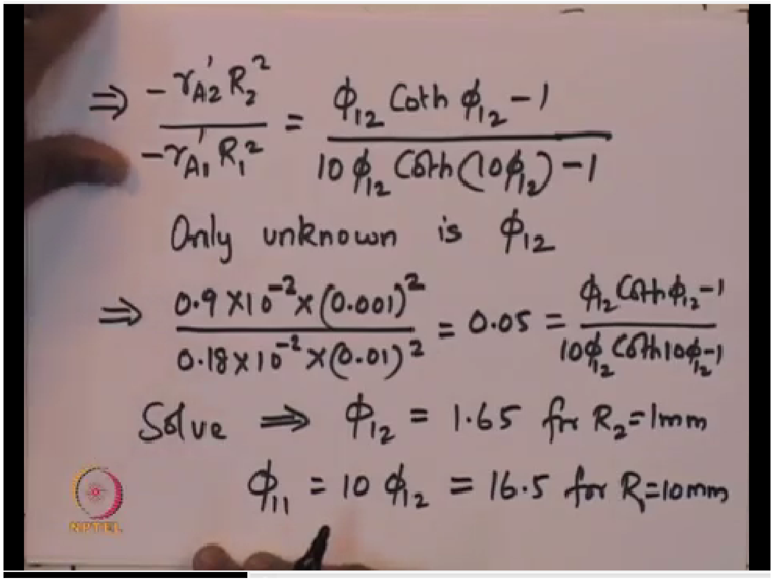

$$\Rightarrow \frac{-r'_{A2} R_2^2}{-r'_{A1} R_1^2} = \frac{\phi_{12}\coth\phi_{12} - 1}{10\phi_{12}\coth(10\phi_{12}) - 1}$$

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 $R = 10\text{mm}$

And that will be -rA2*R2 square/-rA1*R1 square and that should be equal to phi12, which is the Thiele modulus for the second experimental run, *Cot hyperbolic phi12-1/10*phi12*Cot hyperbolic 10*phi12-1. So all the information here is known. The only variable is, only unknown is phi12. So we need to estimate phi12 using all the other information that we already know. So from here, I can plug in the numbers.

So the reaction rate for the second condition will be 0.9*10 power -2*the square of the corresponding radius/0.18*10 power -2*0.01 whole square and that is equal to 0.05 and that will be equal to phi12 Cot hyperbolic phi12-1/10*phi12*Cot hyperbolic 10*phi12-1. So now by solving this expression, we can find out what is the Thiele modulus for the second experimental run.

So solving we can find that phi12 is about 1.65 and this is for R2=1 mm. We also know the relationship between the Thiele modulus of these 2 experimental conditions. So from there, we can find out phi11 which is 10*phi12=16.5 for R1=10 mm. 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 on the Thiele modulus under given experimental conditions are actually related.

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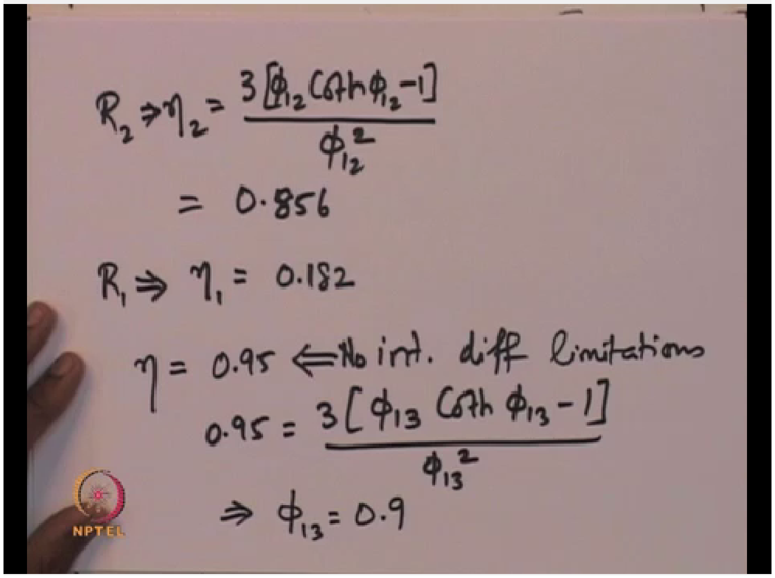

$$R_2 \Rightarrow \eta_2 = \frac{3[\phi_{12} \coth \phi_{12} - 1]}{\phi_{12}^2}$$

$$= 0.856$$

$$R_1 \Rightarrow \eta_1 = 0.182$$

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

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

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

So for R2, which is the second experimental run, eta2=3*phi12*Cot hyperbolic phi12-1/phi12 square and so once we plug in the Thiele modulus data, so we will find out that this effectiveness factor is about 0.856. And then similarly for the first experimental run, the effectiveness factor eta1 will be 0.182. 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 you assume that the effectiveness factor should be 0.95 at which there is no internal diffusion limitations, then we can actually use the relationship between effectiveness factor and the Thiele modulus in order to find out what is the corresponding Thiele modulus. So we know that 0.95=3*phi12 Cot hyperbolic phi13-1/phi13 square.

So by solving this, we can find out that phi13 is about 0.9. So that is the Thiele modulus, that should be the Thiele modulus if the reaction has to be conducted under no internal diffusional limitations. So once we know the Thiele modulus, we also know what is the relationship between the Thiele modulus ratio and the corresponding radii. So we can use that expression in order to find what should be the particle radius in order for the internal diffusion limitations to not exist.

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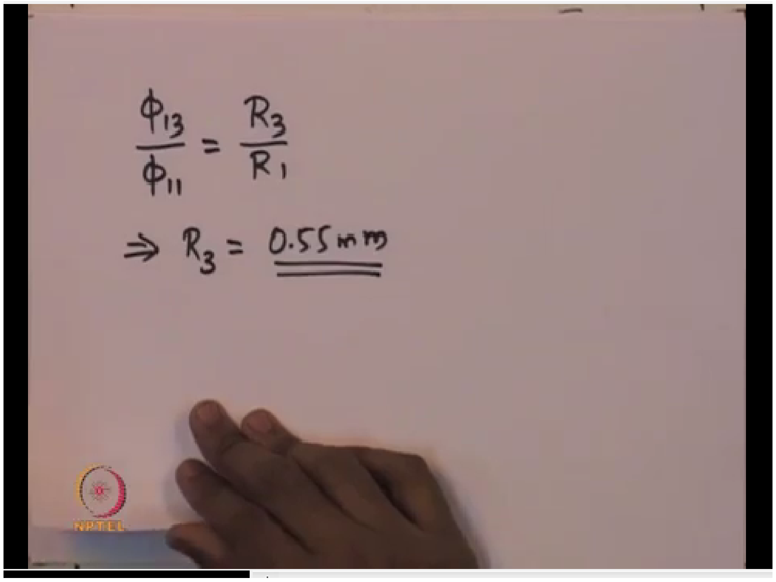

$$\frac{\phi_{13}}{\phi_{11}} = \frac{R_3}{R_1}$$

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

So phi13/phi11, so phi11 is the Thiele modulus corresponding to one of the already conducted experiments and so that will be R3/R1. So from here we can find out that R3 should be equal to about 0.55 mm. The smallest pallet at which the internal diffusion will not limit the reaction is about 0.55 for the given set of experimental conditions. So in this way using some trial experiments, one can actually find out what should be the pellet's 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.