Chemical Reaction Engineering II
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Lecture -16
Implications to rate data interpretation and design – II

Friends, in the last lecture, we looked at Weisz-Prater criterion for deciding from the experimental information whether; the reaction is internal diffusion controlled or not. So, in this lecture we look at what is the reason, why Weisz-Prater scheme works and what are the limitations of this scheme and what is the correction for the same.

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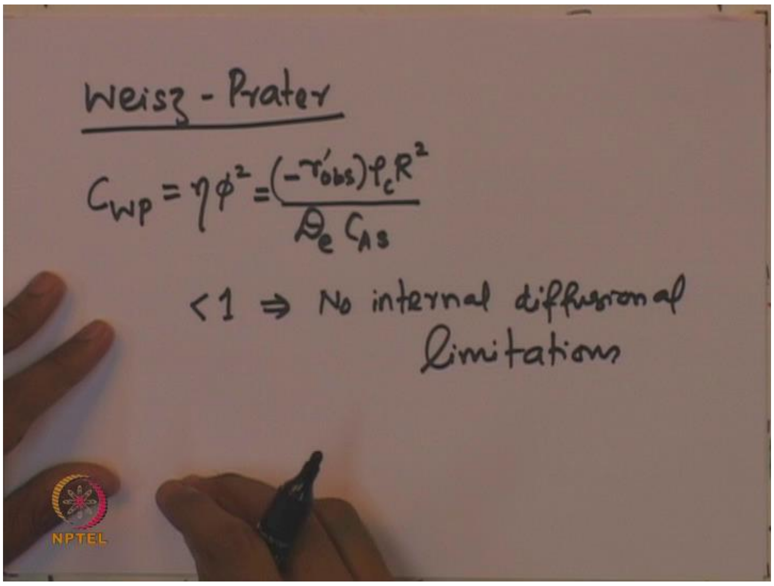

Weisz - Prater

$$C_{WP} = \eta\phi^2 = \frac{(-r'_{obs})\rho_c R^2}{D_e C_{As}}$$

$< 1 \Rightarrow$ No internal diffusional limitations

So, the Weisz-Prater criteria. Weisz-Prater criterion, is basically uses a parameter called C w p, which is equal to the internal effectiveness factor multiplied by the a Thiele modulus; square of phi square and that is equal to the r observed; the observed reaction range multiplied by the density of the catalyst multiplied by the square of the length scale of the pellet that is been used divided by the diffusivity into the corresponding concentration of the species at the surface of the catalyst.

So, if this is less than 1, then this suggests that, there is no internal diffusional limitations. The reaction is not limited by the internal diffusion. So, now, a question is; what is the validity of this criteria when does it work? Does it work for all reactions and all catalytic reactions? So, in order to understand this, let us look at; why the wipe

Weisz-Prater criteria works and why is it being, why is it the correct criteria in order to estimate whether, the diffusion limitations are present. So, in order to establish that, let us look at the classical plot of Thiele modulus versus the internal effectiveness factor eta.

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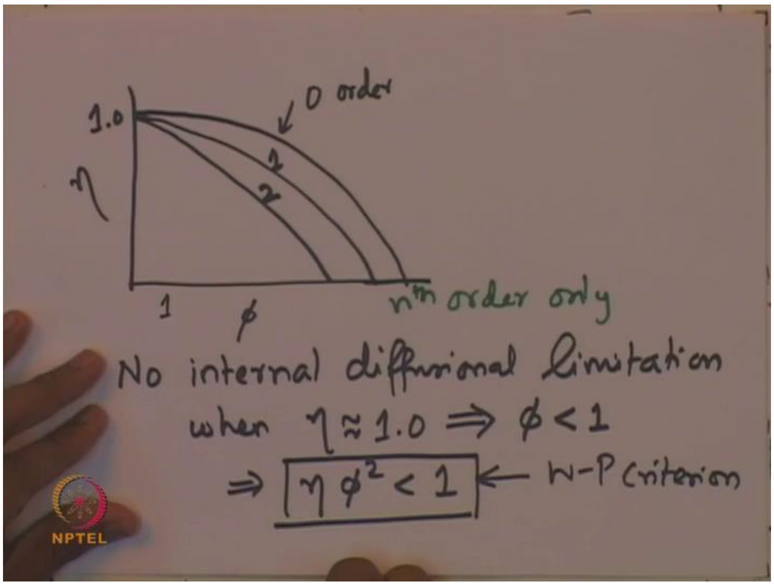

No internal diffusional limitation when $\eta \approx 1.0 \Rightarrow \phi < 1$

$$\Rightarrow \boxed{\eta \phi^2 < 1} \leftarrow \text{W-P Criterion}$$

So, now, if it is a first order reaction, if it is a 0 order reaction, then this is for the 0 order reaction, zeroth order reaction. Now, if it is a first order reaction, the curve looks like this and if it is a second order reaction the curve looks like this and so on. So, this is the first order reaction, this is for the second order reaction and you can now look at other n orders the n’th order reaction.

So, from this graph; 1 can decipher that, there is no internal diffusion limitations, if when; the internal effectiveness factor is approximately equal to 1. So, the effectiveness factor and the here starts at 1. So, its approximately when it is approximately equal to 1, then it means that there is no internal diffusional limitations.

Now from the graph; 1 can easily decipher that, when eta is approximately equal to 1 or slightly less than 1, then the Thiele modulus phi is less than 1. So, therefore, clearly eta times phi square should be less than 1, which is the Weisz-Prater parameter. So, the Weisz-Prater parameter; this is basically the Weisz-Prater criterion. So, therefore, as long as the eta phi relationship behaves the way as it is depicted in this picture, the Weisz-Prater criterion would usually work.

And in fact, the eta versus phi curve, it looks like this only for a typically for an n'th order reaction; any n for n'th order reaction. If it is not an n'th order reaction, for example: if there is adsorption of a species or product inhibition, or if it is a nonisothermal, then the eta versus phi can be different from what is depicted in this picture here. It does not mean that, it will not follow this picture, but if it approximately follows an n'th order reaction, then this is the kind of profile that 1 would get.

Now, if suppose if it is not a simple n'th order reaction, then it is possible that the eta versus phi graph will not look like this. And therefore, this condition of eta phi square less than 1, is not always valid, according to the definition that is given by Weisz-Prater criterion; that is the Weisz-Prater parameter.

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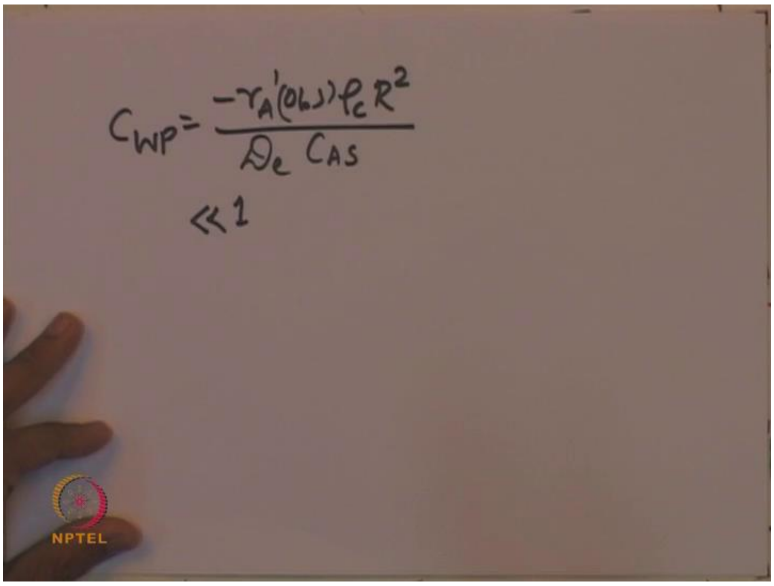

$$C_{WP} = \frac{-r'_A(obs)\,\rho_c R^2}{D_e\, C_{AS}}$$

$$\ll 1$$

The Weisz-Prater parameter C w p equal to minus r a observed reaction rate into the density of the catalyst into square of the length scale divided by the diffusivity into C a s. So, this being less than 1, is not always valid, if the Thiele modulus and the internal effectiveness graph does not look, like the way which is were depicted. Let us look at what happens, if there is a reaction which does not necessarily follow, such a effectiveness factor Thiele modulus relationship.

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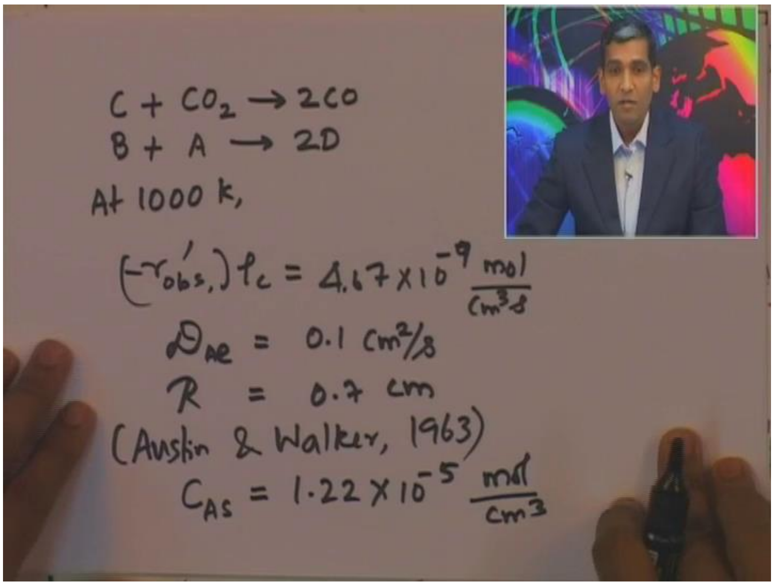

$C + CO_2 \rightarrow 2CO$

$B + A \rightarrow 2D$

At 1000 K,

$(-r'_{obs.})\rho_c = 4.67 \times 10^{-9} \frac{mol}{cm^3 s}$

$\mathcal{D}_{Ae} = 0.1\ cm^2/s$

$R = 0.7\ cm$

(Austin & Walker, 1963)

$C_{As} = 1.22 \times 10^{-5} \frac{mol}{cm^3}$

A 1 particular example is; the reaction of carbon when it reacts with the carbon dioxide it leaves out 2 moles of carbon monoxide. So, suppose I represent this as B plus A giving 2D. So, that is the reaction. So, if I say B species B is carbon and species A is CO2 gas and species D is carbon monoxide.

So, at 1000 Kelvin, which is; where the reaction is conducted, Austin Walker in 1963 measured the rate of reaction rate and other parameters. So, the reaction rate; the observed reaction rate multiplied by the density of the catalyst, was found to be 4.67 into 10 power minus 9 moles per centimeter cube second. So, that was the reaction rate that was observed. And the diffusivity of species A; effective diffusivity of species A is about 0.1 centimeter square per second and the effective radius; radius of the particle pellet that was used is 0.7 centimeters.

So, this information is basically measured by the group of Austin and Walker in 1963. So, the data was measured by these 2 coworkers in 1963. And the surface concentration of the species was measured to be 1.22 into 10 to the power of minus 5 moles per centimeter cube. So, now let us calculate the Weisz-Prater parameter from this expression and then see whether the internal diffusional limitations exist or not. So, if I calculate the Weisz-Prater parameter.

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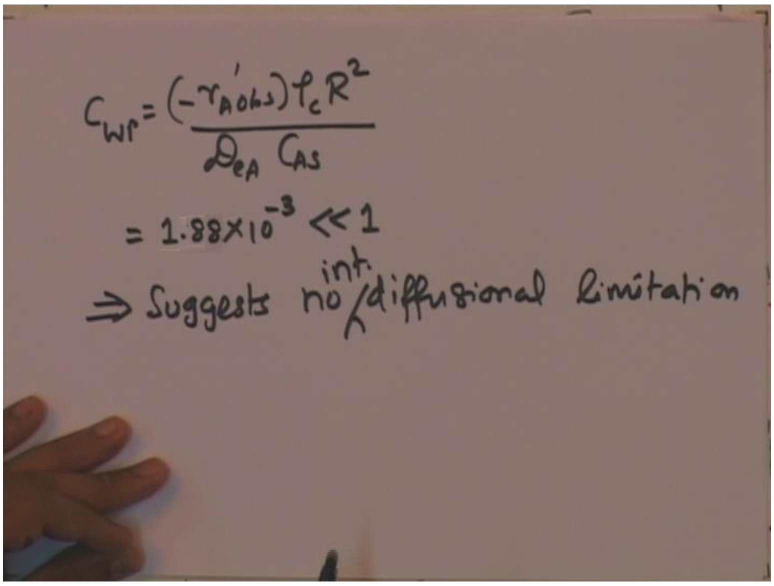

$$C_{WP} = \frac{(-r'_{A\,obs})\rho_c R^2}{D_{eA} C_{AS}}$$

$$= 1.88 \times 10^{-3} \ll 1$$

$\Rightarrow$ Suggests no int. diffusional limitation

So, C w p which is basically the minus r a observed, that is the observed reaction rate multiplied by the density of the catalyst into r square divided by the density, effective diffusivity of the species multiplied by C A S. That turns out to be about 1.88 into 10 power minus 3, which is significantly smaller than 1. Now, this would mean that, this particular reaction does not have a diffusional limitation.

So, this suggests that no diffusional limitation; that means, that the overall reaction is not controlled by the internal diffusional limitations. So, which means that it suggests that there is no internal diffusional limitations for this particular reaction. Carbon and the carbon dioxide heterogeneous reaction; it leads to 2 molecules of carbon monoxide.

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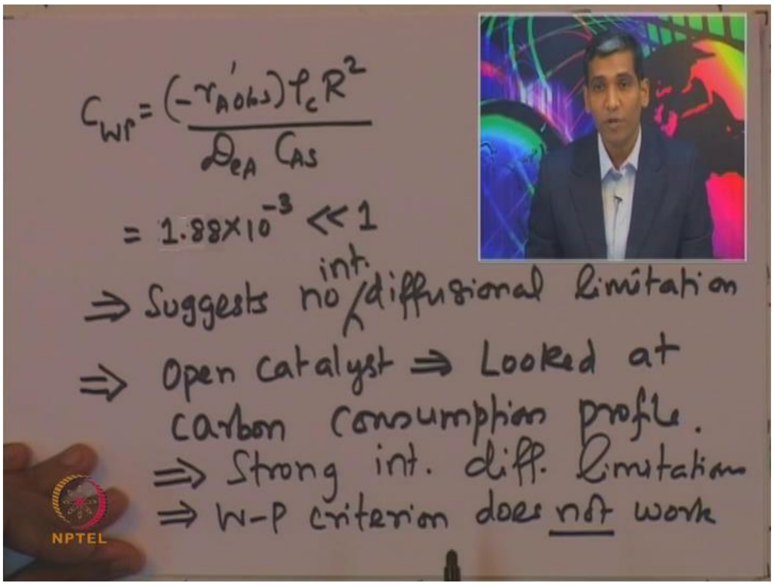

$$C_{WP} = \frac{(-r'_{A\,obs})\,\rho_c R^2}{\mathcal{D}_{eA}\, C_{As}}$$

$$= 1.88\times10^{-3} \ll 1$$

⇒ Suggests no int. diffusional limitation

⇒ Open catalyst ⇒ Looked at carbon consumption profile.

⇒ Strong int. diff. limitation

⇒ W-P criterion does not work

However, after the reaction was conducted, the same researchers, they were actually cut open the, they open the catalyst. They cut open the catalyst and measured looked at the carbon consumption profile. Measured the carbon consumption profile in the catalyst. And once it was measured, it suggested, profile actually suggested that there was strong internal diffusional limitations. It suggested that the reaction was strongly limited by the internal diffusion. And that shows that the Weisz-Prater criteria does not work for this reaction. This reaction; where the carbon reacts with carbon dioxide to form 2 molecules of carbon monoxide. In this particular case, the Weisz-Prater criterion does not work; it does not predict correctly the presence of the internal diffusional limitations.

So, the question is what is the…. So, because it does not predict, 1 needs to find out what is the corrective measure for this and what is the correct criteria, what is the correctly generalized criteria in order to estimate from the experimental observation, whether the external internal diffusional limitations are present or not for a given heterogeneous catalytic reaction.

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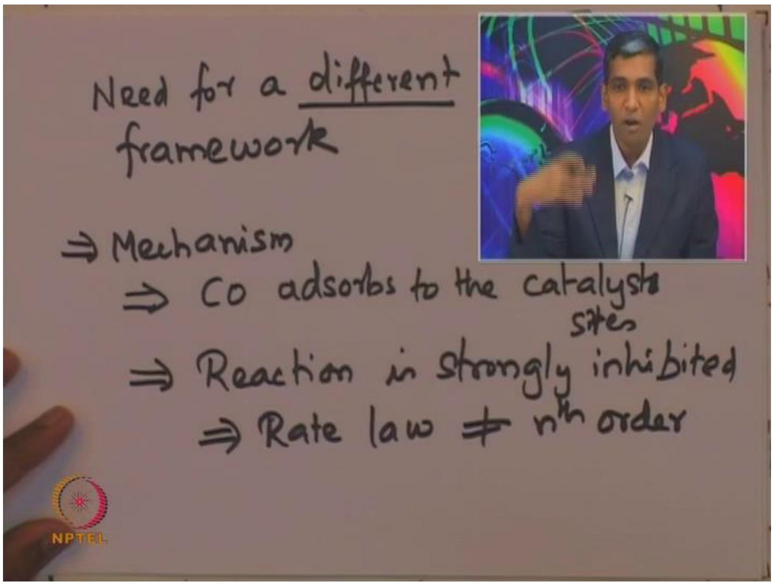

Need for a different framework

⇒ Mechanism

⇒ CO adsorbs to the catalysts sites

⇒ Reaction is strongly inhibited

⇒ Rate law ≠ n^th order

So, clearly there is a need for a different framework. Why do we need a different framework for this reaction? Because, when we look at the mechanism of this particular reaction, we look when you go deep into the mechanism, you try to understand the mechanism of this particular reaction. It was observed that the carbon monoxide, which is a product, it strongly adsorbs onto the catalyst site and then it inhibits the reaction.

So, clearly this mechanism suggests that, the mechanism behind this heterogeneous catalytic reaction, it suggests that the carbon monoxide adsorbs onto the catalyst sites. So, it adsorbs onto the catalyst sites. And therefore, the reaction is strongly inhibited. Which means that, it is not going to follow the classical n'th order reaction, the catalytic reaction is not the… The rate law is not an n'th order reaction, does not have an n'th order dependence on the concentration of the species, because the product is now adsorbing onto the catalyst sites and it is strongly inhibiting the reaction. So, therefore, there is a limitation that is present here. So, now the question is; if I look at the Thiele modulus effectiveness factor graph in general.

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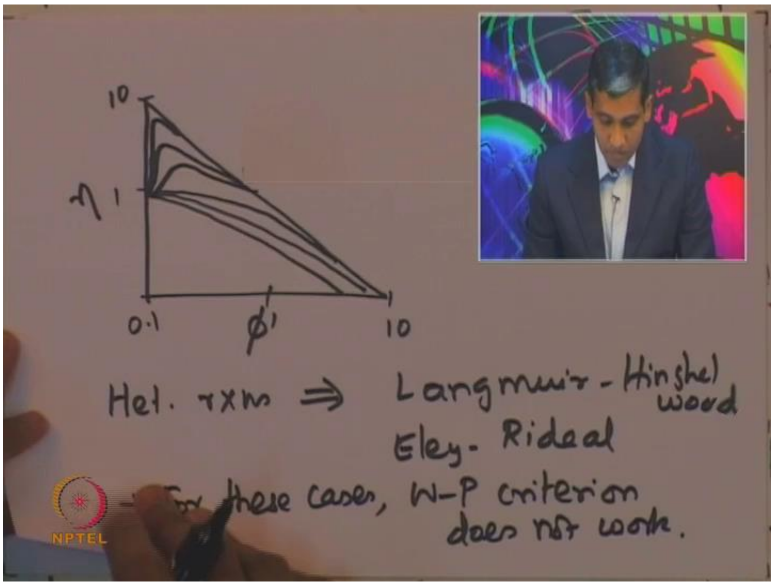

Het. rxn ⇒ Langmuir-Hinshelwood
Eley-Rideal

For these cases, W-P criterion does not work.

And it goes from 0.1 to 10 and this is 1 here. And for an n’th order reaction; first order, second order etcetera, 0’th order, first order, second order; the eta versus phi graph it looks like this. On the other hand, for other types of rate laws, for example, adsorption rate law, Langmuir-Hinshelwood or Ely-Rideal type of mechanisms and for exothermic reactions. The effectiveness Thiele modulus graph can actually look like this.

So, therefore, when eta is equal to 1, when eta is, when the Thiele modulus is very small, it does not necessarily mean that, the effectiveness factor is actually almost equal to 1. So, as a result the Weisz-Prater criterion, which hinges on the fact that; when for a certain type of reactions, the effectiveness factor is almost equal to 1 the Thiele modulus is less than 1. So, that factor does not work for the situations where, the rate law depends upon or rate law mechanism or rate law follows the Langmuir-Hinshelwood type or the Eley-Rideal type, that is, when there is an adsorption; product adsorption or adsorption of the species.

So, heterogeneous reaction several heterogeneous reactions. So, heterogeneous reaction; several heterogeneous reactions, they actually follow the Langmuir-Hinshelwood type kinetics or Eley-Rideal type kinetics, which basically uses the adsorption isotherm, in which is adsorption isotherm is now, incorporated into the rate law. So, therefore, in these cases, the W-P criterion; the Weisz-Prater criterion does now work.

So, now, we need to find out what is the generalized criteria, which works for all types of rate laws. So, the exercise is now to find out what is this generalized criterion.

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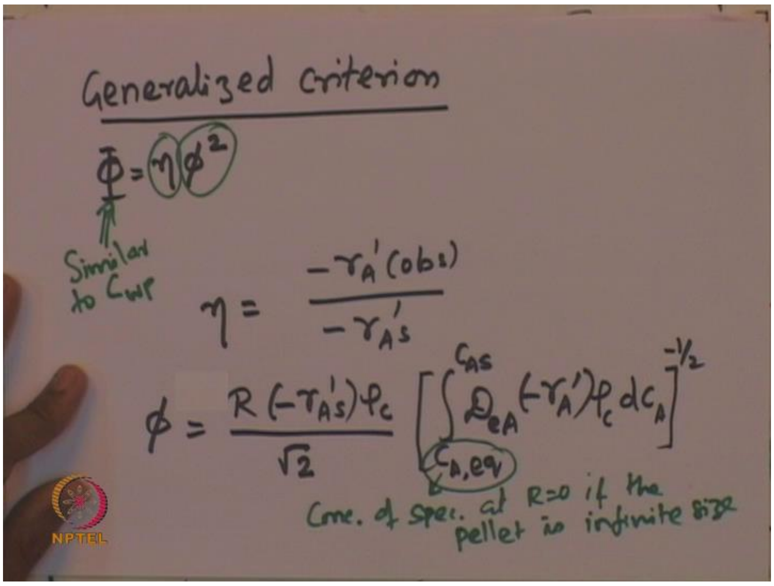

Generalized criterion

$$\Phi = \eta \phi^2$$

Similar to C_{wp}

$$\eta = \frac{-r'_A(obs)}{-r'_{As}}$$

$$\phi = \frac{R(-r'_{As})\rho_c}{\sqrt{2}} \left[\int_{C_{A,eq}}^{C_{As}} D_{eA}(-r'_A)\rho_c \, dC_A \right]^{-1/2}$$

Conc. of spec. at R=0 if the pellet is infinite size

What is this generalized criterion? So, suppose we define Phi as eta into phi square and this is now very similar to that of the Weisz-Prater criterion. This is very similar to C w p that is, the Weisz-Prater parameter. Now the, in order to come up with the generalized criterion, we need to define a generalized, we need to find out what is the generalized effectiveness factor, what is the general definition of the effectiveness factor and what is the generalized definition of the Thiele modulus. So, the generalized definition for the internal effectiveness factor, is basically given by r a prime observed, that is, the observed reaction rate divided by the corresponding reaction rate on the at the surface of the catalyst.

On the other hand, the generalized Thiele modulus can actually be is defined as; the length scale, whatever is the radius of the pellet effective radius of the pellet into minus r A s that is, the reaction rate at the surface concentration multiplied by the density of the catalyst divided by square root of 2 into integral the equilibrium concentration of the species at the center of the catalyst if, the catalyst was of infinite size, integral from C A to C A s, where C A s is the concentration of the surface into the effective diffusivity of the species D e A into minus r A into rho c into D c A. That to the power of minus 1 by 2.

So, that is the generalized Thiele modulus. And it should be noted here that C a is the concentration of species at r equal to 0. Either it is at the center of the catalyst pellet if, the pellet is of infinite size. Now this quantity C A equilibrium is actually going to be 0 if, it is a nonreversible reaction that is, it is a forward or a back 1 of 1 side reaction. Then the C A equilibrium here, would actually take a value of 0.

So, if it is a an nonreversible reaction, then because it is an infinite size pellet, then the amount of time that it takes for the species to actually diffuse into the pellet and go all the way to the center, will be infinite time. And therefore, the concentration of the species at the center of the pellet can be assumed to be 0 if, it is a nonreversible reaction. Now, if it is a reversible reaction, then it will be an equilibrium concentration.

So, now if I look at this expression, if I plug in the generalized effectiveness factor in the generalized Thiele modulus expression into this modified.

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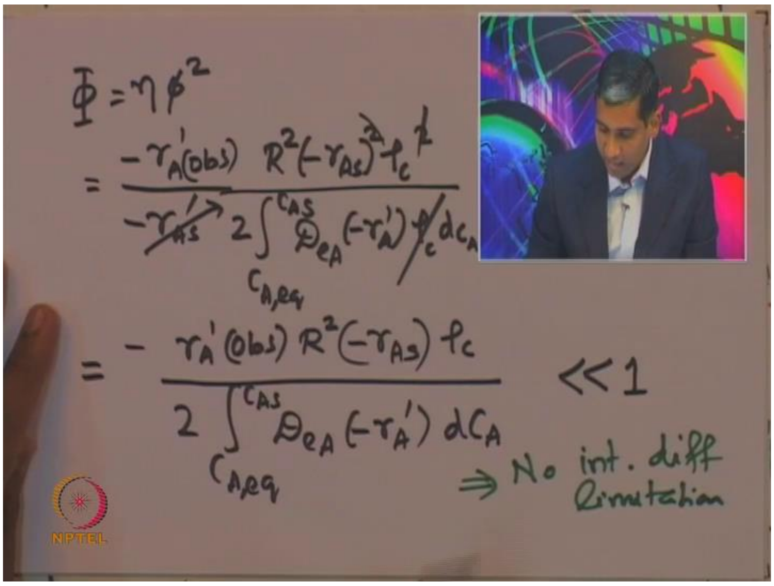

$$\Phi = \eta \phi^2$$

$$= \frac{-r'_{A(obs)} \, R^2 (-r_{AS})^{\cancel{2}} \rho_c^{\cancel{2}}}{\cancel{-r'_{AS}} \, 2\int_{C_{A,eq}}^{C_{AS}} D_{eA} (-r'_A) \cancel{\rho_c} \, dC_A}$$

$$= -\frac{r'_A(obs) \, R^2 (-r_{AS}) \, \rho_c}{2\int_{C_{Aeq}}^{C_{AS}} D_{eA} (-r'_A) \, dC_A} \ll 1$$

$\Rightarrow$ No int. diff limitation

Or new generalized criterion, will be eta phi square and that should be equal to minus r A that is, the observed rate divided by at the surface, at the rate at the surface concentration multiplied by R square into minus r A s square into rho c square divided by 2 times integral C A equilibrium, that is, the equilibrium concentration at the center into C A s into the effective diffusivity of that species into minus r A into rho c into d C into d C A.

So, that is the expression for the modified or generalized criterion for deciding, whether the internal diffusion is going to exist or not internal diffusional limitation is going to exist or not. So, suppose if this quantity so now, we can rewrite this as by cancelling some of these terms.

So, we can cancel this term with this square and this if, assume that the cat density of the catalyst does not change, and then we can cancel of these. And so we can rewrite this as the observed rate into R square, that is, the square of the length scale, that is, the rate evaluated at the surface concentration multiplied by the density divided by 2 times integral C A equilibrium, that is, the equilibrium concentration of the species at the center of the pellet, if the pellet is infinitely large. And the integral goes from the equilibrium concentration to the, at r equal to 0 to the surface concentration multiplied by the corresponding diffusivity into the reaction rate into d C A. So, now, the modified criterion is that if this quantity phi is less than 1, then there is no internal diffusional limitations.

In fact, this quantity here; this generalized modulus here, if we plug in the rate expression for an n’th order reaction and actually reduces to the Weisz-Prater criterion. So, therefore, this is a generalized modeled, which also includes the Weisz-Prater criterion of desire or Weisz-Prater criterion which is used for deciding whether the internal diffusional limitation is present or absent, based on the experimental data. So, now let us look at the specific example we had initiated today.

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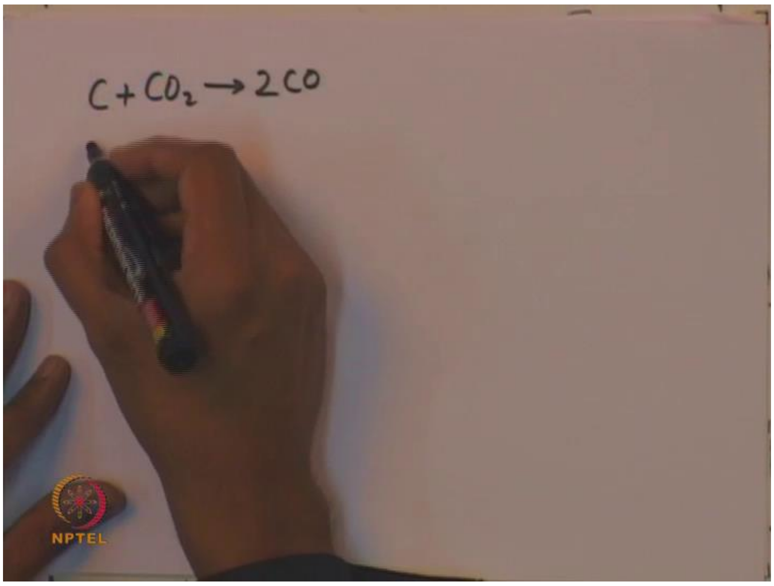

$C + CO_2 \rightarrow 2CO$

That is the reaction of C plus CO2 giving 2 times CO. So, let us look at what happens what is the act, whether at the diffusional limitation is actually predicted by the modified or generalized criterion. So, remember that the Weisz-Prater criterion, did not predict the presence of the internal diffusional limitations. However, by cutting open the catalyst, the experimental evidence, by looking at the profile of the carbon contents suggest that, the diffusional limitations was strongly present and it strongly inhibited the reaction. So, let us now plug in that plug in the rate law into the generalized modulus and look at whether the internal diffusional limitations, was present or absent.

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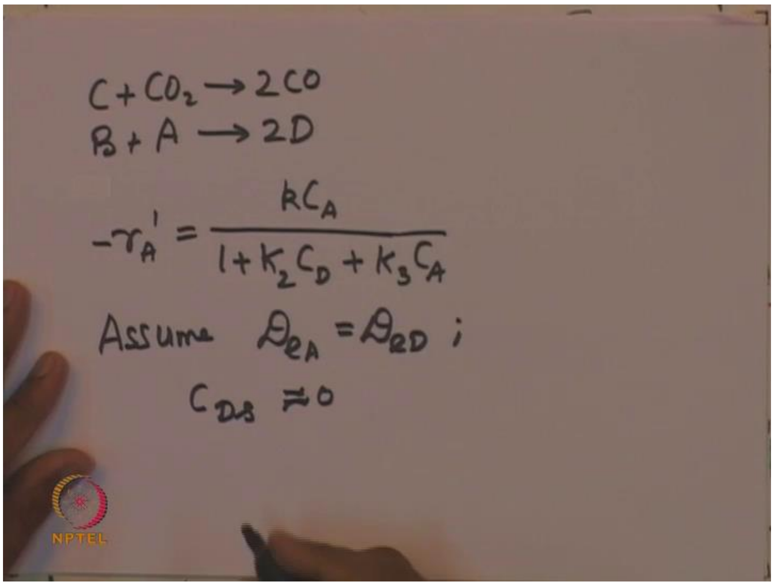

$C + CO_2 \rightarrow 2CO$

$B + A \rightarrow 2D$

$$-r_A' = \frac{kC_A}{1 + K_2 C_D + K_3 C_A}$$

Assume $\mathcal{D}_{eA} = \mathcal{D}_{eD}$;

$C_{DS} \simeq 0$

So, the reaction scheme is B plus A giving 2 times D. So, B is the species B is the carbon and A is CO2 and D is the product carbon monoxide. So, the reaction rate law, by looking at the detailed mechanisms that is involved in the heterogeneous catalytic reaction, has been found to be k into C A divided by 1 plus K 2 into C D that is the adsorption constant for adsorption equilibrium constant for carbon monoxide plus K 3 into C A; this is the adsorption constant correspondingly for the carbon dioxide.

So, if we assume that the diffusivity; effective diffusivity of species A is equal to the effective diffusivity of species D and by assuming that it is a equimolar counter diffusion system. And we also assume that, the concentration of the product species which is carbon monoxide at the surface; is approximately 0. Now this is valid because, the experiment suggests that, there is a strong adsorption of the product onto the catalyst site. So, therefore, we can expect that the amount of carbon monoxide, which is actually left the catalyst and the amount that is present n the surface is negligible.

So, therefore, we can assume that the concentration of D s on the surface is approximately equal to 0.

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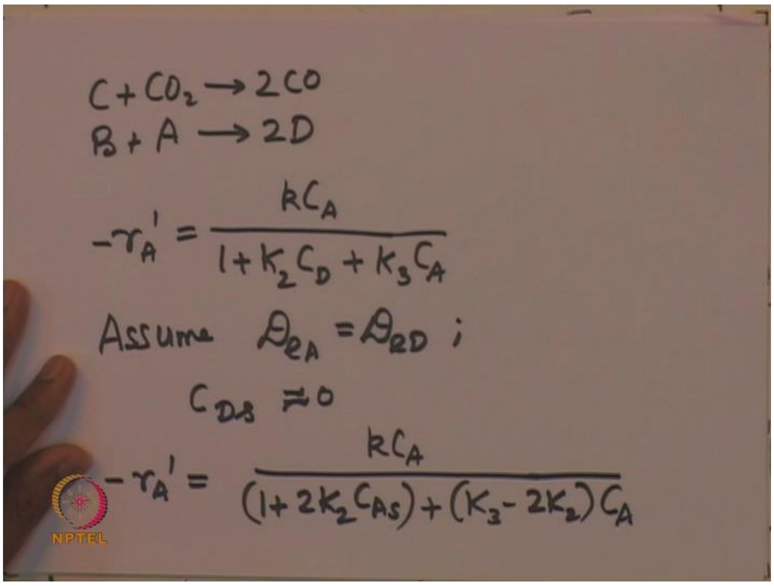

$C + CO_2 \rightarrow 2CO$

$B + A \rightarrow 2D$

$$-r_A' = \frac{kC_A}{1 + K_2 C_D + K_3 C_A}$$

Assume $D_{eA} = D_{eD}$;

$C_{Ds} \approx 0$

$$-r_A' = \frac{kC_A}{(1 + 2K_2 C_{As}) + (K_3 - 2K_2) C_A}$$

So, therefore, using these assumptions, the rate law can now be rewritten as k into C A divided by 1 plus 2 K 2 C A s. That is the concentration of carbon dioxide at the surface of the catalyst. Plus K 3 which is the equilibrium constant for the adsorption of CO2 minus 2 times K 2, that is the equilibrium constant for adsorption of carbon monoxide product carbon monoxide on to the surface of the catalyst multiplied by the concentration of the species C A.

So, now integrating the expression for the generalized modulus, we will find that Phi which is the generalized modulus generalized criterion.

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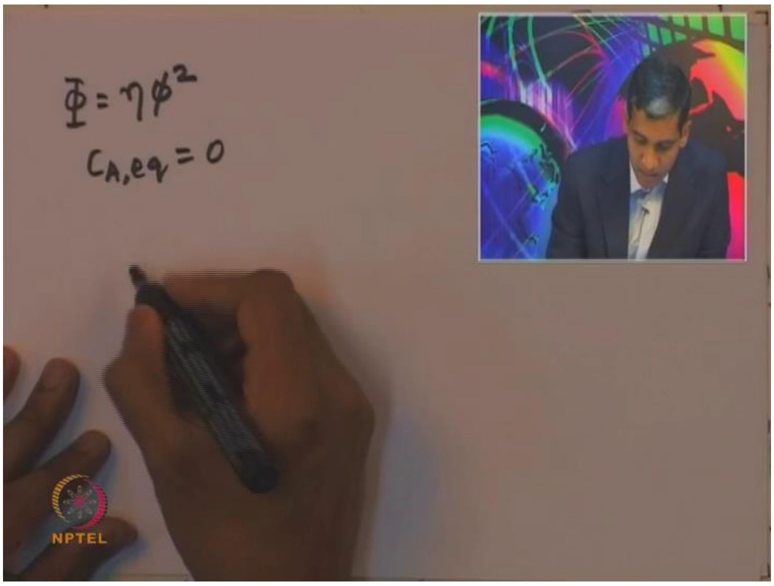

$$\Phi = \eta \phi^2$$

$$C_{A,eq} = 0$$

That is equal to internal effectiveness factor multiplied by phi square. Now because its it is not a reversible reaction, we can assume that C A equilibrium is equal to equilibrium is equal to 0. So, we assume that C A equilibrium, that is the concentration of the species that is, carbon dioxide at the center of the pellet, if the pellet was infinitely long if that is a approximately equal to 0 because, it is a nonreversible reaction.

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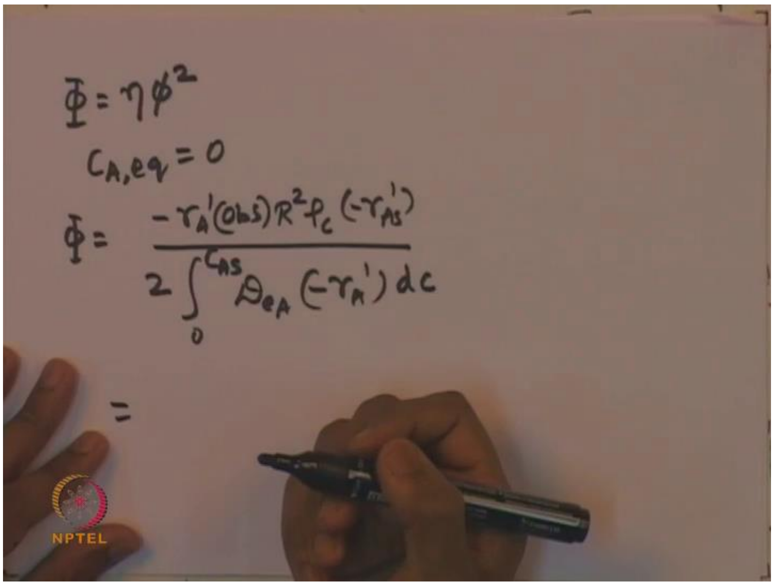

$$\Phi = \eta \phi^2$$

$$C_{A,eq} = 0$$

$$\Phi = \frac{-r_A'(obs) R^2 \rho_c (-r_{AS}')}{2\int_0^{C_{AS}} D_{eA} (-r_A') \, dc}$$

$$=$$

And therefore, phi is equal to minus r a prime the observed reaction rate multiplied by R square into rho c evaluated at the surface divided by 2 times integral 0 to C A s that is the integral into the diffusivity of the species D e A into minus r A prime into d c. So, now plug in we can plug in the rate expression here. Remember that the rate expression is given by the k times C A divided by 1 plus 2 times K 3 into K 2 into C A plus K 3 minus 2 K 2 into C A. So, the first 1 is the product of 1 plus 2 K 3.

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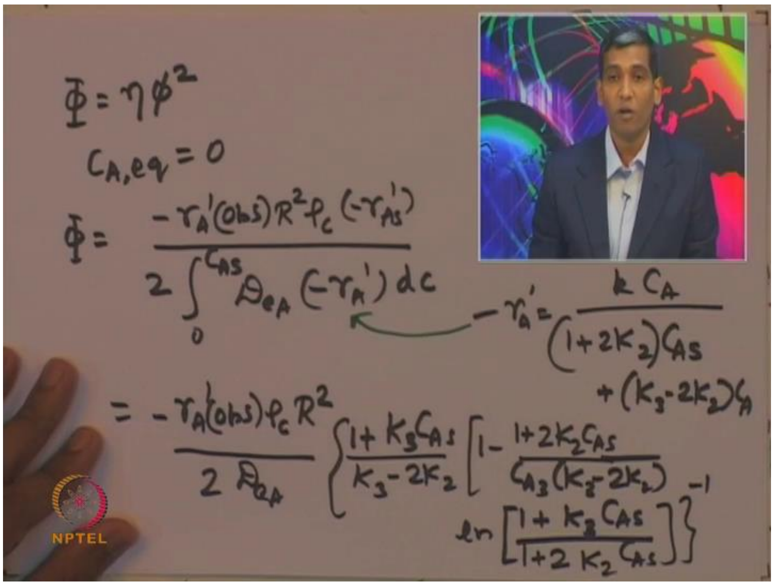

$$\Phi = \eta \phi^2$$

$$C_{A,eq} = 0$$

$$\Phi = \frac{-r_A'(obs) R^2 \rho_c (-r_{AS}')}{2\int_0^{C_{AS}} D_{eA} (-r_A') \, dc}$$

$$-r_A' = \frac{k C_A}{(1+2K_2)C_{AS} + (K_3-2K_2)C_A}$$

$$= \frac{-r_A'(obs) \rho_c R^2}{2 D_{eA}} \left\{ \frac{1+K_3 C_{AS}}{K_3 - 2K_2} \left[1 - \frac{1+2K_2 C_{AS}}{C_{AS}(K_3-2K_2)} \right.^{-1} \left. \ln\left[\frac{1+K_3 C_{AS}}{1+2K_2 C_{AS}}\right] \right] \right\}$$

So, the r A is given by minus r A prime is given by k into C A divided by 1 plus 2 K 2 1 plus 2 K 2 into C A s plus K 3 minus 2 K 2 into C A. So, that is the reaction rate. So, now, if we can that is the rate law for the catalytic reaction. Now, plug in this rate law. So, we can plus in this rate law into this expression here and then we can integrate the expression. So, performing the integration, it turns out that phi is equal to observed into the density of the catalyst multiplied by R square divided by 2 times the corresponding effective diffusivity D e A into 1 plus K 3 C A s divided by K 3 minus 2 K 2 into 1 minus 1 plus 2 K 2 C A s divided by C A 3 into K 3 minus 2 K 2 multiplied by logarithm of 1 plus K 3 C A s divided by 1 plus 2 K 2 C A s inverse of this.

So, that is the expression for the modified generalized criterion phi that is equal to eta internal effectiveness factor and multiplied by the corresponding Thiele modulus multiplied by phi square.

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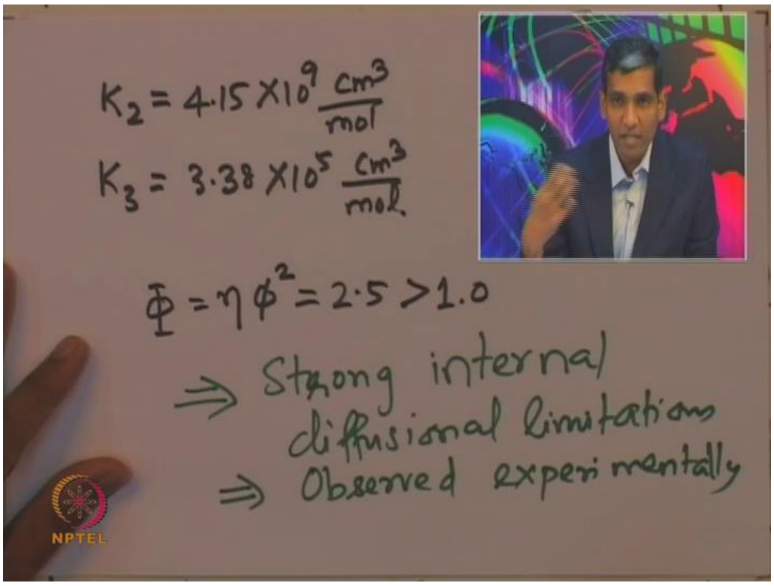

$K_2 = 4.15 \times 10^9 \frac{cm^3}{mol}$

$K_3 = 3.38 \times 10^5 \frac{cm^3}{mol}$

$\Phi = \eta \phi^2 = 2.5 > 1.0$

$\Rightarrow$ Strong internal diffusional limitations

$\Rightarrow$ Observed experimentally

So, now the same experimental group Austin and Walkers group; they have also while performing these experiments they estimated that, K 2 which is the adsorption constant for carbon monoxide is given by 4.15 into 10 to the power of 9 centimeter cube per mole. Similarly K 3 was also estimated as 3.38 into 10 to the power of 5 centimeter cube per mole. So, plugging in these numbers, we can find that the generalized phi which is equal to eta times phi square; which is the parameter in the generalized criterion; that should be equal to 2.5 which is certainly greater than 1.

So, clearly the generalized model generalized criterion; suggest that there is strong internal diffusional limitations. In fact, that is what was observed experimentally. So, that was what; was the experimental observation as well. So, therefore, in order to find out whether there is internal diffusional limitation or not, depending upon what is the nature of the rate law, a simple Weisz-Prater criterion can be used if it is a simple n'th order reaction.

But, if it is a the rate law is not as simple as that, then 1 has to use these generalized criterion phi, which is given by earlier expression that we just derived, where 1 needs to find out what is integrate the expression of the diffusivity; multiplied by the rate going from the concentration of the species at the center of the pellet if it is infinitely long and all the way up to the concentration of the species at the surface of the catalyst.

So, now let us look at; what if there is network of first order reactions. So, this is we looked at what is the experimental criteria and what is the Thiele modulus and effectiveness factor and what is their relationship and how to use that information in order to find out, whether there is internal diffusional limitations or not for a single reaction.

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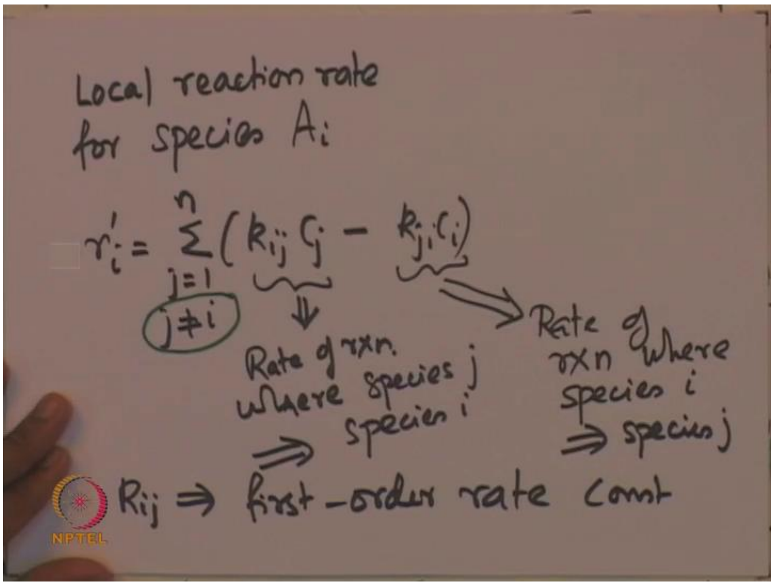

Local reaction rate for species A_i

$$r_i' = \sum_{\substack{j=1\\ \boxed{j\neq i}}}^{n} \left(\underbrace{k_{ij} C_j}_{\Downarrow} - \underbrace{k_{ji} C_i}_{\Rightarrow} \right)$$

Rate of rxn where species j ⇒ species i

Rate of rxn where species i ⇒ species j

k_{ij} ⇒ first-order rate const

Suppose, if there is network of first order reactions, then can we develop is there a general framework in order to find out what is the effectiveness factor and what is the Thiele modulus for each of these first order reactions. And it is very useful in turn in practice because, the diffusional limitations of 1 species can now strongly affect the selectivity of the desired product.

So, therefore, it is important to understand; what is the Thiele modulus of each of these species and the corresponding effectiveness factor. So, let us now look at what is the general framework.

So, this was actually done by Bischoff, in 1967. So, now, suppose if the first set of network of first order reactions is carried out in a porous catalyst, where all the species which are reactants, they diffuse in to the catalyst. And moment they diffuse in to the catalyst, the reaction happens at, some of the species they get adsorbed onto the surface of the catalyst sites and then the reaction happens on the catalyst site. And moment the reaction is completed, the product actually desorbs if it is in the, if it is still adsorbed onto the active sites. Then it desorbs of from the surface and the product leaves the catalyst.

Now it may be that, some of the species directly go into the gas stream and so they will leave the catalyst without the desorption step which may be present.

So, therefore, suppose if I assume that, A i are the end species which is participating in this network of first order reactions. So, A i for all i going from 1 to n. So, there are n species which are present and end species which is participating in this network of first order reactions. Now if c j for all j going from 1 to n is the concentration of the species j if c j is the concentration of species j for all values going from j equal to 1 to n.

So, now the local rate; the local rate for species A i, because it is a network of first order reactions. So, the local reaction rate for species A i is given by r i which is the rate r i. That will be sum j equal to 1 to n and j not equal to i k i j into c j minus k j i into c i. Now k i j, so this term here corresponds to the rate of reaction, where species j is converted to species i. So, basically here the reactant is species j and the product is species i. Now, the second term here is this corresponds to the rate of reaction, where species i leads to formation of species j. Species i acts as a reactant and leads to formation of species j.

So, that is the reaction rate. So, this is the rate of reaction, where species i leads to formation of species j. And the first term corresponds to the rate of reaction, where the species j is consumed and species i is the product that is formed.

So, now, if I assume that all k i j, they are all first order rate constants and they have units of time inverse. And it is important to note that there cannot be a situation where the species j is converted to itself; that is why this summation does not include, this summation should not include the i'th species. So, therefore, it is represented as j not equal to i. That is this summation is for n minus 1 species with the j equal to i is not included in this summation. So, now if we assume that the diffusivity of each of this species is D i.

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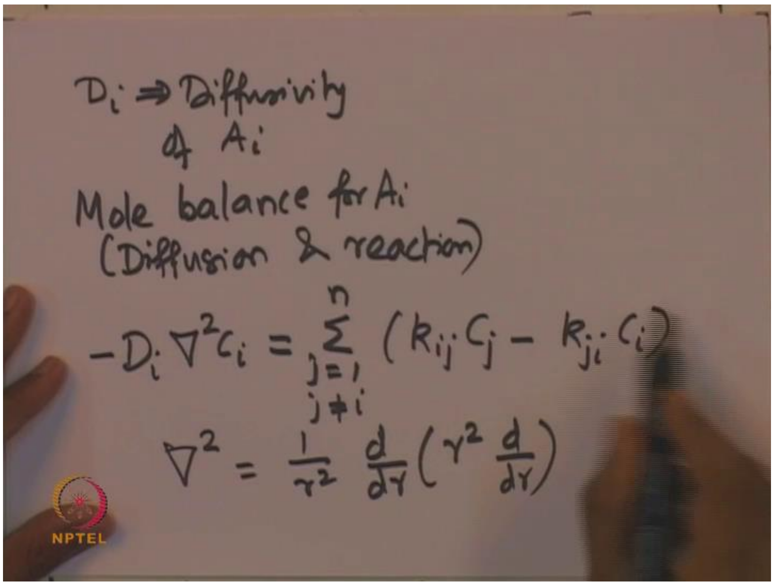

$D_i \Rightarrow$ Diffusivity of A_i

Mole balance for A_i

(Diffusion & reaction)

$$-D_i \nabla^2 C_i = \sum_{\substack{j=1 \\ j \neq i}}^{n} \left(k_{ij} C_j - k_{ji} C_i\right)$$

$$\nabla^2 = \frac{1}{r^2} \frac{d}{dr}\left(r^2 \frac{d}{dr}\right)$$

So, if D i is the diffusivity of A i; D i is the diffusivity of species A i, then 1 can write a mole balance for species A i. So, 1 can write a mole balance; that incorporates diffusion and reaction. Mole balance for A i incorporating diffusion and reaction. So, the mole balance will be minus D i into del square C i. So, this is the Laplacian in particular coordinate system, whichever coordinates in which the reaction is; whichever coordinates the pellet is actually designed or the geometry of the pellet.

And that should be equal to 1 to n j not equal to i k i j C j minus k j i C i. Now, del square suppose, if it is spherical coordinates if it is a spherical catalyst, then del square will be 1 by r square into d by d r into r square d by d r. So, that is the Laplacian in spherical coordinates if the catalyst were to be spherical particle. And remember that, the first term here corresponds to the species reactant being j and the product which is formed is species i. And the second term corresponds to the reactant being species i which is being consumed in order to form a product j.

So, that is the nomenclature that will be used for demonstrating the Thiele modulus and effectiveness factor for network of first order reactions. Now, this mole balance is valid for each and every species i for all n species and so 1 can write this in a vectorial form.

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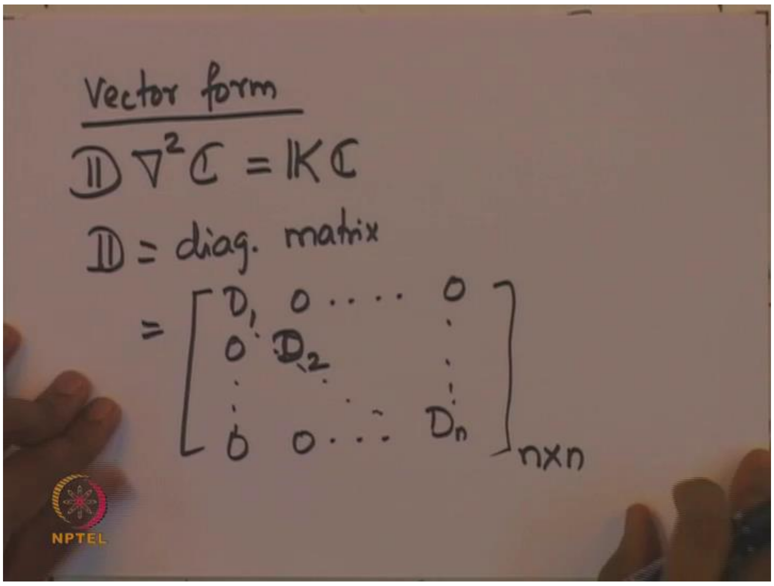

Vector form

$$\mathbb{D}\nabla^2\mathbb{C} = \mathbb{K}\mathbb{C}$$

$\mathbb{D}$ = diag. matrix

$$= \begin{bmatrix} D_1 & 0 & \cdots & 0 \\ 0 & D_2 & & \vdots \\ \vdots & & \ddots & \vdots \\ 0 & 0 & \cdots & D_n \end{bmatrix}_{n\times n}$$

In the vector form, this can be written as the diffusivity D multiplied by the Laplacian diffusivity matrix D multiplied by Laplacian of the concentration vector C; that should be equal to the rate constant matrix K multiplied by the concentration vector C. So, now, the diffusivity matrix; is essentially a diagonal matrix, it is a diagonal matrix and that looks like D 1 D n D 2. So, it is an n cross n matrix, where the diagonal elements are the diffusivity of each of the molecular n molecular species. Now, similarly the concentration c the concentration vector can be written.

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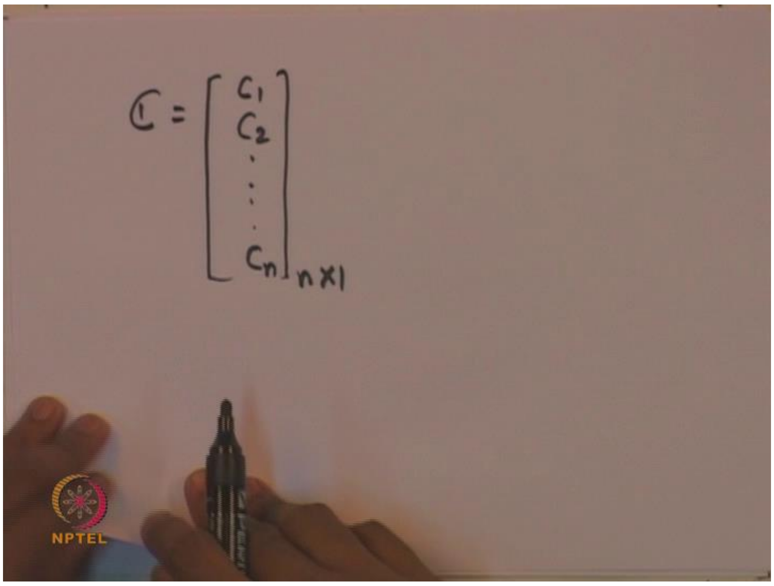

$$\mathbb{C} = \begin{bmatrix} C_1 \\ C_2 \\ \vdots \\ C_n \end{bmatrix}_{n \times 1}$$

The concentration vector C is essentially a vector of concentration C 1 C 2 etcetera upto C n. So, that is a n cross 1 vector; so n rows and 1 column. So, n cross 1 vector, where containing the concentration of this n species, which is actually participating in the network of first order reactions. Then, 1 can look at the rate constant matrix. So, the rate constant matrix is essentially looks like this.

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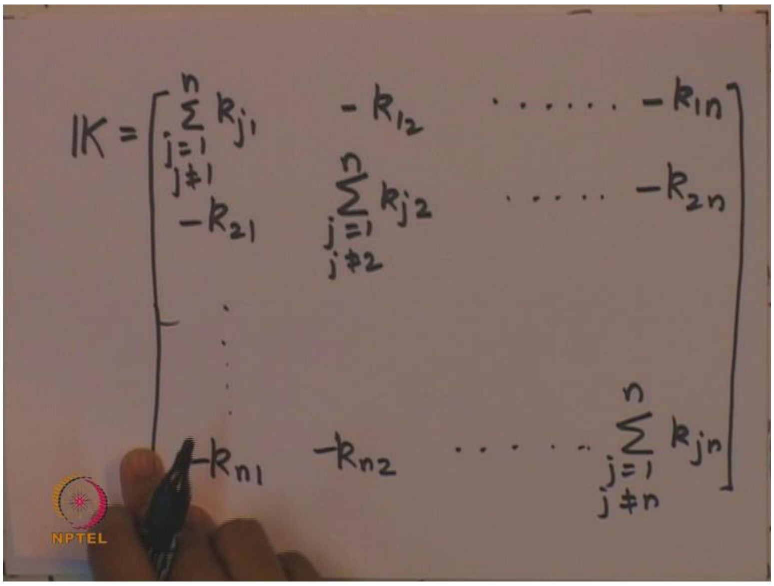

$$\mathbb{K} = \begin{bmatrix} \sum\limits_{\substack{j=1 \\ j \neq 1}}^{n} k_{j1} & -k_{12} & \cdots\cdots & -k_{1n} \\ -k_{21} & \sum\limits_{\substack{j=1 \\ j \neq 2}}^{n} k_{j2} & \cdots\cdots & -k_{2n} \\ \vdots & & & \\ -k_{n1} & -k_{n2} & \cdots\cdots & \sum\limits_{\substack{j=1 \\ j \neq n}}^{n} k_{jn} \end{bmatrix}$$

So, where K is rate constant matrix and that is given by sum j equal to 1 to n k j 1, where j is not equal to 1 minus k 1 2 all the way upto minus k 1 n. And the second term will be k 2 1, this will be sum j equal to 1 to n k j 2, where j is not equal to 2 minus k 2 n. And similarly we can fill this matrix and that will be minus k n 1 minus k n 2 and that will be sum j equal to 1 to n j is not equal to n k j n. So, that is the rate constant matrix.

So, this contains all the information about the rate constants for first order rate constants, for all the reactions which is involved in the network that is being considered. So, now 1 can actually find out. So, because of the presence of diffusion, because of the diffusional limitations; the observed kinetics based on the observed reaction rate, can be different from the; what is the actual true kinetics. So, the kinetics is falsified because of the presence of the diffusional limitations. And that can actually be expressed in terms of vectorial form for the network of first order reactions.

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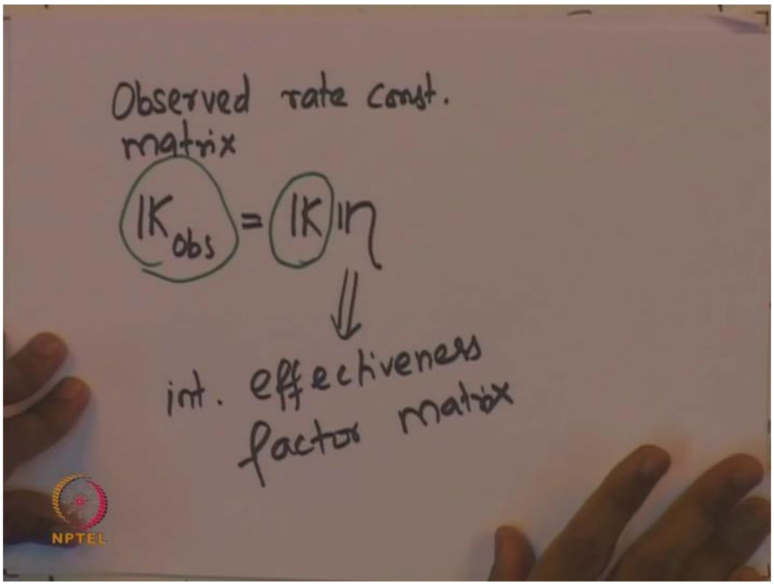

And that is given by this is observed reaction rate constant matrix. Observed rate constant matrix is given by; suppose if K observed is the observed rate constant matrix. So, that should be equal to the true rate constant matrix which is what we just wrote in the in the last slide and multiplied by the corresponding effectiveness factor matrix. So, this is the internal effectiveness factor matrix. In the presence of the internal diffusion, the reaction rate that is observed is actually falsified and the observed reaction rate which is given by this matrix which contain; it is an n cross n matrix containing all the reaction kinetics rate constants and that is given by the true rate constants multiplied by the corresponding effectiveness factor matrix.

So, what is this effectiveness factor vector? So, it can defined as the if we solve the equations and find out what is the effectiveness factor.

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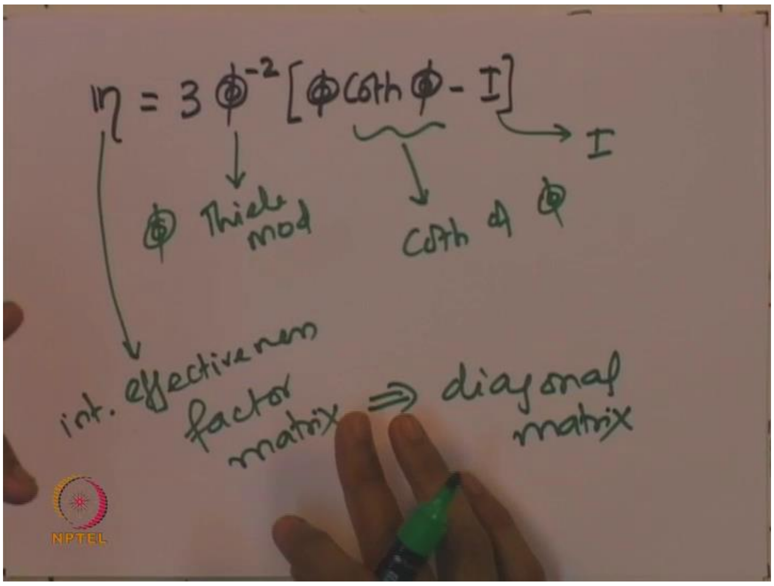

So, the effective factor matrix is given by 3…. That is the matrix of Thiele modulus; it is the square of the inverse, inverse of the square of the matrix of Thiele modulus multiplied by matrix of Thiele moduli into cot hyperbolic of the; it is a matrix of cot hyperbolic minus the identity matrix. So, this is the Thiele modulus. So, phi is the Thiele modulus matrix and this is the cot hyperbolic of the Thiele modulus matrix.

So, that is the matrix cot hyperbolic and it is a diagonal matrix. And the I is the identity matrix and eta is the effectiveness factor matrix, theta is the internal effectiveness factor matrix and this is essentially a diagonal matrix. And this is diagonal because, the Thiele modulus matrix turns out to be a diagonal matrix and the cot hyperbolic function of the diagonal matrix also is a diagonal matrix. And therefore, the effectiveness factor matrix is also a diagonal matrix, consisting of the individual effectiveness factor of each of these network of reactions.

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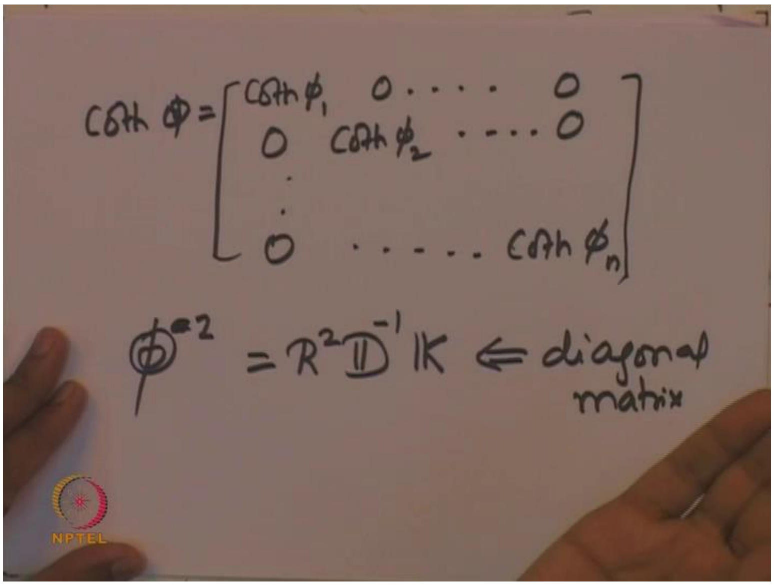

$$\coth \Phi = \begin{bmatrix} \coth\phi_1 & 0 & \cdots & 0 \\ 0 & \coth\phi_2 & \cdots & 0 \\ \vdots & & & \\ 0 & \cdots & & \coth\phi_n \end{bmatrix}$$

$$\Phi^{2} = R^2 \mathbb{D}^{-1} \mathbb{K} \Leftarrow \text{diagonal matrix}$$

So, now, the cot hyperbolic of the Thiele modulus matrix that is matrix is given by it is a diagonal matrix it is the cot hyperbolic of phi 1 0 cot hyperbolic of phi 2 etcetera, cot hyperbolic of phi n. So, that is a diagonal consisting of the cot hyperbolic each of the Thiele modulus corresponding to each of the species. And the overall Thiele modulus matrix, which is again a diagonal matrix square of that, is given by R square which is the length scale of the catalyst multiplied by the diffusivity matrix which is again a diagonal matrix inverse of that multiplied by the corresponding rate constant matrix first network of first order reaction rate constant matrix.

So, this is again a diagonal matrix. And so the network of the …. So, once we know the Thiele modulus matrix, we should be able to find out what is the cot hyperbolic and we can substitute that in the expression for the relationship between the Thiele modulus matrix and the effectiveness factor matrix and from that the effectiveness factor matrix can be found out. And using that 1 can actually find out what is the actual observed kinetics and express that in terms of the true kinetics.

So, from experiments, if we measure the actual kinetics and from the effectiveness factor, we will be able to use that expression to find out what is the true kinetics we have to the network of first order reactions. So, this is important because, the diffusional effects; strongly affects the selectivity of the product that is designed.

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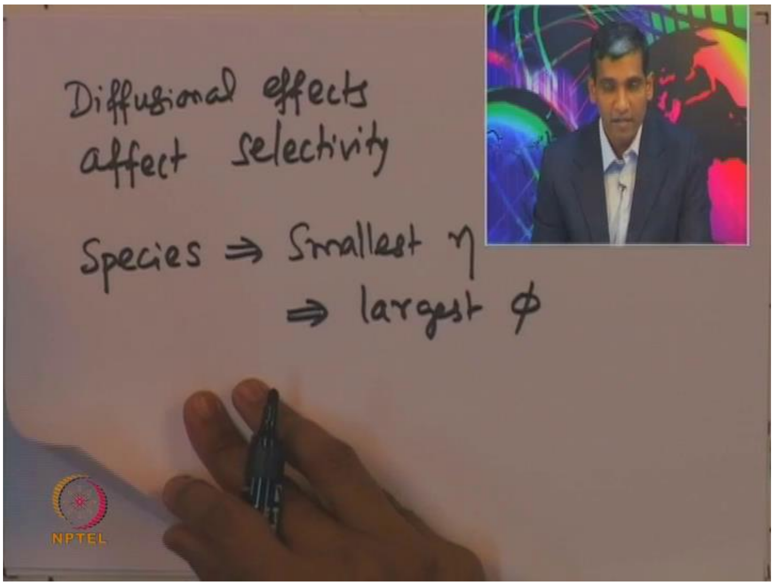

Diffusional effects affect selectivity

Species $\Rightarrow$ Smallest η

$\Rightarrow$ largest ϕ

So, the diffusional effects; they affect selectivity. And so because the effectiveness factor matrix is a diagonal and the Thiele modulus matrix is also a diagonal matrix, 1 can easily deduce that, the species with that has smallest eta; smallest internal effectiveness factor, will actually have the largest Thiele modulus. So, species n whose Thiele modulus is the largest, will have the correspondingly smallest effectiveness factor or that is that can be deduce simply from the expressions.

So, now let us look at; what are all the experimental limiting cases from what how to deduce these limiting cases from the experimental data. So, if you want to summarize, what are the features of the experiments or what are the information from the experiments; that needs to be used in order to deduce whether a particular limiting case exists in a given heterogeneous catalytic reaction. So, that can be summarized quite nicely, depending upon the dependence of the rate on various parameters or various system parameters.

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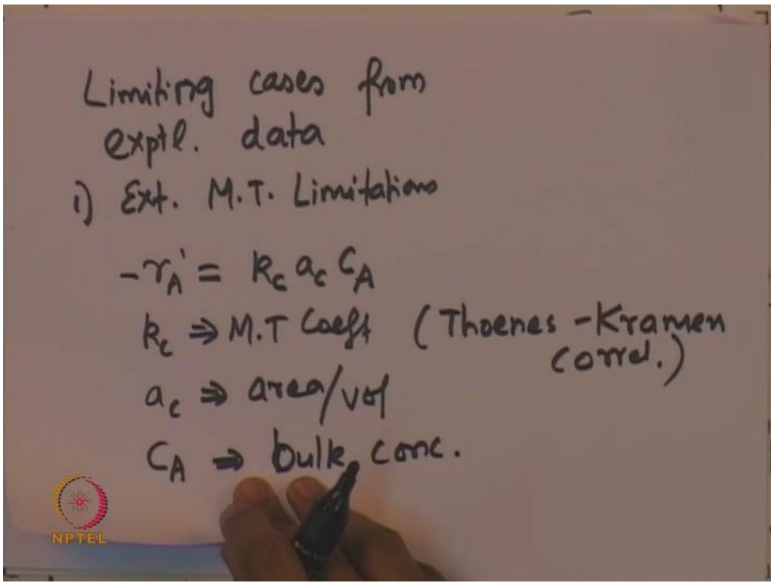

Limiting cases from
exptl. data
i) Ext. M.T. Limitations

$-r_A' = k_c a_c C_A$

$k_c \Rightarrow$ M.T Coeft (Thoenes-Kramen corrl.)

$a_c \Rightarrow$ area/vol

$C_A \Rightarrow$ bulk conc.

So, let us look at the limiting cases from experimental data; look at the limiting cases from experimental data. So, suppose if we look at the external mass transport limitations, then the reaction; suppose if the reaction is controlled by the external mass transfer, then the reaction rate minus r A is given by the mass transport coefficient k c multiplied by the area per unit volume of the catalyst into the concentration of the species C bulk concentration of the species. So, where k c is the mass transport coefficient. And this can typically be estimated using various correlations appropriate correlations. For example, 1 could use Thoenes-Kramer correlation.

So, 1 could use a Thoenes-Kramer’s correlation, in order to estimate what is the mass transport coefficient. And the a c is the area per unit volume of the catalyst and C A is the concentration bulk concentration of the species. Now if we look at these; the dependence of the mass transport coefficient on various system parameters. So, we could now look at the Thoenes-Kramer correlation because, the mass transport is go given by these correlation.

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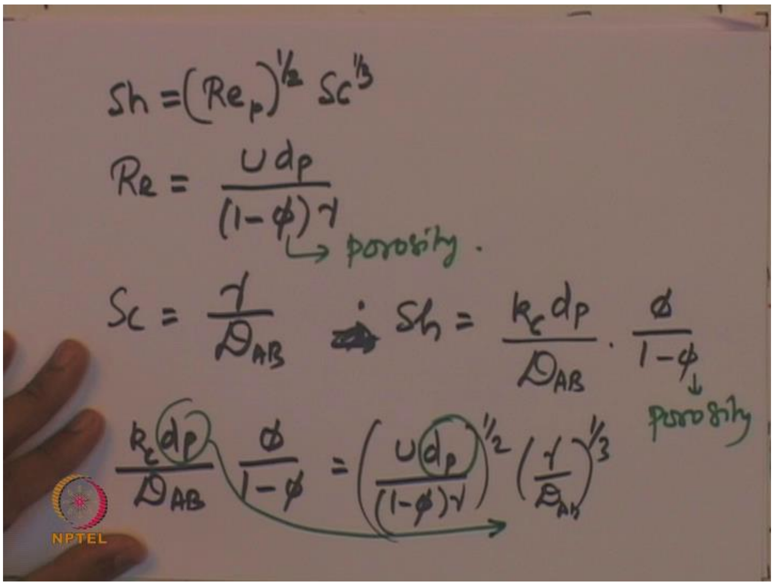

$$Sh = (Re_p)^{1/2} Sc^{1/3}$$

$$Re = \frac{U d_p}{(1-\phi)\nu}$$

↳ porosity.

$$Sc = \frac{\nu}{D_{AB}} \quad \therefore Sh = \frac{k_c d_p}{D_{AB}} \cdot \frac{\phi}{1-\phi}$$

↓ porosity

$$\frac{k_c d_p}{D_{AB}} \frac{\phi}{1-\phi} = \left(\frac{U d_p}{(1-\phi)\nu}\right)^{1/2} \left(\frac{\nu}{D_{AB}}\right)^{1/3}$$

So, that will be that is given by the Sherwood number is equal to the Reynolds number based on the particle diameter. So, to the power of half multiplied by the Schmidt number to the power of 1 by 3. So, that is the dependence of the Sherwood number on the Reynolds number of the based on the particle diameter multiplied by the Schmidt number. What is Reynolds number? Reynolds number is given by; the superficial velocity U multiplied by the diameter of the particle dp divided by 1 minus porosity into the kinematic viscosity.

So, remember that phi here is not Thiele modulus; this is the porosity of the bed of the catalyst bed in which the reaction is being conducted. And the Schmidt number S c is given by kinematic viscosity divided by the diffusivity of that species matrix diffusivity of that species. And so from here and Sherwood number is given by mass transport coefficient k c multiplied by the diameter of the particle dp divided by the corresponding diffusivity into phi by 1 minus phi. Once again here phi refers to the porosity of the bed. So, from here we can substitute these expressions into the Thoenes-Kramer relationship. So, this is the Thoenes-Kramer relationship.

So, from here we can see that k c dp by D A B into phi by 1 minus phi, that should be equal to U into dp divided by 1 minus phi into nu to the power of half into nu by D to the power of 1 by 3. So, now from here, we can deduce that t he mass transport coefficient k c is a function of square root of dp which appears in the Reynolds number term. And then if we bring this dp, if we divide this expression by dp. So, we will find that we can bring this to the diameter and we will find that the mass transport coefficient k c is now a function of is now a function of.

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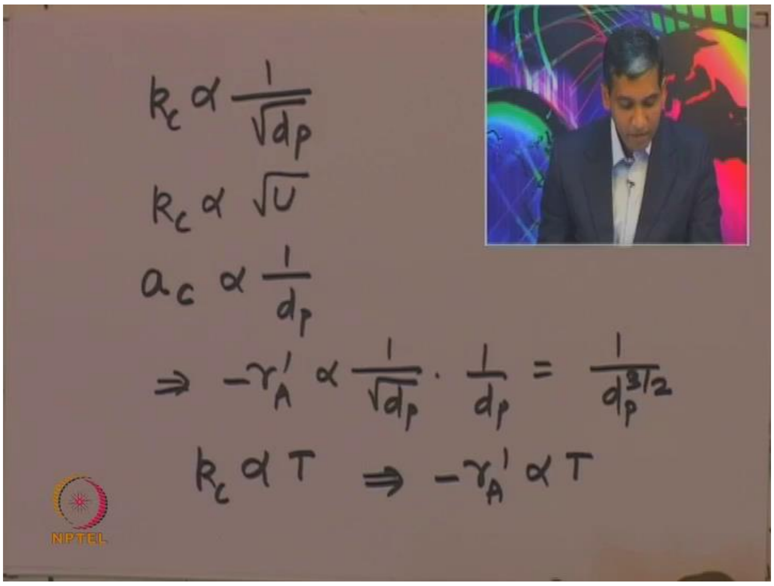

$$k_c \propto \frac{1}{\sqrt{d_p}}$$

$$k_c \propto \sqrt{U}$$

$$a_c \propto \frac{1}{d_p}$$

$$\Rightarrow -r_A' \propto \frac{1}{\sqrt{d_p}} \cdot \frac{1}{d_p} = \frac{1}{d_p^{3/2}}$$

$$k_c \propto T \Rightarrow -r_A' \propto T$$

k c is now proportional to 1 by square root of d p. Now, in addition to this; the mass transport coefficient is proportional to square root of the superficial velocity. Now the surface area per unit volume of the catalyst is essentially proportional to 1 by d p because, it is the surface area per unit volume. And therefore, we can say that the reaction rate of that particular species is proportional to 1 by square root of dp into 1 by diameter of the particle and that is equal to 1 by dp to the power of 3 by 2. And the mass transport coefficient k c is proportional to the temperature at which the reaction is being conducted, which means; that the reaction rate is now proportional to temperature.

So, what we have looked at in this lecture so far is; we have looked at the generalized criterion for determining what is the way whether based on the experimental data, whether the internal diffusion controls the overall catalytic reaction; heterogeneous catalytic reaction. And then we had looked at; what if there is a network of first order reactions, what is the general framework for finding the effectiveness factor, Thiele modulus of various species; that participate in a network of first order reaction. And then we initiated discussion on how to use experimental data and to identify, what are the various kinds of limitations and how the rate depends upon various systems parameter. So, we will continue with this in the next lecture.

Thank you.