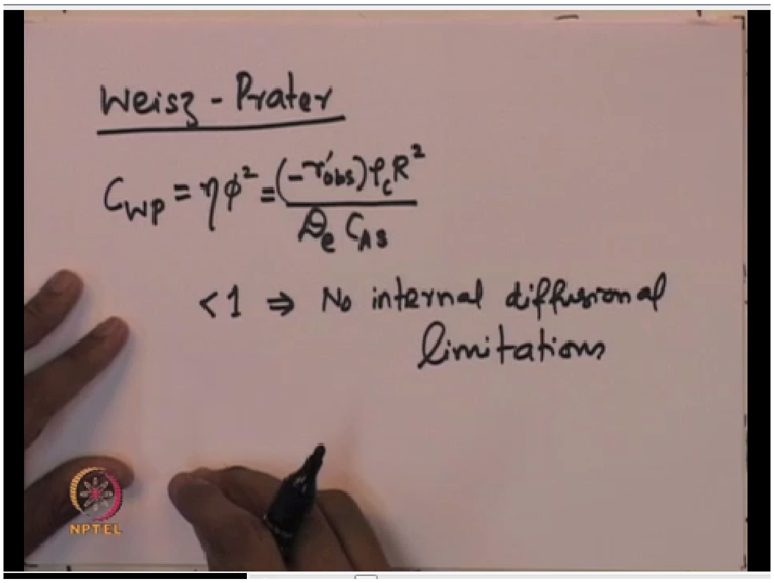
Chemical Reaction Engineering - II
Prof. Ganesh A Viswanathan
Department of Chemical Engineering
Indian Institute of Technology - Bombay

Lecture – 35
Generalized Criterion for Diffusion- and Reaction-Limited Conditions

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 the scheme and what is the correction for the same.

(Refer Slide Time: 01:02)



Weisz - Prater

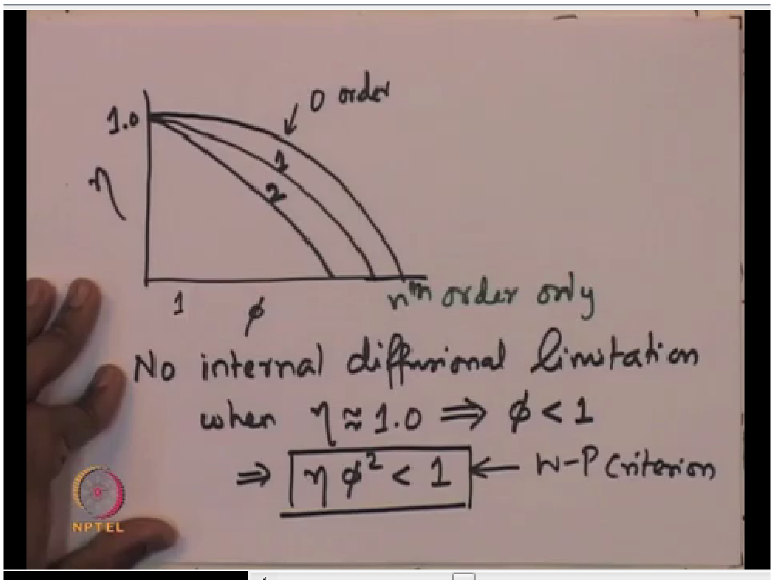
$$C_{WP} = \eta\phi^2 = \frac{(-r'_{obs})\rho_c R^2}{D_e C_{As}}$$

< 1 ⇒ No internal diffusional limitations

So the Weisz–Prater criterion is basically uses a parameter called CWP which is equal to the internal effectiveness factor*the Thiele modulus, square of, phi square, and that is equal to the r observed, the observed reaction rate*the density of the catalyst*the square of the length scale of the pellet that is being used/the diffusivity*the corresponding concentration of the species at the surface of the catalyst.

So if this is less than 1 and this suggests that there is no internal diffusional limitations, the reaction is not limited by the internal diffusion. So now the question is what is the validity of this criterion, when does it work? Does it work for all the actions and all catalytic reactions? So in order to understand this, let us look at why the Weisz–Prater criterion works and why is it the correct criterion in order to estimate whether the diffusional limitations are present.

(Refer Slide Time: 02:24)



No internal diffusional limitation

when $\eta \approx 1.0 \Rightarrow \phi < 1$

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

So in order to establish that, let us look at the classical plot of Thiele modulus versus the internal effectiveness factor, eta. So now if it is a first order reaction, if it is a 0 order reaction, then this is for the 0 order reaction, 0th order reaction and 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 nth order reaction.

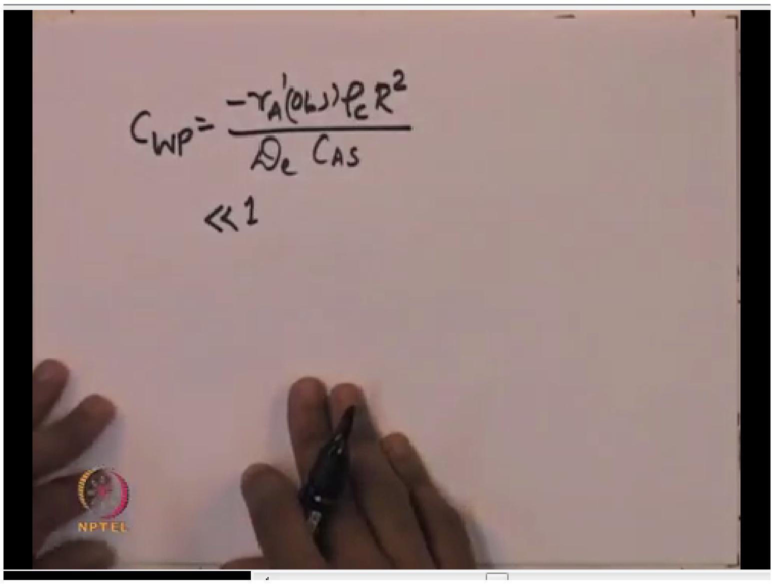
So from this graph, one can decipher that there is no internal diffusional limitations if when the internal effectiveness factor is approximately equal to 1. So the effectiveness factor here starts at 1. So it is approximately and it is approximately equal to 1, then it means that there is no internal diffusion limitations. Now from the graph, one 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*phi square should be less than 1. So which is the Weisz–Prater parameter. So 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 usually work. And in fact, the eta versus phi curve, it looks like this only for, typically for an nth order reaction, any n for nth order reaction.

If it is not an nth order reaction, for example if there is adsorption of species or product inhibition or if it is a non-isothermal, then the eta versus phi can be different from what is depicted in this picture here. Does not mean that it will not follow this picture but if it approximately follows an nth order reaction, then this is the kind of profile that one would get.

Now suppose if it is not simple nth 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 CWP=-rA observed reaction rate*the density of the catalyst*square of the length scale/the diffusivity*CAS.

(Refer Slide Time: 05:14)

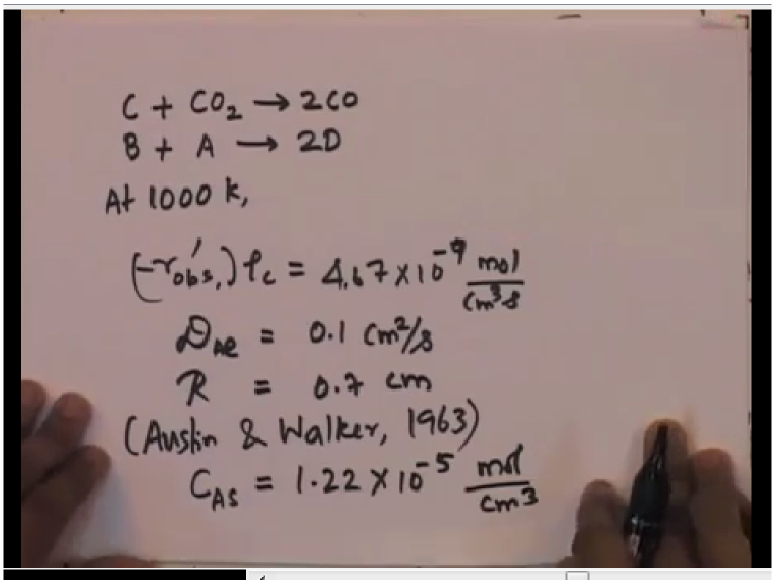


$$C_{WP} = \frac{-r'_A(obs)\,\rho_c R^2}{\mathcal{D}_e\, C_{AS}}$$

$$\ll 1$$

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 we just see in the picture. Let us look at what happens if there is a reaction which does not necessarily follow such an effectiveness factor Thiele modulus relationship.

(Refer Slide Time: 05:48)



$C + CO_2 \rightarrow 2CO$

$B + A \rightarrow 2D$

At 1000 k,

$$(-r'_{obs.})\rho_c = 4.67\times10^{-9}\ \frac{mol}{cm^3 s}$$

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

$$R = 0.7\ cm$$

(Austin & Walker, 1963)

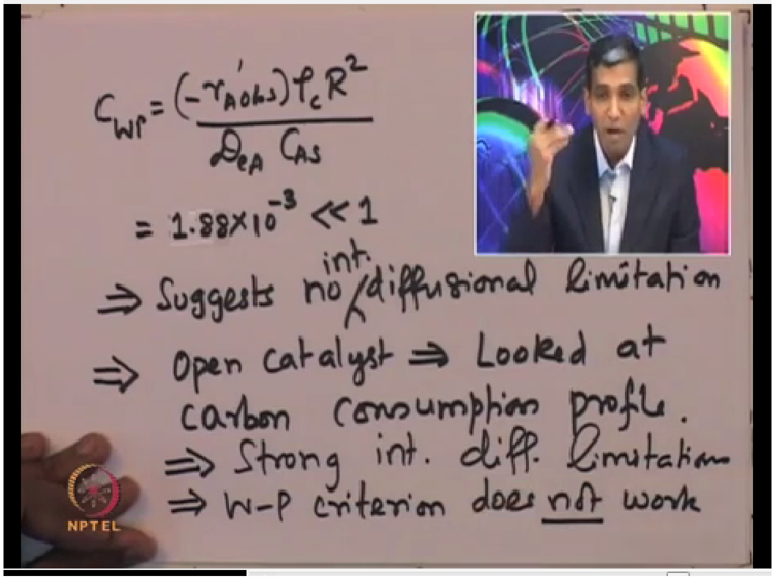
$$C_{As} = 1.22\times10^{-5}\ \frac{mol}{cm^3}$$

One 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+A giving 2D, so that is the reaction. So if I say 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 and Walker in 1963 measured the rate of, reaction rate and other parameters.

So the reaction rate, the observed reaction rate*the density of the catalyst was found to be 4.67*10 power -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 cm square/second and the effective radius, radius of the particle pellet that was used is 0.7 cm. So this information is basically measured by the group of Austin and Walker in 1963.

So the data was measured by these 2 co-workers in 1963 and the surface concentration of the species was measured to be 1.22*10 to the power of -5 mol/cm cube. So now let us calculate the Weisz–Prater parameter from this expression and then see whether the internal diffusional limitations exist or not.

(Refer Slide Time: 07:44)



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

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

⇒ Suggests no $\overset{\text{int.}}{\wedge}$ diffusional limitation

⇒ Open catalyst ⇒ Looked at carbon consumption profile.

⇒ Strong int. diff. limitation

⇒ W-P criterion does not work

So if I calculate the Weisz–Prater parameter, so CWP which is basically the -rA observed that is the observed reaction rate*the density of the catalyst*R square/the density, effective diffusivity of the species*CAS, that turns out to be about 1.88*10 power -3 which is significantly smaller than 1. Now this would mean that this particular reaction does not have a diffusional limitations.

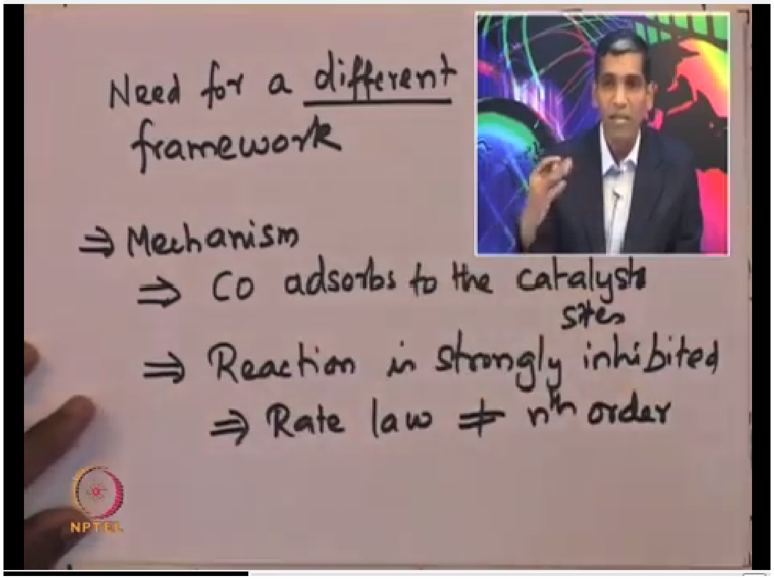
So this suggests that, suggests no diffusion limitation that means the overall reaction is not controlled by the internal diffusion limitations. So which means that it suggests that there is no internal diffusion limitations for this particular reaction, carbon and the carbon dioxide, heterogeneous reaction, it leads to 2 molecules of carbon monoxide. However, after the reaction was conducted, the same researchers, they actually cut open the, they open the catalyst.

They cut open the catalyst and measured, looked at the carbon consumption profile. They measured the carbon consumption profile in the catalyst and once it was measured, it suggested, the profile actually suggested that there was strong internal diffusion limitations. It suggested that the reaction was strongly limited by the internal diffusion and that shows that the Weisz–Prater criterion 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 results of the internal diffusion limitations. So question is, what is the, so because it does not predict, one needs to find out what is the corrective measure for this and what is the correct criterion.

What is the correct generalized criterion in order to estimate from the experimental observation whether the internal diffusional limitations are present or not for a given heterogeneous catalytic reaction?

(Refer Slide Time: 10:33)



Need for a different framework

⇒ Mechanism

⇒ CO adsorbs to the catalyst sites

⇒ Reaction is strongly inhibited

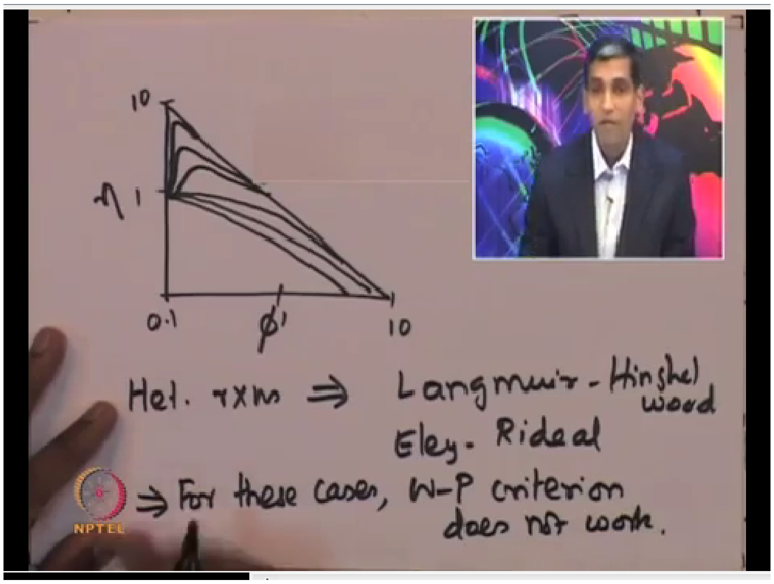
⇒ Rate law $\neq$ n^{th} order

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, 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 on to the catalyst side. 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 on to the catalyst's sides and therefore, the reaction is strongly inhibited which means that it is not going to follow the classical nth order reaction that a catalytic reaction is not, the rate law is not an nth order reaction, does not have an nth order dependence on the concentration of the species because the product is now adsorbing on to the catalyst's sides 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, now if I look at the Thiele modulus effectiveness factor graph, in general.

(Refer Slide Time: 12:24)



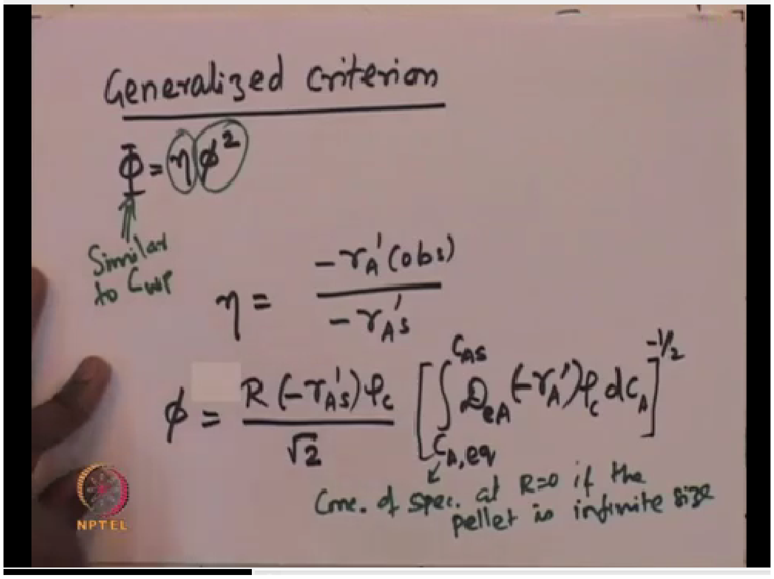
Het. rxns ⇒ Langmuir-Hinshelwood
Eley-Rideal
⇒ For these cases, W-P criterion does not work.

And it goes from 0.1 to 10 and this is 1 here. And for a nth order reaction, first order, second order, etc. 0th 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 Eley-Rideal type of mechanisms and for exothermic reactions, the effectiveness Thiele modulus graph can actually look like this.

So therefore, when eta=1 and eta is, I mean, 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, 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 reactions, several heterogeneous reactions, they actually follow the Langmuir Hinshelwood type kinetics or Eley-Rideal type kinetics which basically uses the adsorption isotherm which is adsorption isotherm is now incorporated into the rate law. So therefore, in these cases, the WP criterion, the Weisz–Prater criterion does not work. So now we need to find out what is the generalized criterion which works for all types of rate laws. So the exercise is now to find out what is this generalized criterion.

(Refer Slide Time: 14:36)



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 capital phi as eta*phi square and this is now very similar to that of the Weisz–Prater criterion. This is very similar to CWP, that is the Weisz–Prater parameter. Now in order to come up with a 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.

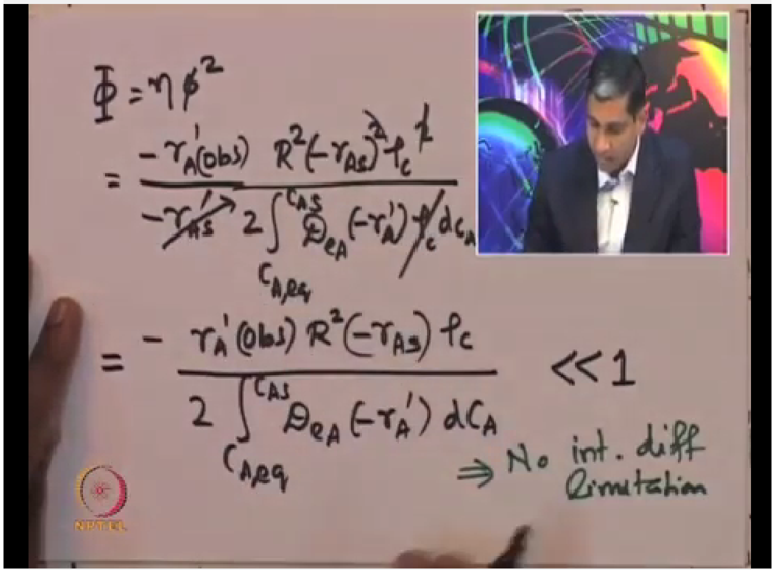
So the generalized definition for the internal effectiveness factor is basically given by rA prime observed, that is the observed reaction rate, /the corresponding reaction rate at the surface of the catalyst. On the other hand, the generalized Thiele modulus can actually be defined as the length scale, whatever is radius of the pellet, effective radius of the pellet, *-rZ, that is the reaction rate at the surface concentration, * the density of the catalyst/square root of 2*integral the equilibrium concentration of the species at the center of the catalyst.

If the catalyst was of infinite size, integral from CA to CAS, where CAS is the concentration of the surface, *the effective different of the species DeA*-rA*rho c*dCA, that to the power of

-1/2. So that is the generalized Thiele modulus and it should be noted here that CA is the concentration of species at R=0 or that is at the center of the catalyst pellet if the pellet is of infinite size. Now this quantity CA equilibrium is actually going to be 0 if it is a non-reversible reaction, that is it is a forward or a back, one side reaction.

Then the CA equilibrium here would actually take a value of 0. So if it is a non-reversible 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 non-reversible reaction. But if it is a reversible reaction, then it will be an equilibrium concentration.

(Refer Slide Time: 17:41)



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

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

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

$\Rightarrow$ No int. diff limitation

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 or new generalized criterion, will be eta phi square and that should be equal to -rA, that is the observed rate, /at the surface, rate at the surface concentration*R square*-rAS square*rho c square/2*integral CA equilibrium, that is the equilibrium concentration of the center, *CAS*the effectiveness diffusivity of that species*-rA*rho c*dCA.

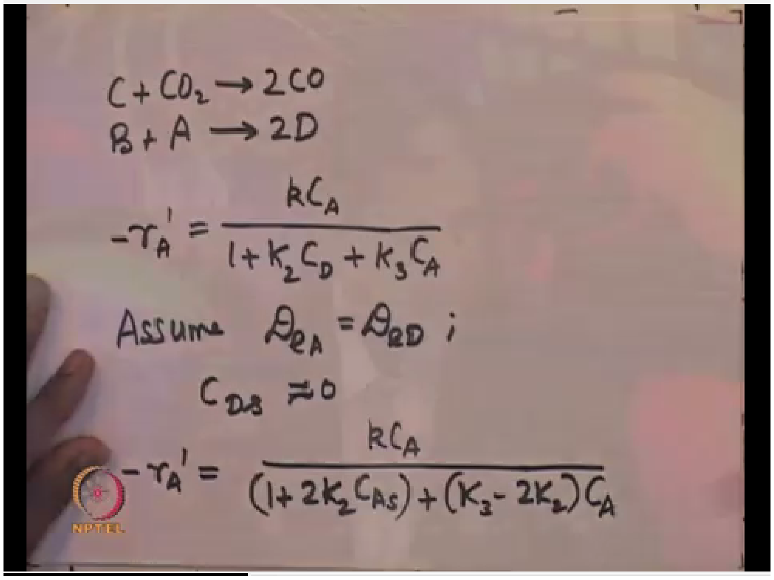
So that is the expression for the modified or generalized criterion for deciding whether the internal diffusion is going to exist or not, internal diffusion limitation is going to exist or not. So suppose if this quantity, so now we can rewrite this as by cancelling some of these terms, we can cancel this term with the square and this if assume that the density of the catalyst does not change, then we can cancel off these.

And so we can rewrite this as the observed rate*R square, that is the square of the length scale, that is the rate evaluated at the surface concentration, *the density/2*integral CA 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 equilibrium concentration to the, at R=0 to the surface concentration, *the corresponding diffusivity*the reaction rate*dCA.

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 is generalized modulus here. If we plug in the rate expression for nth order reaction, it actually reduces to the Weisz–Prater criterion. So therefore, this is a generalized model which also includes the Weisz–Prater criterion, or Weisz–Prater criterion which is used for deciding whether the internal diffusional limitation is present or absent based on the experimental data.

Now let us look at this specific example we had initiated today.

(Refer Slide Time: 20:25)



$C + CO_2 \rightarrow 2CO$

$B + A \rightarrow 2D$

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

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

$C_{DS} \approx 0$

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

That is the reaction of C+CO2 giving 2 times CO. So let us look at what happens, what is the, whether 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 or by looking at the profile of the carbon content, suggest that the diffusion limitations were strongly present and they strongly inhibited the reaction.

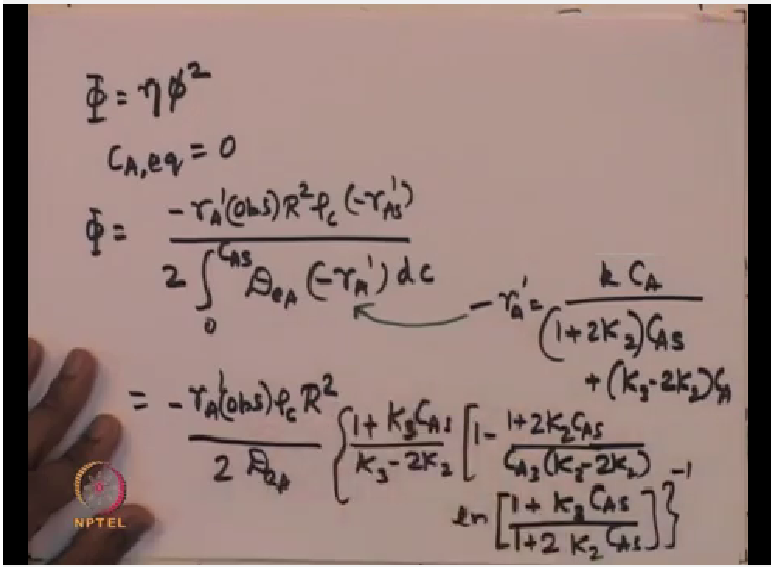
So let us now plug in that, plug in the rate law into the generalized modulus and look at whether the internal diffusional limitation was present or absent. So the reaction scheme is B+A giving 2 times D. So B is the, species B is the carbon and A is CO2. And D is the product carbon monoxide. So the reaction rate law by looking at the detailed mechanisms that is involved in the heterogeneous catalytic reaction has been found to be k*CA/1+K2*CD.

That is the adsorption constant for, adsorption equilibrium constant for carbon monoxide, +K3*CA, this is the adsorption constant correspondingly for the carbon dioxide. And so if you assume that the diffusivity, effectiveness diffusivity of species A=the effectiveness diffusivity of species D and by assuming that it is an equimolar counter diffusion system and if you 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 experiments suggest that there is a strong adsorption of the product on to the catalyst side. So therefore, we can expect that the amount of carbon monoxide which has actually left the catalyst and the amount that is present on the surface is negligible. So therefore, we can assume that the concentration of DS on the surface was approximately equal to 0. So therefore, using these assumptions, the rate law can now be rewritten as k*CA/1+2K2CAS.

That is the concentration of carbon dioxide at the surface of the catalyst+K3, which is the equilibrium constant for the adsorption of CO2, -2*K2, that is the equilibrium constant for adsorption of carbon monoxide, product carbon monoxide on to the surface of the catalyst*the concentration of the species CA.

(Refer Slide Time: 23:19)



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

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

$$\Phi = \frac{-r_A'(obs) R^2 \rho_c (-r_{AS}')}{2\int_0^{C_{AS}} D_{eA} (-r_A')\, dc} \longleftarrow -r_A' = \frac{k C_A}{(1+2K_2)C_{AS} + (K_3-2K_2)C_A}$$

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

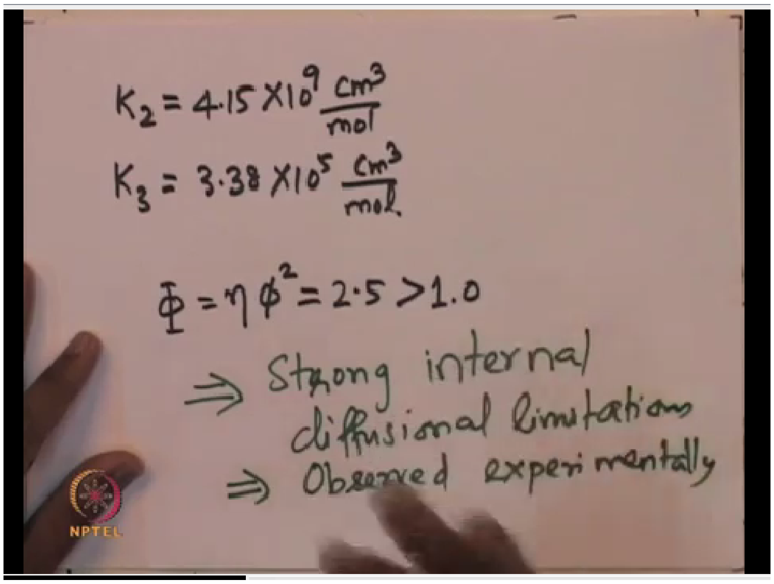
So now integrating the expression for the generalized modulus, we will find that phi, capital phi which is generalized modulus, generalized criterion, that is equal to internal effectiveness factor*phi square. Now because it is not a reversible reaction, we can assume that CA equilibrium=0. So we assume that CA 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 say approximately equal to 0.

Because it is a non-reversible reaction and therefore, phi=-rA prime, the observed reaction rate, *R square*rho c evaluated at the surface/divided by 2*integral 0 to CAS, that is the integral, *the diffusivity of species DeA*-rA prime*dC. So now plug in, we can plug in the rate expression here. Remember that the rate expression is given by the k*CA/1+2*K2*CA+K3-2K2*CA. So the first one is the product of 1+2K3, so the rA is given by, -rA prime is given by k*CA/1+2K2*CAS+K3-2K2*CA. 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 plug in this rate law into this expression here and then we can integrate the expression. So performing the integration, it turns out that phi=observed * the density of the catalyst*R square/2*the corresponding effectiveness diffusivity, DeA*1+K3CAS/K3-2K2*1-1+2K2CAS/CA3*K3-2K2*logarithm of 1+K3CAS/1+2K2CAS, inverse of this.

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

(Refer Slide Time: 26:24)



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

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

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

$\Rightarrow$ Strong internal diffusional limitations

$\Rightarrow$ Observed experimentally

So now the same experimental group, Austin and Walker's group, they have also while performing these experiments, they estimated that K2 which is the adsorption constant for carbon monoxide is given by 4.15*10 to the power of 9 cm cube/mole. Similarly, K3 was also estimated as 3.38*10 to the power of 5 cm cube/mol. So plugging in these numbers, we can find that the generalized phi which is equal to eta*phi square which is the parameter in the generalized criterion, that should be equal to 2.5 which is certainly > 1.

So clearly the generalized model and 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, you depending upon what is the nature of the rate law, a simple Weisz–Prater criterion can be used if it is a simple nth order reaction.

But if it is a, the rate law is not as simple as that. Then one has to use these generalized criterion phi which is given by earlier expression that we just derived but one needs to find out what is integrate the expression of the diffusivity * 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.