

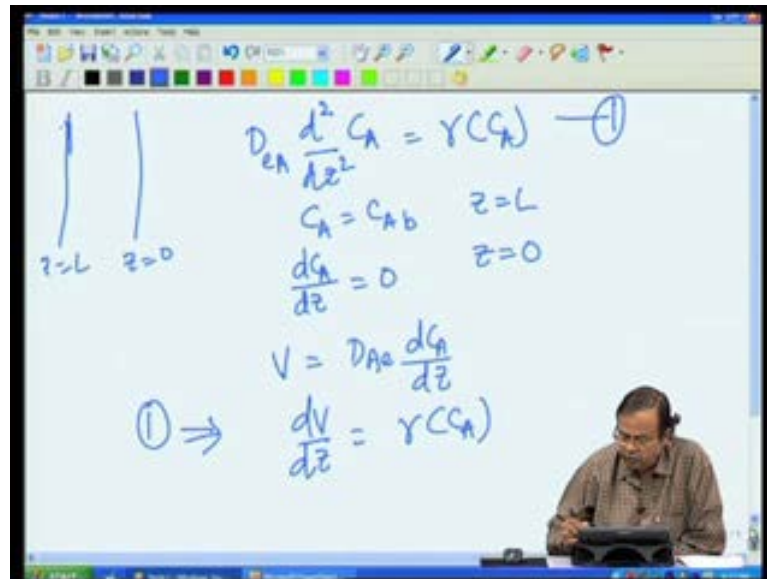
Chemical Reaction Engineering
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Lecture No. # 21
Gas-solid Catalytic Reactions - Diffusion and Reaction II

Friends, we are discussing gas-solid catalytic reaction and we looked at in depth a scenario where a first order irreversible, isothermal reaction takes place in a catalyst, which is of slab geometry. I also mentioned that we will relax all these restrictions one by one and in last session we looked at relaxing the condition of geometry and saw that even for spherical geometry even for cylindrical geometry or for any irregular shape, if we define the Thiele modulus appropriately then the relationships between the effectiveness factor and Thiele modulus for a first order reaction is almost unique may be few percentage point difference.

But under the extremes of reaction controlling the whole process or diffusion controlling the whole process, the behavior is unique that is effectiveness factor is one if reaction is controlling the process and effectiveness factor goes as inverse of Thiele modulus if diffusional limitation are controlled. Let us now relax the constrained on the order of reaction saying that instead of considering only first order reaction what happens if the kinetics is more general and we will take a look at this situation today.

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So coming back to diffusion mass balance equation, the mass balance equation is same as same as before that is if we are if we are considering let us say reaction A going to B in a slab geometry. Now we understand that we do not have to worry about whether it is slab geometry or whether it is a cylindrical geometry or for that matter any irregular shape. So our mass balance equation for slab geometry for example, is as shown over here $D_{eA} \frac{d^2 C_A}{dz^2} = r(C_A)$. With the boundary conditions that C_A is equal to C_{Ab} at the outer surface namely z equal to L .

So let me draw a sketch here this is my inner centre point this is my outer surface. So concentration at this location over here is C_{Ab} and then at the centre point the flux is zero because of symmetric condition so these are the boundary conditions and the mass balance or diffusion reaction equation. Now we solve this for r equal to $K C_A$ that is the first order kinetics. Now let us see how what can we do if the kinetics is not first order but any general reaction rate r of r of C_A . to address this we will now follow the following method. let us first of all define V as $D_{eA} \frac{dC_A}{dz}$ let us let us define this V . So in terms of V if we go back to our mass balance equation one we can write that equation one as $\frac{dV}{dz} = r(C_A)$.

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$$\textcircled{1} \Rightarrow \frac{dV}{dz} = r(C_A) \quad \text{--- 2 } V=0 \text{ at } z=0$$

$$\frac{dC_A}{dz} = -\frac{V}{D_{Ae}} \quad \text{--- 3 } C_A = C_{Ab} \text{ at } z=L$$

$$\frac{dC_A}{dV} = -\frac{V}{D_{Ae} r(C_A)} \quad \text{--- } \textcircled{4}$$

$$\frac{V^2}{2} = \int_{C_{A0}}^{C_A} D_{Ae} r(C') dC' \quad C_{A0} = C_{Ab}$$

Our definition of definition of V says that dc_A/dz is equal to one over D_{Ae} into V . Now so this is my equation two this is my definition of V . So we have these two equations now if I combine these two equations. Now if I combine this two equations that is equation two and equation three I can alternatively write dc_A/dV that is just three by two dc_A/dV is nothing but one over D_{Ae} V by r of C_A and what is the boundary conditions of this two equations V is equal to zero when z is equal to zero and C_A is equal to C_{Ab} when z is equal to L . We are trying do now look at a combination of this two equations as written over here, which we can integrate and will give us V^2 by 2 is equal to integral C_A zero to C_{Ab} D_{Ae} of $r(C')$.

Let us say that diffusibility is also a function of C_A so we have just integrated this equation four and use the boundary condition that V is zero at z equal to zero. This C_{A0} is nothing but some concentration at that is C_{A0} is C_A at z equal to zero we do not know that value but let us say that that concentration is C_{A0} so what we are saying using our catalyst I know the concentration here is C_{Ab} I do not know what the concentration here is there is going to be diffusion and reaction let us call this concentration C_{A0} .

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$$V = \left[2 \int_{c_{A0}}^{c_{Ab}} D_{Ae} (c') \gamma(c') dc' \right]^{1/2} = D_{Ae} \frac{dc_A}{dz}$$

$$\int_0^L dz = \int_{c_{A0}}^{c_{Ab}} D_{Ae} \frac{dc_A}{V}$$

$$L = \int_{c_{A0}}^{c_{Ab}} D_{Ae} \frac{dc_A}{V}$$

So if you do that then I can write my V square in this particular manner or in other words I can write this equation five in a equivalent form namely V is equal to two integrates c A zero to c A b D A e raise to half and this is nothing but D A e dc A dz as we defined earlier. Let us work with these equation little more and integrate this one more time that is we have dz will be D A e dc A by V. Let us keep it in term of V because it is little complicated equation so instead of repeating it we will keep it in the in the in the same term. So if we integrate both the sides between the limit zero to L with concentration limit c A zero to c A b we will get L equal to integral c A zero to c A b D A e dc A by V. So this equation gives us where V is this particular term over here.

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$$L = \int_{c_{A0}}^{c_A} \frac{D_{Ae}}{V} dz$$

$$\eta = \frac{r_{obs}}{r(c_{A0})} = \frac{1}{L} \frac{1}{r(c_{A0})} \left(D_{Ae} \frac{dc_A}{dz} \right)_{z=L}$$

$$\eta = \frac{1}{L} \frac{1}{r(c_{A0})} \left[2 \int_{c_{A0}}^{c_A} D_{Ae}(c') r(c') dz \right]^{1/2}$$

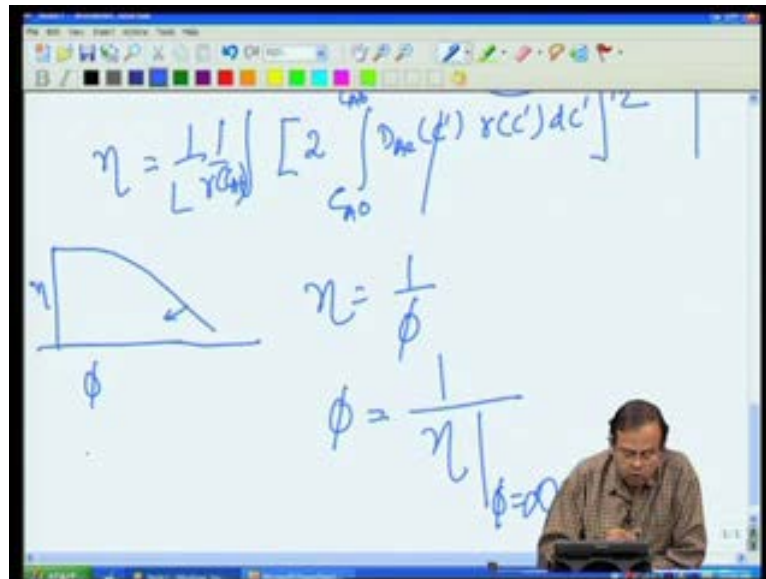
So the last equation over here tells us, what this c_A zero is implicitly. We do not know what this integral value is because that is not a simple equation it is little involved equation. We do not know what that that equation is but we know implicitly that is in these integral if we know the length of your slab width that is the catalyst half width. Then we know the c_A zero value implicitly. But we are interested in knowing what the effectiveness factor is and what is what is what the Thiele modulus is.

So let us define effectiveness factor η as r observed by r if the concentration is c_A same as same as before and using the similar manipulation that we did earlier we can write this as which is which actually this term is nothing but this term is nothing but V at z equal to L . So if we put all this things together we will get an equation for effectiveness factor as raise to half.

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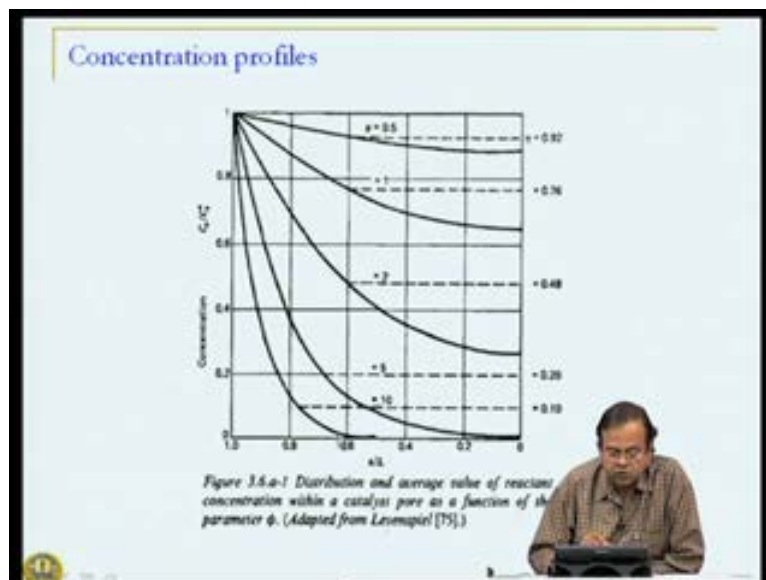
All we have done is we have used the definition of η coupled it along with the value of V at z equal to L and we get this particular expression. So we know what is effectiveness factor but we do not know what is the what is the Thiele modulus and to do that definition to get the definition of Thiele modulus for a generalized kinetics let us use an idea that we saw earlier for a first order reaction the idea was that the idea was as follows.

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If you look at eta versus Thiele modulus plot the plot looks something like this with Thiele modulus being very high that is when you have diffusion limitation eta was one over Thiele modulus. So let us now define the Thiele modulus for the generalized kinetics as Thiele modulus is one over eta at Thiele modulus being very large and this gives us the definition of definition of Thiele modulus. Now if we take this definition of eta and what is the meaning of Thiele modulus been very large that is the diffusion limitations are very strong.

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So what happens when diffusion limitations are very strong? For example, for the first order reaction we saw these results earlier that are when Thiele modulus is very large the concentration of reactant at the centre point is almost zero. So let us make use of this observation and say that when Thiele modulus is very large my centre point concentration is going to be going to be zero.

Now it need not be actually physically zero because if the reaction is reversible than we can have the centre point concentration as equilibrium concentration that is at very large Thiele modulus values. We will get concentration lower limit or lower limit on concentration as equilibrium concentration. So c_A^b to c_A^e and if the reaction is irreversible c_A^e is nothing but zero and that is what we saw for a first order kinetics when the reaction was irreversible.

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$$\phi = \frac{V_p}{S_p} \frac{k_v}{\sqrt{2}} \left[\frac{c_A^b}{c_A^e} \right]^{1/2}$$

$$r(c_A) = k_v c_A$$

$$= L \frac{k_v c_A^b}{\sqrt{2}} \cdot \frac{1}{D_{ac}} \left[\int_0^{c_A^b} k_v c' dc' \right]^{1/2}$$

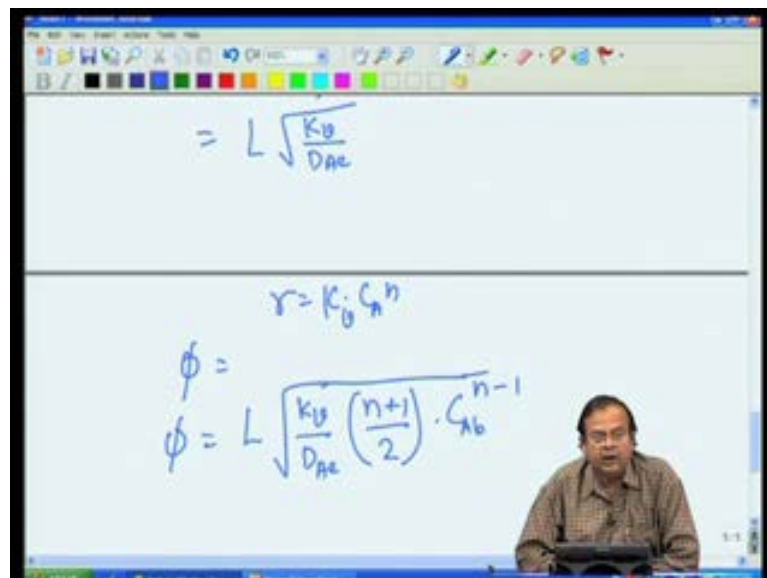
$$= L \frac{k_v c_A^b}{\sqrt{2}} \frac{1}{\sqrt{D_{ac}}} \cdot \frac{1}{k_v^{1/2}} \cdot \frac{\sqrt{2}}{c_A^b}$$

$$= L \sqrt{\frac{k_v}{D_{ac}}}$$

So if you do all this we get now that is what we have is effectiveness factor value eta now put c_A^b equal to c_A^e or the equilibrium value and the appropriate rearrangement will give us the effectiveness factor for a generalized kinetics as volume of the particle to spherical surface area of the particle, this take care of the geometry of the catalyst pellet r of c_A^b by square root of 2. So this gives us now the definition of Thiele modulus for spherical for generalized kinetics. Let us see how this simplifies for first order reaction. So for first order reaction for first order reaction our r of c_A is k_v into c_A .

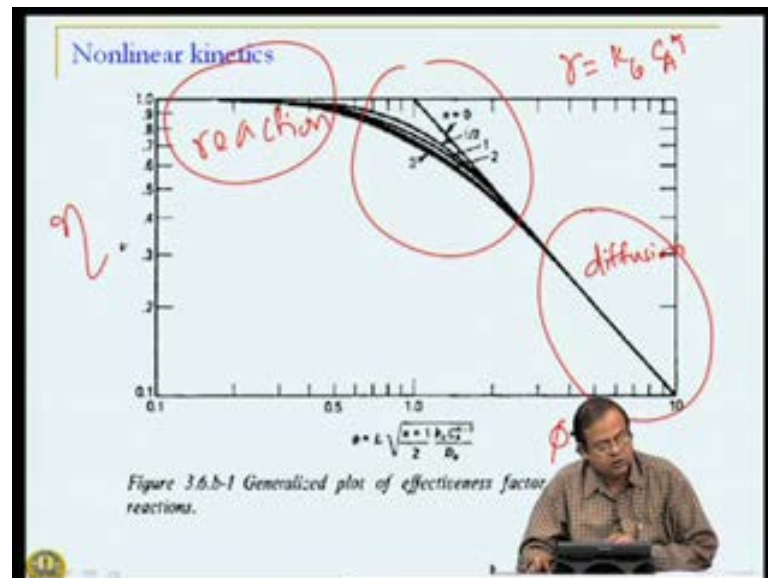
So if we if we or if we put all this individual terms assuming diffusivity is constant then and for slab geometry for example, V_p by S_p is L this is k_v into $c_A c_A b$ divided by square root of square root of 2 into D_{Ae} D_{Ae} into this should be minus half because that is inverse. So D_{Ae} raise to minus half into integral first order reaction $c_A b$ r of c prime so k_v into c prime dc prime raise to minus half and if you if you now simplify this simplify this relationship will be left with L into k_v by into $c_A b$ by square root of 2 into one over square root of D_{Ae} into one over k_v raise to half into square root of 2 by $c_A b$ this integral. So these terms will cancel out and we are left with the definition of Thiele modulus which we got which we got earlier.

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What if the reaction is general n th order kinetics? What if the reaction is general n th order kinetics? So if we substitute now r equal to k_v into c_A raise to n we will get Thiele modulus equal to L square root of k_v by D_{Ae} into $n + 1$ by 2 into $c_A b$ raise to $n - 1$ this is our Thiele modulus for a general kinetics.

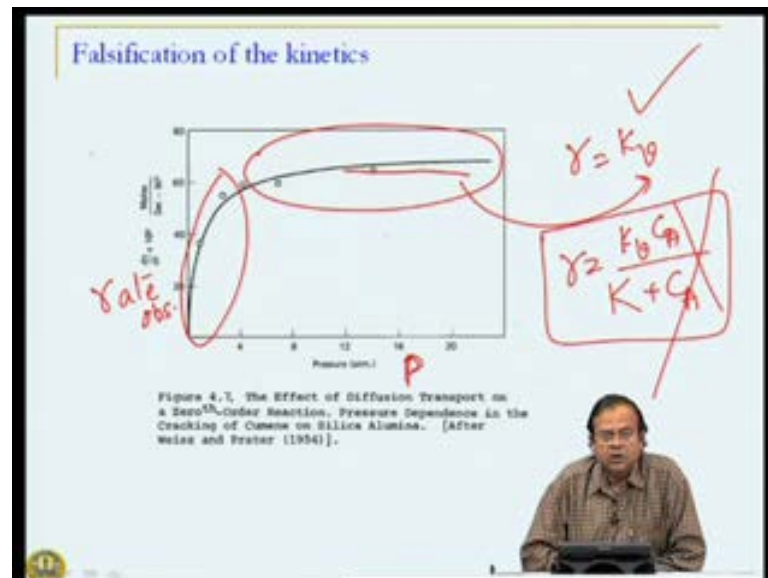
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And if we now look at the behavior of Thiele modulus versus effectiveness factor, Thiele modulus Thiele modulus phi versus effective factor eta for power law kinetics that is r is equal to $k_v c A^n$ and for different values of n one half zero two three etcetera. Once again we see that two limiting cases the behavior for effectiveness factor and Thiele modulus is unique. Diffusion control, reaction control, reaction control so both this both these extremes you have the same behavior of Thiele modulus and eta whereas, during the transition period there are variations for different kinetics but the behavior qualitatively is very much very much similar.

So this is how diffusion resistances or mass transfer phenomena interferes with the kinetics or chemical reaction to produce results, which are different than if the diffusion was not playing any role. Now when you actually do the experiment you do not know a priori whether diffusion is playing a role or not so that is something that we would like to find out so to find, what is the criteria? But before we do that let us look at what happens if the diffusion limitations are there? How does your measurement give you incorrect or falsified data?

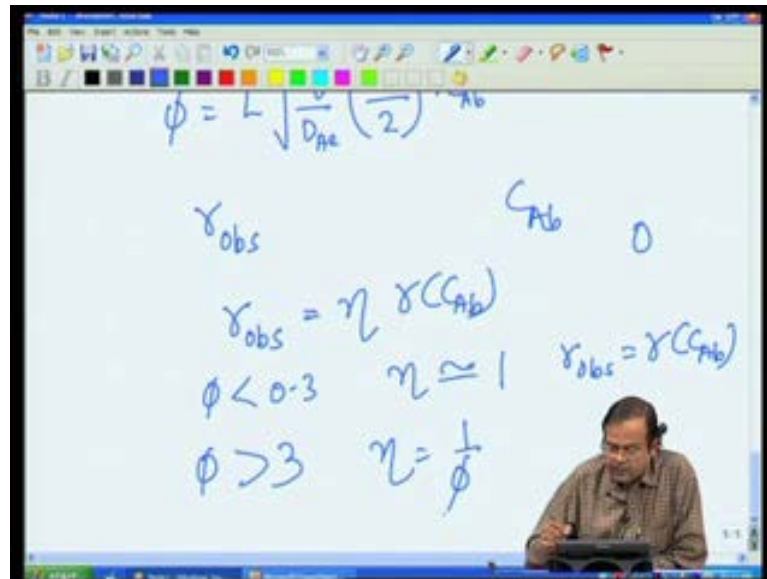
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So to look at that first let us look at an example and to illustrate what do I mean by falsification of kinetics. Now this is this is an experimental result of cracking of cumen and this the rate of cracking as measured experimentally. So rate observed as a function of pressure. Now in reality this cracking of cumen is a zero order reaction. So kinetics is namely $r = k_0$ or simply a constant k_0 vs pressure is an indication of concentration. Now if you examine this observed rate data we see that as we are increasing the pressure the rate is increasing from a low value and reaching a saturation point.

This is a behavior of a zero order reaction that is rate is some constant k_0 . But what about this regime, clearly there is something else that is happening that is the true kinetics is zero order but if you measure these data and try to determine the kinetics you will conclude that this is some kind of a saturation kinetics. That is the kinetics is actually something like this. We saw this in langre absorption isothermal behavior. So one may conclude that this is the kinetics if we just try to fit the rate experimental data to some model equation, but this is not the true kinetics. True kinetics is this zero order reaction so that means there is some falsification of kinetics as we measure it how why do we get falsification of kinetics.

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Let us try to first look at look at that aspect. So what we are saying is that we observed rate and we measure bulk concentration. So we measure both these quantities and because there are some diffusion limitations or there is a likelihood of diffusion limitations we do not actually see the true kinetics. This is a falsification of kinetics. So how do we how do we how do we try to try to explain that. So let us go back to our r observed which is effectiveness factor into r of c A b.

So when you are in the reaction control regime when phi value so how will this equation behave when phi is less than 0.3 let us say eta is close to unity. So r observed is same as r of c A b. So you will measure the observed rate which is the true kinetic rate. But what happens if phi value is greater than 3, then eta is one over one over phi.

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The whiteboard contains the following handwritten equations:

$$n = \frac{d \ln r(C_A)}{d \ln C_A} \quad r = k_0 C_A^n$$

$$n_{obs} = \frac{d \ln r_{obs}}{d \ln C_{Ab}} \leftarrow$$

$$r_{obs} = \eta r(C_{Ab})$$

$$\ln r_{obs} = \ln \eta + \ln r(C_{Ab}) \leftarrow$$

$$n_{obs} = \frac{\ln \eta}{d \ln C_{Ab}} + \frac{d \ln r(C_{Ab})}{d \ln C_{Ab}}$$

So let us try to see what the implication of this particular behavior is. Now first we will try to see how the order of reaction may get falsely reported. Now if you recall what is the order of reaction earlier we said order is $d \ln r$ of $c A$ by $d \ln c A$. This is how we define our order this comes from the fact that if rate is defined as $c A$ raise to n then this n is nothing but $d \ln r$ of $c A$ $d \ln c A$. So now let us let us try to see what happen if diffusion limitations are there. So let us now say that observed rate will be first of all $d \ln r$ observed by $d \ln c A b$.

Because my observed rate is r observed concentration is concentration is $c A b$. Now let us let us go back to our equation my r observed is $\eta r c A b$. So I will take a log of this because I want to see how the $\ln r$ observed changes so this is $\ln \eta$ plus $\ln r$ of $c A b$. So this equation coupled with my definition of observed order gives me $\ln r$ observed is $\ln \eta$ by $d \ln c A b$ plus $d \ln r$ of $c A b$ $d \ln c A b$.

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$$n_{obs} = \frac{d \ln r}{d \ln C_{A b}} + \frac{d \ln \eta}{d \ln C_{A b}}$$

$$= n + \frac{d \ln \eta}{d \ln C_{A b}} \Leftarrow$$

$$\phi(C_{A b}) \eta = \frac{1}{\phi}$$

$$n_{obs} = n + \frac{n-1}{2} \frac{d \ln \eta}{d \ln \phi}$$

$$n_{obs} = \frac{n+1}{2}$$

Now I can write $d \ln r$ of $C_{A b}$ as n , so this will be n plus $d \ln \eta$ over $d \ln C_{A b}$. Now why should η change as $C_{A b}$ because if you recall our definition of Thiele modulus is a function of $C_{A b}$ η is one over Thiele modulus if diffusion limitations are strong. So η depends upon $C_{A b}$. So if you now put this information into this equation we will get n_{obs} as n plus $(n-1)$ by 2 $d \ln \eta$ over $d \ln \phi$. All I have done is instead of writing $d \ln \eta$ over $d \ln C_{A b}$ I wrote this as $d \ln \eta$ over $d \ln \phi$ and we get this particular relationship.

Now how does η varies with ϕ . We know η varies with ϕ by minus one that is $d \ln \eta$ over $d \ln \phi$ is minus one. So for power law kinetics you will get observed rate as $(n+1)$ by 2 where n is the true kinetic rate.

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$$\phi(C_{A b}) \eta = \frac{1}{\phi}$$

$$n_{obs} = n + \frac{n-1}{2} \frac{d \ln \eta}{d \ln \phi}$$

$$n_{obs} = \frac{n+1}{2}$$

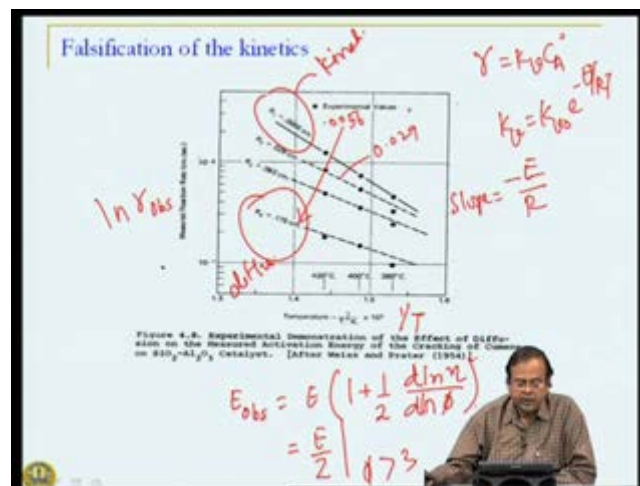
$$n=1 \quad n_{obs} = n$$

$$n=0 \quad n_{obs} = \frac{1}{2}$$

This has several implications for example, let us take a first case that we have seen in depth when n is one first order kinetics n observed is same as n , the true order of the order of the reaction. But what if n is zero then n observed is half and in fact if you go back and look at this behavior. This particular behavior is a part of r actually effectively r observed r observed is actually $k v c A$ raise to half be actually this behavior. True kinetics is this behavior. So this is my true kinetics this is my diffusion limitations strong diffusion limitations so the actual behavior is a combination of combination of these two.

Now how it is related to relate to the pressure. Now if we look at look at our Thiele modulus definition for a zero order kinetics it turns out Thiele modulus is inversely proportional to pressure. So lower the value of pressure higher is the value of Thiele modulus using our idea of generalized Thiele modulus so lower is the pressure higher is the pressure of Thiele modulus higher is the pressure lower is the value of Thiele modulus true kinetic control diffusion control.

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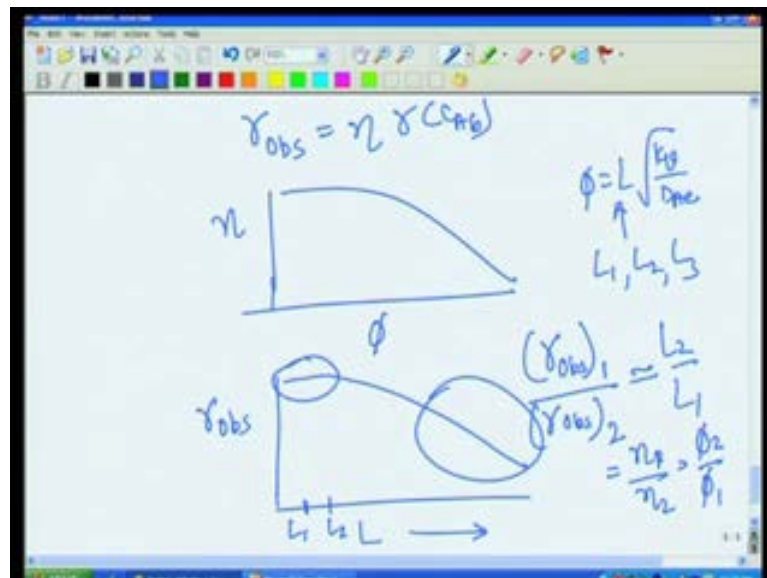


Let us look at another example of how kinetics get falsify. This is again same cracking of cumin but now the observed rate as a function of one over one over T having particle sizes, which are increasing in this order. This is 0.0056 centimeter this is second one is 0.029 and so on. Now what do we see in this figure we see in this figure that r observed versus one over T is a straight line this is a \ln plot so this is \ln and that comes from the fact that r is $k v$ into concentration let us say. In this case concentration rise to zero and $k v$ is a function of temperature namely let us say that Arrhenius rate form.

So if we now plot $\ln k_v$ versus $1/T$ or $\ln r$ versus $1/T$ you will get a straight line with slope equal to $-E/R$ is the slope from which we get our activation energy. So if we now look at this figure let us say that for a value of small radius to a large radius. We see that the slope is decreasing our lines are becoming less steep and steeper that means the activation energy activation energy is decreasing. This is again a falsification of kinetics and in fact if you do the same exercise with it for the order of a reaction we will get the activation energy the activation energy observed is true activation energy into $1 + \frac{1}{2} \frac{d \ln \eta}{d \ln \phi}$.

So under the case of strong diffusion limitations the activation energy observed will be actually when ϕ is greater than $3E/2$ and this is in fact what we are saying here when the particle radius is very large diffusion resistances are strong, so Thiele modulus is high and at that point we get the slope which is the smallest roughly half of what when the kinetics was controlling, this will happen when the particle size is small. So this is the kinetics true kinetics this is the diffusion effect or falsification because of because of diffusion limitations.

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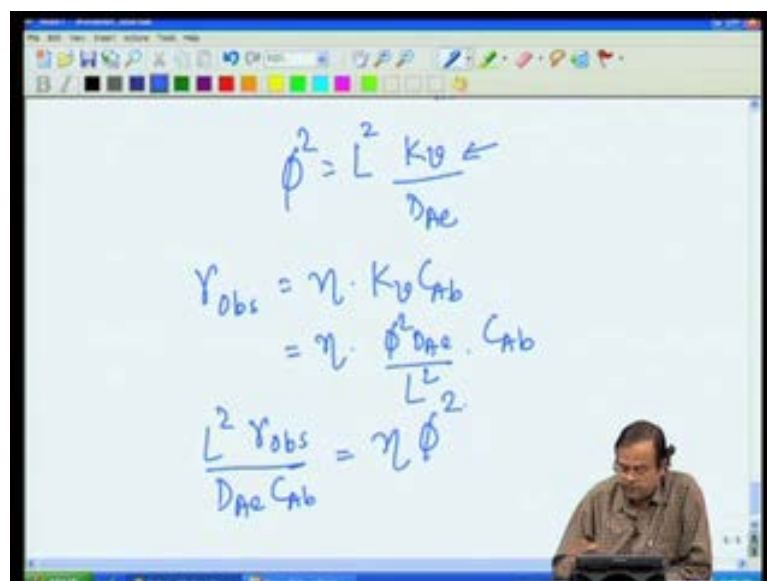
Now experimentally, how do we determine whether our reaction is in a diffusion regime or in a kinetic regime? Now qualitatively we can argue and find out in the following manner. Let us go back to our discussion and we said that we define observed rate as ηr of C_A and we also know that η versus Thiele modulus behavior is of something of

this kind. Now we also know Thiele modulus is $L \sqrt{k_v / D_{Ae}}$. So now suppose we do experiments by changing Thiele modulus. How we change Thiele modulus by choosing different value of catalyst L_1, L_2, L_3 and so on.

So instead of η versus ϕ my experimental measures as L on x axis so different values of L and I measure the rate of reaction at different catalyst half width. So I am maintaining all other condition same bulk concentration is same temperature is same and all other characteristic of catalyst are same except the half width is different. Then what kind of behavior will we get ϕ and L same that is ϕ is nothing but L times some constant. So as we change L $r_{observed}$ will change as η changes because this all conditions are same so the bulk concentration is same so rate at bulk concentration is same. So this also will be a behavior, which is very similar to η versus ϕ .

So let us say that we do experiment at two different lengths L_1 and L_2 and we say that $r_{observed}$ one by $r_{observed}$ two that is at two different length if this ratio is unity we are in this particular regime. But on the other hand if this ratio $r_{observed}$ one by $r_{observed}$ two is L_2 / L_1 is L_2 / L_1 why L_2 / L_1 because from our definition this is strictly speaking η_1 / η_2 . But η is inversely proportion to Thiele modulus so ϕ_2 / ϕ_1 and ϕ_2 / ϕ_1 is nothing but L_2 / L_1 so if we get ratio of two observed rates related to L_2 / L_1 we can say that we are in this particular diffusion based regime.

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There is another approach also by using what is called as observable Thiele modulus. So to do that let us go back to our definition of Thiele modulus for first order reaction. For first order reaction we said this is or phi square is $L^2 k_v / D A e$. Now our r observed is $\eta k_v c_{A b}$. So for k_v for k_v which we which we may not know let us put this as $\eta \phi^2 D A e / L^2$ from this particular equation into $c_{A b}$.

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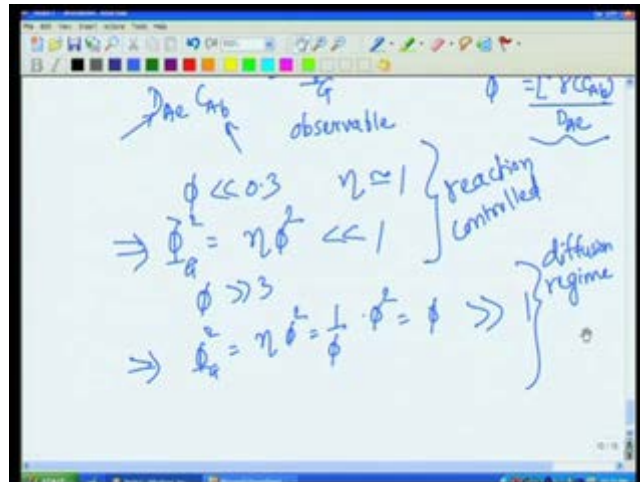
The image shows a whiteboard with handwritten mathematical equations. At the top, there is a small equation: $= \eta \cdot \frac{\phi^2 D A e}{L^2} \cdot c_{A b}$. Below it, the main equation is $\frac{L^2 r_{obs}}{D A e c_{A b}} = \eta \phi^2$. A wavy line is drawn under the denominator of this equation. Below a horizontal line, the equation is rearranged: $\frac{L^2 r_{obs}}{D A e c_{A b}} = \frac{\phi^2}{\eta} = \eta \phi^2$. The term $\frac{\phi^2}{\eta}$ is labeled as 'observable'. To the right, two definitions are given: $\phi^2 = \frac{L^2 k_v c_{A b}}{D A e}$ and $\phi^2 = \frac{L^2 r_{obs}}{D A e}$.

So let us rearrange this equation little bit $L^2 r_{obs} / D A e$ into $c_{A b}$ as $\eta \phi^2$. Now what is this quantity what is this quantity $L^2 r_{obs} / D A e$ into $c_{A b}$. This quantity is similar to our Thiele modulus why because we can write this r_{obs} see we earlier defined our true Thiele modulus as $L^2 k_v / D A e$. So let us write k_v by $D A e$ as k_v by $c_{A b}$ divided by $c_{A b}$. So if we now look at this Thiele modulus is nothing but $L^2 r_{obs} / D A e$. This quantity over here that we have got is very similar to this quantity except instead of r_{obs} in our true Thiele modulus we have r_{obs} .

Or in other words we can treat $L^2 r_{obs} / D A e$ into $c_{A b}$ as observable Thiele modulus ϕ or ϕ^2 as it is also sometimes refer to as so this is an observable quantity. Why is this observable quantity? It is observable quantity because we know exactly what the half width of catalyst is. We have observed or measured the rate of reaction we know what is the bulk concentration and we

presumably have done some diffusion characterization of the catalyst so we know $D A e$. So all these four quantities are actually observable and so this observable Thiele modulus is η into ϕ square.

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Now how will this change actually as Thiele modulus or as the experiments are conducted. So this if for example, if ϕ is less than 0.3 let us say. Then we know η is close to unity and therefore, $\eta \phi^2$ or $\frac{r_{cat}}{r_{cat,0}}$ will be very much less than one because ϕ^2 will be square of this number which is already small so that will be very much less than one. Let us say that if ϕ is very much greater than 3 what is very much is all relative but ϕ is very much greater than 3. So let me put this then what do we get for $\frac{r_{cat}}{r_{cat,0}}$? η is one over ϕ into ϕ^2 so ϕ or in other words very much greater than one for sure.

So in other words we will know whether we are working under diffusion limitations or not by conducting an experiment measuring the rate of reaction calculating the observable Thiele modulus and if its value is very small that means we are in a reaction controlled regime. If the value is very much greater than one we know that we are in a diffusion controlled regime. So this is how we can experimentally find out without knowing the kinetics of the process. The whole idea of doing this was that we earlier to calculate this Thiele modulus ϕ^2 we need to know for example, what is the true kinetics.

But to measure true kinetics we must carry experiments which are not under a kinetically controlled regime. How do we know that a priori this is how we know that that is if your

observable modulus and here there is no mention of any kinetic rate constant or any such value? These are all purely measurable quantities without knowing about the kinetics of the reaction. So if that value is less than one we have a reaction controlled regime, if that value is very much greater than one we have diffusion control regime. So you must carry out your experiments where the observable Thiele modulus is very much less than one, so that whatever is the rate of reaction that you get is a true kinetic rate and then you can find activation energy true kinetic activation energy true order of reaction or whatever may be the expression for that particular rate.

With that we will stop for today by concluding the discussion on diffusion internal diffusion and reaction for an isothermal case. We will bring in external diffusion and see how external diffusion combines with internal diffusion to create rates of reactions, which can be truly different than the true kinetics of the process. This discussion is for the next session and then we will relax the final constrain we had namely the temperature effects or the reaction is occurring under isothermal condition. We will relax that also and look at non-isothermal behavior. Thank you.