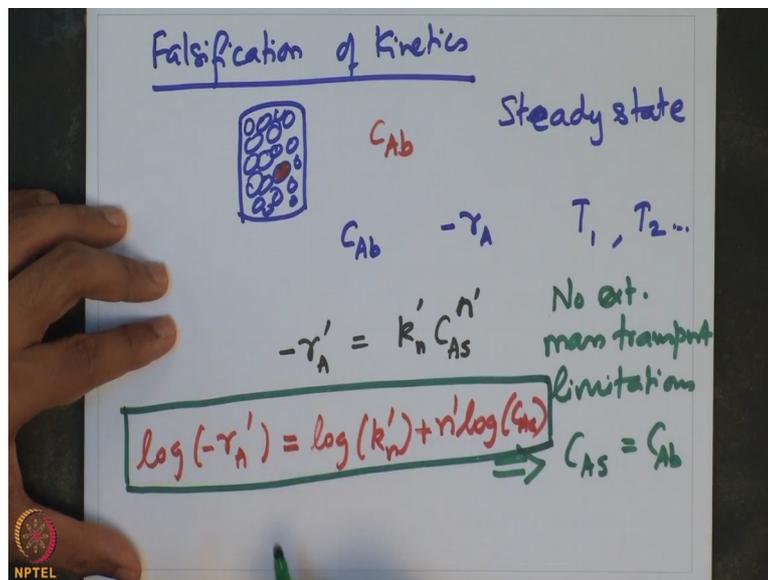


Chemical Reaction Engineering - II
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Module - 5
Lecture - 24
Falsification of Kinetics

In the last lecture, we looked at the effectiveness factor thiele modulus relationship, when the reaction may be exothermic or endothermic that is happening inside the catalyst pellet. In this lecture, we will look at an important concept called falsification of kinetics.

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So, typically, when a reaction is conducted, let us say in a differential reactor; what is it that we measure? The possible measurable quantities are the concentration of the species in bulk. Because the catalyst is very tiny particle. And in a given reactor, there are several of these particles which are packed inside. And then we pass gas through it or fluid through it. And so, what we can at best measure is the concentration of the species in bulk.

It is not possible to measure the local concentration of the species inside the catalyst pellet. It is rather challenging to measure even the concentration of the species at the surface of the catalyst pellet. So, suppose we have a reactor. And it is packed with catalyst. So, what we just observed is that, it is not possible to measure the concentration of the species inside the catalyst pellet. All we can do is, we can measure only the bulk concentration.

So, what do we typically get? We would typically observe the concentration of the species, bulk concentration of the species. Let us say, species A is undergoing reaction. And if you assume that it is at steady-state. If we assume that it is at steady-state. Then we can measure what is the rate at which the species is actually being consumed; which is a reflection of the overall rate at which the reaction is happening inside the catalyst.

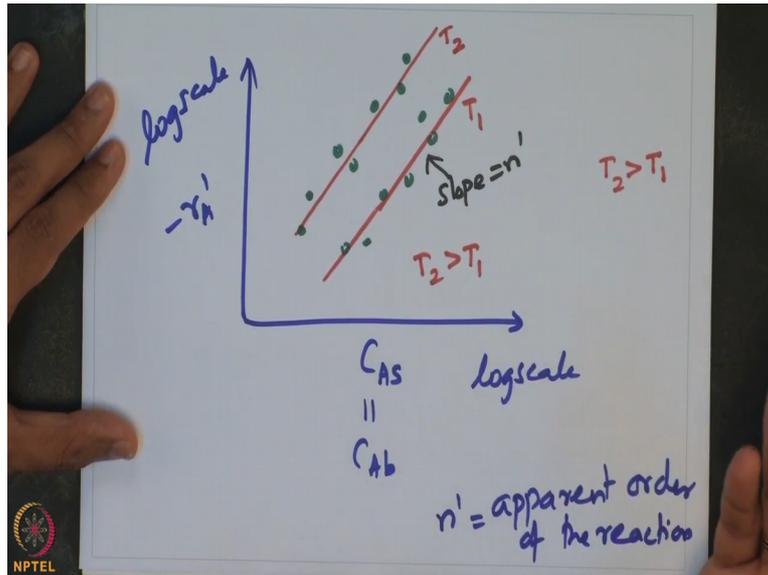
So now, if we measure this at, we can measure this at different temperatures. Let us say T_1, T_2 , so on and so forth. So now, if I plot the concentration of the species versus rate, by assuming that the rate is some rate constant k_n multiplied by, let us say the surface concentration $C_{A,S}$. And let us say that the order of the reaction, observed order of the reaction is some n or apparent order is some n .

Suppose, if we assume that there are no external mass transport limitations, which means that the concentration of the species at the surface is = concentration of the species in bulk. Which means that the time that is taken for diffusion of the species, from the bulk, all the way to the surface of the catalyst pellet is actually very fast. And therefore, the concentration of the species at the surface is almost equal or perhaps just about = the concentration of the species in bulk.

Now, what does this mean? It means that, if I measure the concentration of the species in bulk, it is as good as measuring the concentration of the species at the surface of the catalyst pellet. So, making this observation, if I now take log on both sides of this expression. So, if I take a log, natural logarithm of r_A . And that should be = log of $k_n + n$ into log of $C_{A,S}$. So, if I take a log, it is essentially $\log - r_A$, is log of $k_n + n$ into log $C_{A,S}$.

Now, I can actually, from experimental data, where I am measuring the bulk concentration, which is as good as measuring the surface concentration. I can now make a plot of the concentration of, the measured concentration of the species.

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So, I can now make a plot of the measured concentration of the species. Remember that, this is = the bulk concentration and let us say it is in log scale. And I plot $-r_A'$, which is the observed rate at which the reaction happens. What should be the nature of this curve? Look at the expression here. So, this expression is, it is like $y = m x + C$. So, it is like $y = C + \text{some slope}$. Some constant + slope into some x .

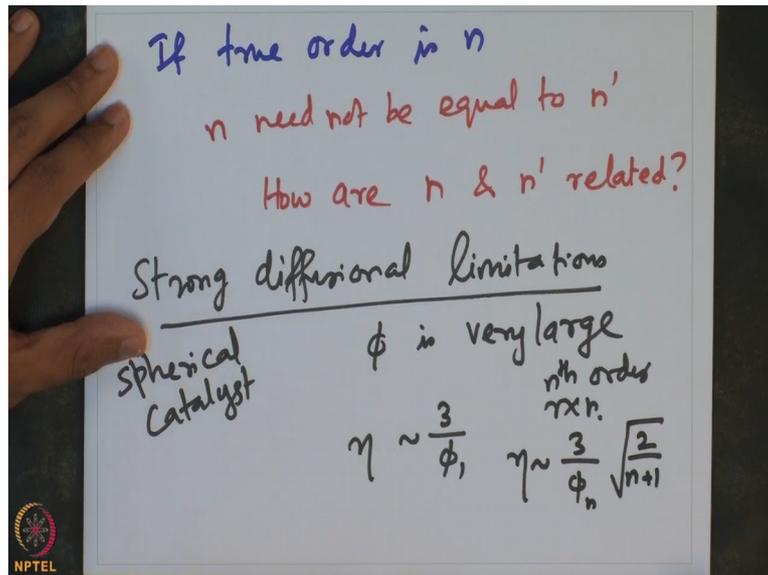
So it, clearly it is a linear relationship. So, I can now appreciate that the data should actually fall in a linear curve. And let us say, this is at temperature T_1 . Suppose if I conduct the same experiment at different temperature, let us say at temperature T_2 , which is let us say, greater than T_1 . So, what will be the nature of this curve? Where will the experimental data lie? Will it lie below the lines of temperature 1 or above the line corresponding to temperature 1?

Remember that, when temperature increases, the rate at which the reaction is increasing. So, therefore it should essentially lie for the same concentration; it should essentially lie above the; the experimental data points should essentially lie above the line corresponding to temperature T_1 . So, this should correspond to temperature T_2 . And from here, what will be the slope?

So, the slope of this line essentially will give you n' , which is the apparent order with which the reaction actually happens. So, this is the apparent order. So, n' is the apparent order of the reaction, based on the observables, which is the concentration of bulk or the concentration of the species at the catalyst pellet; in this case, because there is no external mass transport diffusion.

Now, let us try to relate these to the actual order of the reaction. So, note that the true order of the reaction is essentially the intrinsic property of the reaction. That is the order with which the, actually the reaction is happening at the catalyst surface. Now, because the diffusional limitations and other aspects are present, other resistances may be present, the order with which the reaction happens at the surface, may not be reflected in the order that we may predict, based on the observable quantities. That is, concentration of the species in bulk and in surface.

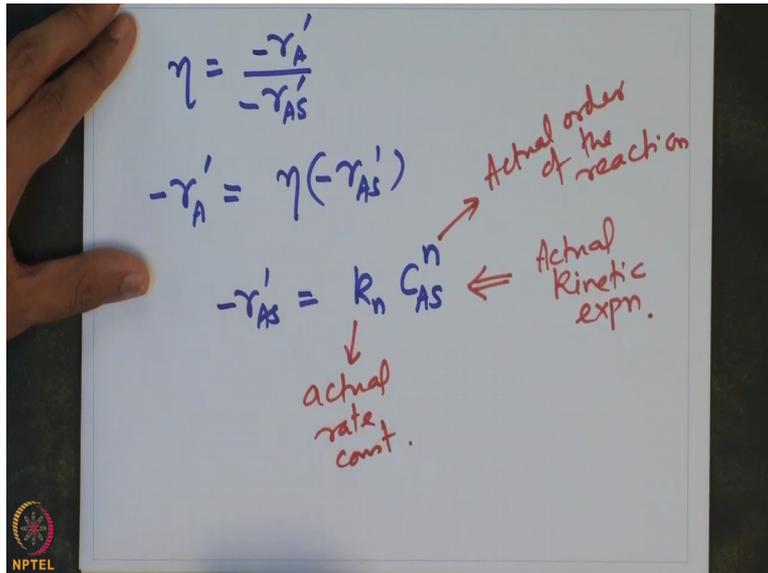
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So, if true order is n , is let us say n , and clearly, this can be different. n need not be = n prime. In fact, in strong diffusional limitation scale, it will not be = n . And so, let us see how to relate this n and n prime. So, how are, and n prime related. So, let us consider first the strongly diffusional limitation case. Let us consider the strong diffusional limitations case. Now, what is strong diffusional limitation case?

Let us say that we use the spherical catalyst pellet. In fact, this idea can actually be extended to any geometry in principle. So, if is, takes strong diffusional limitations case, which means that the thiele modulus is very large. And eta for a first order reaction let us say, it essentially scales as 3 divided by phi 1. And I can actually do the same exercise for any order reaction. So, for any n th order reaction, eta essentially scales as 3 divided by phi n into square root of 2 by $n + 1$. So now, we know what is the effectiveness factor in terms of the rate at which the reaction happens.

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So η , effectiveness factor is essentially given by $-r_A'$ by $-r_{AS}'$. We can use the fact that, effectiveness factor is a ratio of these 2 quantities. And so, from here, the observed rate $-r_A'$, which is based on the catalyst, weight of the catalyst. And that should be $= \eta$ times $-r_{AS}'$. And $-r_{AS}'$ is essentially given by the intrinsic kinetics.

So, $-r_{AS}'$ is essentially given by some k_n , which is the true rate constant. That multiplied by the surface concentration to the power of n . So, this is the intrinsic kinetics. This is the actual kinetics. And n is the actual order of the reaction. And k_n is the actual rate constant for that particular case. Now, if you substitute this here, if you substitute this expression here, we will see that $-r_A'$ is essentially η into $-r_{AS}'$; which is $= \eta$ into $k_n C_{AS}^n$. But we know that η is essentially, can be expressed as $\frac{\sqrt{2n+1}}{2}$.

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$$\begin{aligned}
 -r'_n &= \eta - r'_{As} = \eta k_n C_{As}^n \\
 \eta &= \frac{3}{\phi_n} \sqrt{\frac{2}{n+1}} \\
 -r'_n &= \frac{3}{\phi_n} \sqrt{\frac{2}{n+1}} k_n C_{As}^n \\
 &= \frac{3}{R \sqrt{\frac{k_n C_{As}^n}{D_e}}} \sqrt{\frac{2}{n+1}} k_n C_{As}^n
 \end{aligned}$$

So therefore, eta is = 3 by phi n into square root of 2 by n + 1. So, substitute in this we find that -r A prime is essentially = 3 by phi n into square root of 2 by n + 1 into k n into C A S to the power of n. Now we can substitute the expression for phi n. What is phi n? phi n is 3 divided by R into square root of k n divided by the effective diffusivity. And that multiplied by square root of 2 by n + 1 into k n into C A S to the power of n.

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$$\begin{aligned}
 -r'_n &= \frac{3}{R} \sqrt{\frac{2}{n+1}} \sqrt{D_e} \sqrt{k_n} C_{As}^n C_{As}^{\frac{1-n}{2}} \\
 &= \frac{3}{R} \sqrt{\frac{2}{n+1}} \sqrt{D_e} \sqrt{k_n} C_{As}^{\frac{2n+1-n}{2}} \\
 &= \frac{3}{R} \sqrt{\frac{2}{n+1}} \sqrt{D_e} \sqrt{k_n} C_{As}^{\frac{n+1}{2}} \\
 \text{if } n' &= 1 \quad n = 2 \times 1 - 1 = 1 \quad n' = \frac{n+1}{2} \\
 &= k'_n C_{As}^{n'} \quad \underline{\underline{n = 2n' - 1}}
 \end{aligned}$$

So, we can further simplify this as -r A prime is = 3 by R, into square root of 2 by n + 1. And that multiplied by D e, square root of D e into square root of k n into C A S to the power of n. So, note that, we missed out C A S. So, it should essentially be, that into C A S to the power of n - 1. That into C A S to the power of 1 - n by 2. So, that is = 3 by R into square root of 2 by n + 1 into square root of D e into square root of k n into C A S to the power of n + 1, 2 n + 1 - n by 2.

And that is $= 3$ by R , square root of 2 by $n + 1$ into square root of D e square root of k n into $C A S$ to the power of $n + 1$ by 2 . Now, the observed rate, essentially, we expressed it as, let us say, some rate constant into $C A S$ to the power of n prime. So, this is the apparent order with which the reaction is happening, based on the surface concentration. And this is the apparent rate constant.

So now, comparing the expression we got based on the effectiveness factor for the overall rate at which the reaction happens, versus what is observed. We can clearly see that n is $= n$ prime which is the apparent order with which the reaction is observed to happen. That is $= n + 1$ by 2 . Where n is the true order of the reaction. So, if I now conduct an experiment and I observe the concentration of the species as a function of the rate at which the reaction is happening at that concentration, then I can estimate the apparent order with which the reaction happens.

And I can use this expression to find out what is the actual order with which the reaction; what is the true order of the reaction. So, if I know n prime, then n is essentially given by 2 into 2 or 2 into n prime $- 1$. So, if I see that the reaction is actually first order, let us say in the observed kinetics. If the observed kinetics or the based on the surface concentration that is measured, if I see that the observed order with which the reaction happens is 1 , then the true order is essentially given as n is $= 2$ into $1 - 1$, if n prime is $= 1$; which is essentially $= 1$.

So, if it is a first order reaction in the observed rate versus the concentration of the species, then the actual order is also $= 1$. But, let us take another example, where if n prime is $= 2$, then the actual true order of the reaction is essentially given by 2 into $2 - 1$; which is basically 3 . So, it is a third order reaction which happens inside the catalyst pellet. But, because of the diffusional limitations, strong diffusional limitations, the actual order that is observed based on the experimental data which is called as the apparent order, is essentially reduced to 2 .

And so, therefore, there is a falsification of the order that is actually be seen based on the experimental data. So, this aspect is what is called as falsification of order, which is 1 component of the kinetics. So, let us look at what happens to the activation energy.

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Falsification of activation energy

$$\begin{aligned}
 r_A &= \frac{3}{R} \sqrt{\frac{2}{n+1}} \sqrt{D_e} \sqrt{A_T \exp\left(-\frac{E}{RT}\right)} C_{AS}^{\frac{n+1}{2}} \\
 &= \frac{3}{R} \sqrt{\frac{2}{n+1}} \sqrt{D_e} A_T^{\frac{1}{2}} \exp\left(-\frac{E}{2RT}\right) C_{AS}^{\frac{n+1}{2}} \\
 &= k_n' C_{AS}^{n'} = A_{T,app} \exp\left(-\frac{E_{app}}{RT}\right)
 \end{aligned}$$

$E_{app} = \frac{E}{2}$

$A_{T,app} = \frac{3}{R} \sqrt{\frac{2}{n+1}} \sqrt{D_e} A_T^{\frac{1}{2}}$

So, there is also falsification of activation energy too. How do we see this? – r_A is essentially given by $\frac{3}{R}$ into square root of $\frac{2}{n+1}$ into D_e into; now I can write my rate constant as some frequency factor. Let us say that, this is my A_T , which is the intrinsic frequency factor. That multiplied by exponential of $-\frac{E}{RT}$, into C_{AS} to the power of $\frac{n+1}{2}$. Now, I can rewrite this as, $\frac{3}{R}$ into square root of $\frac{2}{n+1}$ into square root of D_e into A_T to the power of half, into exponential of $-\frac{E}{2RT}$, into C_{AS} to the power of $\frac{n+1}{2}$.

So now, if I now equate this to the observed kinetics, based on the experimental data. So, that is essentially given by some k_n' into C_{AS} to the power of n' . And I can write this also in terms of the frequency factor and activation energy. So, let us say that, this is the apparent frequency factor. That multiplied by exponential of $-\frac{E}{RT}$, into C_{AS} to the power of n' .

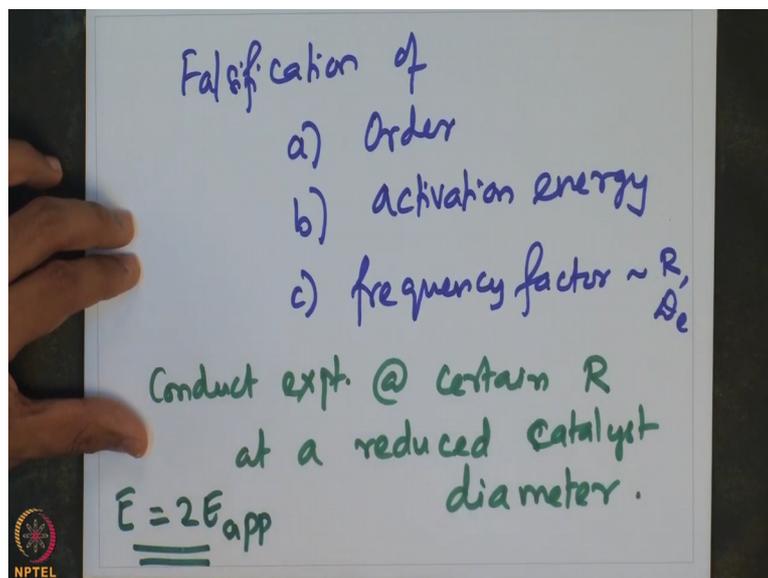
So, simply by comparing these, we can see that the activation energy is not the same; whatever observed activation energy based on experimental data, is not same as the intrinsic activation energy. So, what is it? So, E_{app} . So, if E_{app} is the observed activation energy. So, E_{app} is the observed activation energy, based on experimental data, is actually = half of the actual activation energy.

Now, this has a strong implication in terms of the design which we will see in a few moments. And not just that the frequency factor $A_{T,app}$, which is based on the experimental data, is essentially given by $\frac{3}{R}$ into square root of $\frac{2}{n+1}$ into square

root of D_e into $A T$ to the power of half. So, the falsification of activation energy happens. And it is, because of the diffusional limitations, the apparent activation energy that is measured based on experimental data, is essentially half of the actual activation energy.

On the other hand, the frequency factor that actually estimated based on experimental data, would also be a scale which, will also get scaled up. And in fact, it is proportional only to the square root of the actual frequency factor that is intrinsic to the reaction system that is being considered. So therefore, there is falsification of all 3 aspects of the kinetics.

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So, there is falsification of, a) the order, order of the reaction; b) the activation energy and there is the frequency factor which is actually dependent. And in fact, the frequency factor falsification is actually a function of the radius and the diffusivity of the, effective diffusivity of the species and the radius of the catalyst pellet. Now, why is this important? Suppose, let us say we conduct the reaction at a certain particle diameter R and if we change the diameter of the particle, let us say.

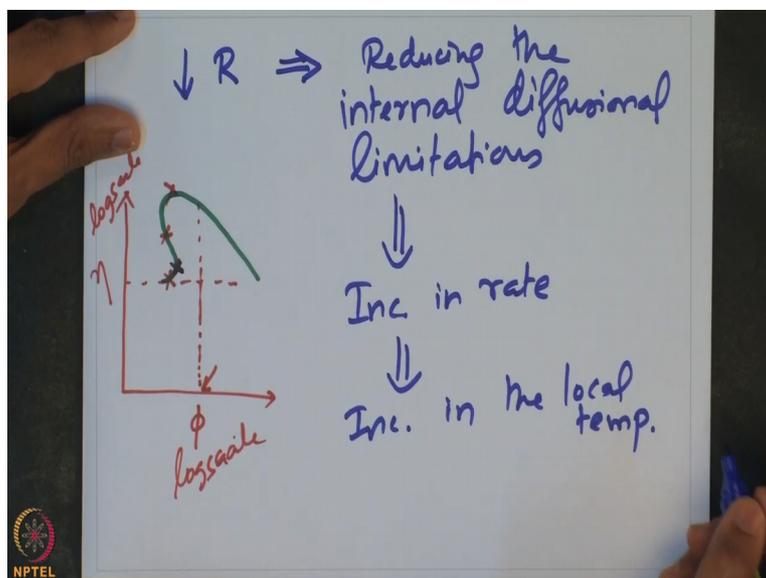
We decrease the particle diameter. So, suppose let us say that we conduct experiment @ certain particle diameter R . And then we suddenly decide to actually reduce the particle diameter. So now, we conduct experiments at a reduced catalyst diameter. What will happen? So, if we now reduce the catalyst particle diameter, then the diffusional limitations; remember that the ϕ^2 which is the thiele modulus is a function of R^2 .

So, if I now reduce my radius, then I am actually reducing ϕ square as well. So, if I reduce my ϕ square, then the species is readily available right inside the catalyst pellet, for the reaction to happen. Now, the apparent activation energy is only half of the actual activation energy. And so, if I now reduce it, then we would be fooled in terms of the, what will be the rate at which the temperature will increase.

Because the rate is now sensitive high, more sensitive to temperature. Because the actual activation energy E , is actually twice the estimated activation energy based on the observed kinetics, observed data. So, the actual true activation energy is essentially twice that of the apparent activation energy. And so, if I now reduce the diameter, we actually remove the diffusional or reduce the internal diffusional limitations.

And we allow the reaction to happen actually faster and it is not limited by diffusion. And more species is available at the catalyst surface for the reaction to happen. And because it is an exothermic reaction, let us say, the temperature increase is going to be significantly higher. So, if the temperature increase is significantly higher, then unfortunately, there is a potential possibility that it might actually cause a runaway of the reaction.

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So, if you decrease the radius catalyst particle, then that will actually lead to reducing the internal diffusional limitations. And that might actually lead to increase in the rate. Because more species is now available for the reaction. And that will actually lead to increase in the local temperature. And remember that we saw in the last lecture, that when there is a, an

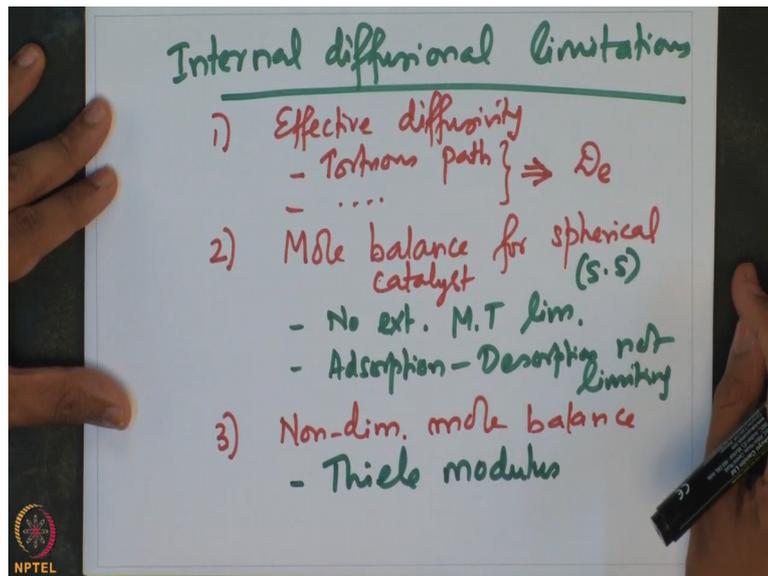
exothermic reaction then it is possible that, possible to have a effectiveness thiele modulus in log scale, let us say.

For a specific value of beta, for certain specific value of beta, you can have what is called as a multiple steady-states possible. You can have 3 steady-states possible, for a given value of thiele modulus. And if this radius that we have chosen, actually falls in this thiele modulus. Suppose, let us say that we initially operate at this radius, at this thiele modulus. And suddenly if we reduce the radius of the catalyst pellet, we may actually fall in this regime here.

And which might actually lead to a situation where there may be a higher effectiveness factor which may be available. Now, when we reduce the size of the particle, we may even land up in this particular location here; which is basically an unstable state, which will lead to a sustained increase in the rate at which the reaction happens. And that might actually lead to increase in the local temperature of the catalyst pellet.

And that may or may not be desirable. For example, if the local temperature suddenly increases very largely. And it reaches, let us say the melting point of the catalyst itself, then what happens is that the catalyst is actually sacrificed. So, it is not desirable to have an uncontrolled increase in the temperature. So therefore, understanding the correct; what is the true order and what is the true activation energy, has a strong implications in terms of the overall design of catalytic reactors. So, what we, let us summarise what we have seen in several lectures now.

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So, we looked at internal diffusional limitations in several lectures. And we particularly looked at what is effective diffusivity. We looked at the concept of effective diffusivity, where we understood the presence of tortuous paths of the pores that may be present. There may be interlinking of pores and so on and so forth. And we tried to see how to capture all of these in a combined quantity called effective diffusivity.

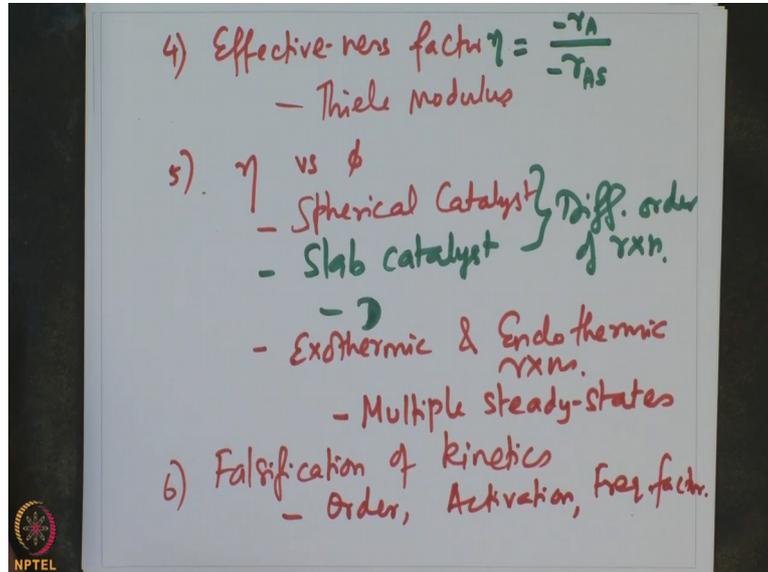
In fact, one could model the diffusion process in every pore which is present. But that is a very futile exercise because there are so many pores that are present. So, it might actually be worthwhile to define an effective diffusivity and model the whole system, the whole catalyst together as 1 piece, by assuming both void and the solids actually together. And so, we define the effective diffusivity, which actually helps in modelling or characterising the reaction, taking the whole catalyst, putting both voids and the solids together and modelling them together.

Then the second aspect we looked at, there is a second aspect where we essentially wrote the mole balance, for spherical catalyst. And here we actually assumed that there are no external limitations, external mass transport limitations. We even assumed that the adsorption desorption is not limited. Adsorption desorption is not limiting. It is only the surface reaction that is actually limiting.

And we wrote the mole balance for steady-state conditions. And then, while doing this, we defined, we non-dimensionalized the mole balance. And we defined an important quantity characterising parameter called thiele modulus, which essentially characterises the rate at

which the reaction happens due to its intrinsic kinetics versus the rate at which the species would diffuse through the catalyst pellet. And then, the next aspect we looked at is, what is called as an effectiveness factor.

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And we specifically looked at the relationship between effectiveness factor and thiele modulus. And we said that the effectiveness factor is essentially, the rate at which the actual reaction happens at the surface, divided by the rate at which the reaction happens if the conditions everywhere inside the catalyst is actually that of the surface conditions. That is, both concentration and temperature.

We looked at the relationship between eta and thiele modulus for the spherical catalyst. We looked at what is the eta versus phi relationship for slab catalyst and for different orders. Each of these, we looked at different orders, different order of reaction. And in fact, one can extend the same principal for cylindrical catalyst as well. And then, we also looked at an important case of the eta versus phi for exothermic and endothermic case, exothermic and endothermic reactions.

And we observed an important characteristic feature which is basically the presence of multiple steady-state solutions, multiple study-states. And lastly, we looked at the falsification of kinetics, particularly the order of reaction, activation energy and the frequency factor. So, with this we complete the major aspects of the internal diffusional limitations. From the next lecture, we will move on to the external diffusional limitations.

If there is mass transport limitation, that is, there is diffusional limitations outside the catalyst pellet, for species which is diffusing from bulk to the surface of the catalyst pellet. Then how do we characterise it? How do we quantify it? And how does that affect the overall rate of the reaction? Thank you.