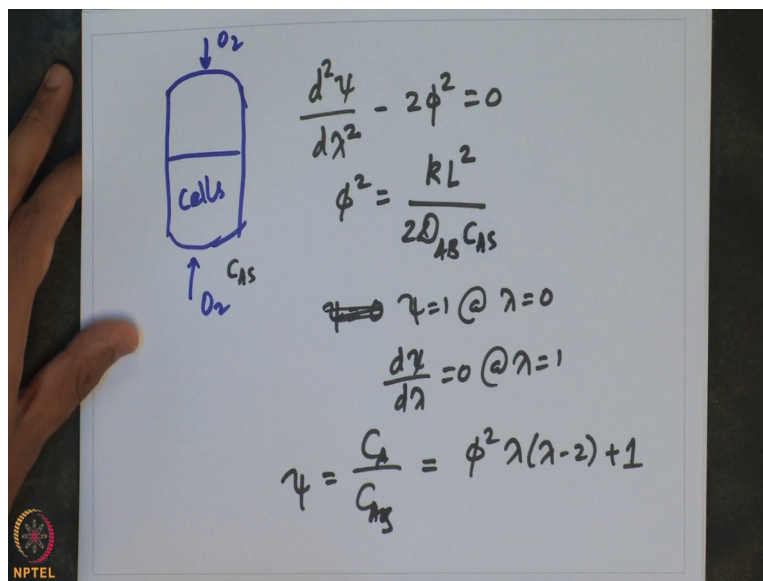**Module - 5**
Lecture - 23
Internal Effectiveness Factor III: Exothermic and Endothermic reactions

In the last lecture we start by looking at the example of cells which are present in hydrogels, which could be used as a replacement for cartilages. So, we, this could be posed as a diffusion reaction problem.

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So, the problem is, we had a hydrogel; which may be having cells inside. And in order for the cells to survive, the oxygen may be supplied from both sides. And so, we wrote the model equation in the last lecture and non-dimensionalize it and found the solution. So, the dimensionless model equation is d square psi by d lambda square – 2 phi square = 0, where phi square is essentially given by k into L square for a 0 order reaction into C A S.

So, the boundary conditions for these are psi = 1 @ lambda = 0. And d psi by d lambda = 0 @ lambda = 1. And we looked at the solution, the solution of which is essentially given by psi = C A by C A not, C A S which is the surface concentration or the concentration at this location where the oxygen goes in. And that should be = phi square lambda into lambda – 2 + 1. So now, let us look at some numbers here.

And in fact, we said that this expression is not valid for all situations. In fact, it is valid only for certain values of phi square. So, if we put some numbers now. So, let us try to put some numbers.

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Suppose, if the rate constant for the 0 order reaction k is essentially given by 10 power – 3 moles per decimetre cube hour. And let us say that the concentration C A S is essentially given by 0.2 into 10 power – 3 moles per decimetre cube. And these are the numbers which are actually available in the example problem, given in Fogler page 824, 4th edition. And if the equimolar counter diffusivity of oxygen is given by 10 power – 5 centimetre square per second, which is essentially = 3600 into 10 power – 5 centimetre square per hour.

So, one can actually calculate phi square which is given by k into L square by 2 D A B into C A S. That is = 70 centimetres – 2 into L squared. We still do not know what is length of the hydrogel is. It is the half length of the hydrogel. So, suppose let us say if you want to find out. If you pose a question that, what should be the, what should be L if oxygen is completely consumed? What is the value of L if oxygen is actually completely consumed?

So, how do we proceed? So, we know that the solution for this equation, for this problem, is essentially given by psi, which is phi square lambda, lambda – 2 + 1. And if the oxygen has to go to complete consumption, then essentially it means that the complete consumption of O 2 happens at, complete consumption of O 2 is @ lambda = 1. So, suppose let us say that if it is complete consumption of the oxygen, then it must be essentially at lambda = 1. So, the first step is, can we find out what is phi square at lambda = 1. So, let us do that exercise.

So now, if we set psi = 1, for complete consumption, psi @ lambda = 1, should essentially be = 0. Because it is completely consumed. And therefore, psi which is a dimensionless concentration, it is essentially, must be = 0. So, from here, if we set psi = 0, is = phi square into lambda is 1 into lambda – 2 + 1. And so, from here we will see that 0 is = – phi square + 1 or phi square is essentially = 1.

But we know that phi square is, for the given set of conditions or the numbers, phi square is essentially given by 70 centimetre – 2 into L square. So, now we can plug this in here and we can find out what L square is? So, L square is essentially 1 by 70. And which means that L is = 0.12 centimetres. Now, if you take the, if you recall the problem that we are looking at, we are essentially looking at a problem where the oxygen is being used by the cells for its survival.

So, complete consumption of oxygen is actually not a desirable situation, because if it is completely consumed, then the cells which are actually present at lambda = 1, would essentially die. So, therefore a better condition would be, what if the oxygen consumption is only half consumed. That is, if it is only partially consumed.
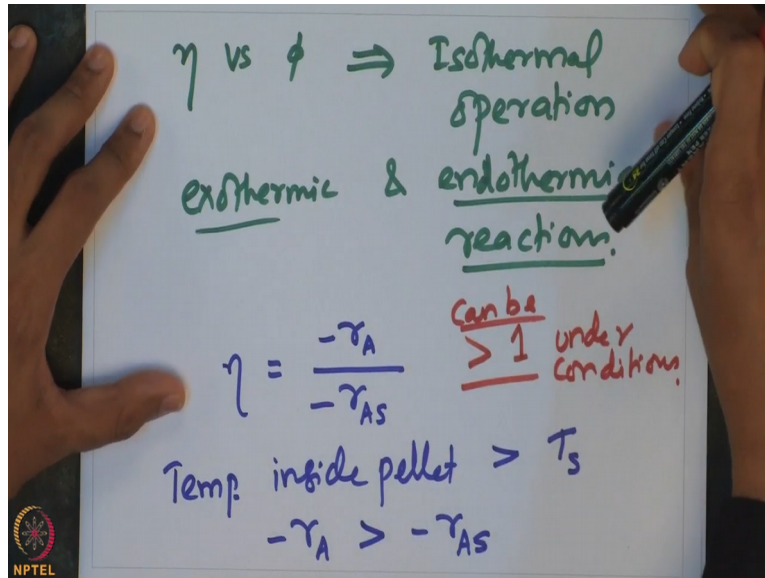
So, if we assume that, psi = 0.5 @ lambda = 1. That is, the oxygen is only 50% consumed. Whatever is coming into the hydrogel, only half of it is consumed; as oxygen goes from the place, location where the oxygen is entering the hydrogel. That is at lambda = 0, all the way up to lambda = 1. So now, the question is, what is the value of L? For this situation, what should be the height. What should be the height of the hydrogel?

So, we can easily find this using the same procedure. So, psi is 0.5, is = phi square into lambda is 1, 1 − 2 + 1. And so, that is = 0.5 = − phi square + 1. Or phi square is = 0.5. So, from here, we can actually find out that L is essentially given by, square root of phi square by 70, which is essentially square root of 0.5 by 70. And that is essentially = square root of 0.5 by 70, which is certainly much smaller than L when psi is = 0.

So, this actually provides a way by which we can actually estimate. So clearly, when psi = 0.5, which is partial consumption of oxygen, the length of the hydrogel required should be smaller than the length of the hydrogel which is required for complete consumption of oxygen. So, all the internal effectiveness factor that we have seen so far, versus phi we have seen so far.

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η vs ϕ $\Rightarrow$ Isothermal operation

exothermic & endothermic reaction.

$$\eta = \frac{-r_A}{-r_{AS}}$$

Can be ≥ 1 under conditions.

Temp. inside pellet $> T_s$

$-r_A > -r_{AS}$

They are all for isothermal conditions. They are all for isothermal operation. But in fact, the concept of effectiveness factor is valid even for non-isothermal operations. So, in fact, it can, it is applicable even for exothermic and endothermic reactions. So, suppose we look at the definition of effectiveness factor, which is the rate at which the reaction is actually happening in the catalyst pellet, divided by the rate as though the concentration or the conditions everywhere inside the catalyst pellet is that of the surface conditions.

That is the concentration of the species which is present at the surface and the temperature of the species at the surface. Now, if it is an exothermic reaction, then it is possible that the temperature inside the pellet, is likely to be higher than the temperature at the external surface of the pellet.

So, if the temperature of the, temperature inside the pellet is greater than the temperature at the surface, then it is likely that the rate of reaction inside the catalyst is likely to be larger than the rate at which the reaction would happen if the conditions everywhere in the pellet is that of the surface conditions. So, it tells out that, in this case, because of this observation that the actual reaction rate can be larger than that of the reaction rate if the conditions inside the catalyst pellet were that of surface conditions.

The ratio of these 2 rates are expected to be larger than one. So clearly, for the case of exothermic and endothermic reaction, this can be larger than 1. It can be larger than 1. It is not that it is larger than 1 always but it can be larger than 1 under certain conditions. Now, suppose we sketch the eta versus phi behaviour for such kind of systems.
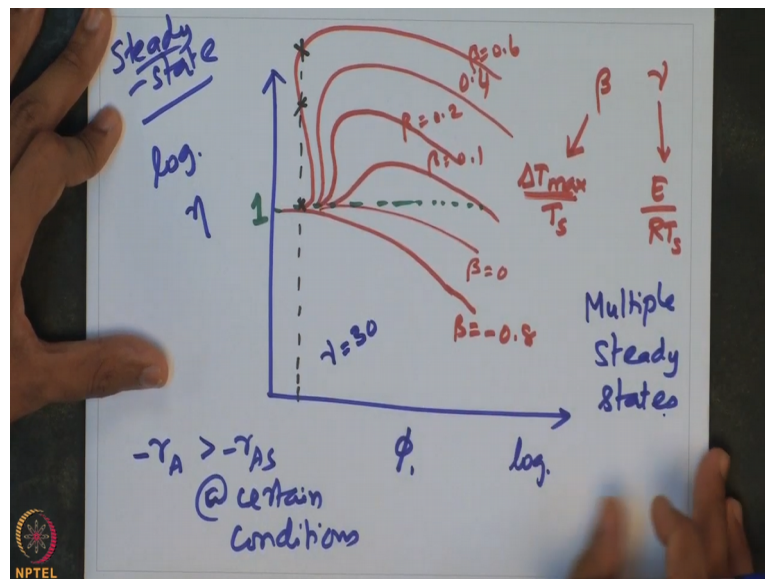
So, suppose this is the, this is phi. That is, let us say, and let us say that we sketch it in log scale again. We sketch it in the log scale. Then we will see that, let us say that eta = 1; is essentially here. And it turns out that the effectiveness thiele modulus relationship for this kind of a system is actually a strong function of 2 important parameters called beta and gamma.

Where beta is essentially given by the delta T max, which is the maximum temperature difference between the temperature inside the pellet and the surface temperature. That divided by the surface temperature itself. And this gamma is essentially dimensionless activation energy evaluated at the surface temperature. So, if I now sketch the effectiveness thiele modulus relationship between these, for exothermic or endothermic reactions, then we will see that, for beta =, this is beta = – 0.8.

And then we can have for a situation where the beta is = 0. So, that will be the graph for beta = 0 and for beta = 0.1; that will be for beta = 0.1. And then, for beta = 0.2; that will be for beta = 0.2. And then we can have for beta = 0.4. This will be for beta = 0.6. So, what it essentially signifies is that, depending on the values of beta and gamma, one can actually have a situation where the effectiveness factor eta can actually be larger than 1.

And this is because we observed, this is simply because we observed few moments ago that the rate of the reaction inside the catalyst pellet can be greater than r A S under, @ certain conditions. Now, an important observation here is that for all, for certain values of beta, let us

say 0.2, 0.4 and 0.6. If I now fix a specific value of phi, let us say in this range here, then I will see that;

Suppose I look at what is the effectiveness factor for this value of thiele modulus, then I can see that the, for specified value of phi, you can actually locate 3 points on this graph here. Which means that there are 3 possible effectiveness factor values for a specified value of phi. And that is only in a particular range of thiele modulus. So, this property of finding 3 possible effectiveness factor for a specific thiele modulus.

And remember that we are actually looking at a steady-state system. We are looking at a steady-state problem. So, this aspect of finding 3 different possible effectiveness factor for certain values of the system parameters, for a given thiele modulus, is actually what is called as, multiple steady-state solutions. Now note that, this is for specific example where gamma is = 30.

So, what it suggests is that, there are 3 possible steady-states for a specified value of the thiele modulus that actually we are looking at for this kinds of a system. And this is a very special property of the case of exothermic or endothermic reactions, for case where the temperature actually plays a role in the reaction rate. Now, let us look at what this multiple steady-states really mean. So, let us zoom up a little bit.

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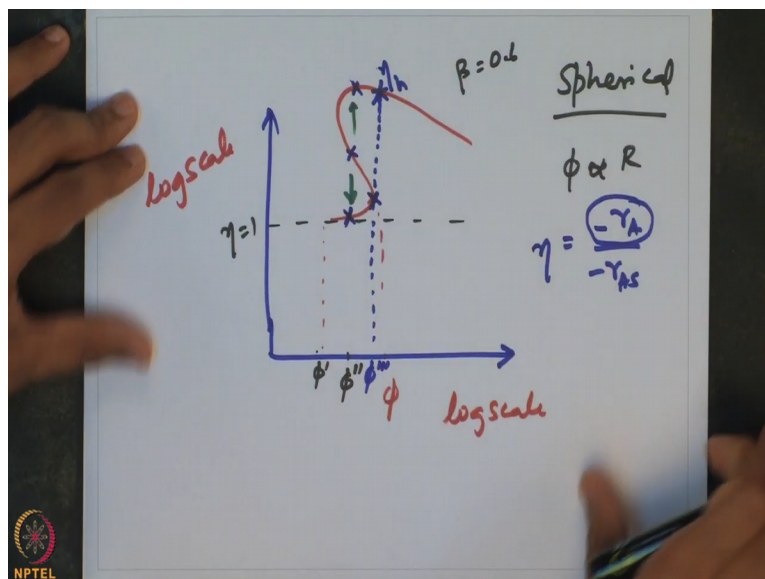
And let us plot only the range. Let us zoom up this region here and specifically look at what is happening in this location. So, let us say that eta = 1 is here. And we have for beta =, let us

say 0.6. We have a situation where the effectiveness thiele modulus graph, essentially looks like this. In this range of, suppose let us say we plotted in this range. So, this is for beta = 0.6. And note that this is log scale. And this is also log scale.

So now, if I fix my thiele modulus, let us say at this value; let us say I start with this value of thiele modulus. Let us call this is phi 1. And now, I can actually change my thiele modulus by changing the radius of the catalyst pellet. Suppose, if it is a spherical catalyst pellet, spherical catalyst pellet, then by changing the radius of the catalyst pellet, which means I now use a different size catalyst pellet.

And I can actually change the thiele modulus that actually is for that particular system. Because phi is actually proportional to the radius of the catalyst pellet. It is actually proportional to the radius of the catalyst pellet. And therefore, I can actually change the radius and I can increase the radius or I can use a slightly larger catalyst pellet. And so that, let us say that I choose a catalyst pellet and where the thiele modulus is this value.

So now, the effectiveness factor is actually at this location here. And so now, if I operate a different values of phi; now depending upon the initial conditions I choose for starting the reactor, the steady-state may be present in this location or the steady-state may be present in the other steady-state. So, there are, remember that there are 3 steady-states here. So, depending upon how I start the reactor and reach a steady-state.

I may actually, the reactor may operator at this steady-state or this steady-state. So, it turns out that the middle steady-state is actually unstable. And even if I start here, I would essentially land either into this side, either into this steady-state or into this steady-state. Now, let us look at a situation where the reactor is actually operated at, let us say, this value of phi. Let us call this is as phi triple prime.

And let us say that we operate at this value of phi. Now, what will happen? Because this value is actually a turning point here. Because the effectiveness factor is actually; so, if there are any perturbations that are actually present in the reactor, then what happens is that, this point is actually unstable. And so, the reactor would actually jump and land into this steady-state. Now, what does that mean?

If, let us say that the effectiveness factor is increasing. We observed that the effectiveness factor is basically given by r A by – r A S. And if effectiveness factor increases for a given conditions, for a specified surface concentration surface temperature, then it automatically implies that the reaction rate is actually increasing. Now, if I now operate under this value of thiele modulus, let us say some value of radius of the catalyst pellet.

Then the temperature inside the catalyst pellet would actually increase in an uncontrollable fashion, in such a way that the effectiveness factor reaches this particular value or the value somewhere, let us say here. Let us say I call this as eta h, the highest value of effectiveness factor for this thiele modulus. It will continue to increase until it reaches this particular effectiveness factor, which means that it is a much higher rate at which the reaction is happening inside the catalyst pellet.

And this has a strong implication in terms of the design. Because, if the catalyst which we use, actually has a certain properties. And the temperature with that can be withstood by the catalyst also is limited. So, if there is a possibility of operating in this particular thiele modulus, then one has to always pick a catalyst, such that it can withstand this particular rate, this particular temperature that may be achieved for achieving this particular rate at which the reaction is happening.

Otherwise, there will be a detrimental effect on the catalysts, which could actually cause deactivation of the catalyst and which will strongly affect the productivity. So therefore, observing the presence of these 3 steady-states and taking a decision as to where it has to be operated is critical. It may be required that for increasing the productivity, one may want to operate the reactor under the highest possible effectiveness factor for a given thiele modulus.

Because, that is going to have a very high rate at which reaction can happen. And that will actually increase the productivity, which directly controls the economy of that particular industry. So clearly, a decision has to be made as to where one has to operate. And depending upon where one has to operate, one has to actually take all these factors into design and ensure that the catalyst and the reactor material could withstand the temperature that the system might reach, if it is operated under this particular effectiveness factor well.

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So, let us look at some examples here of this, what could be the value of this dimensionless parameter called beta, which is basically the ratio of the maximum temperature difference divided by the surface temperature. And that is essentially given by – delta H reaction. Clearly, this is controlled by the heat liberated due to reaction, multiplied by the effective diffusivity, into the concentration of the species at the surface, divided by the conductivity into T S.

And this typically has a wide range for, let us say exothermic reactions. And this is approximately about 0.025 for vinyl chloride synthesis, from HCL and acetone. And the value of corresponding value of gamma is approximately 6.5. Now, for the case of ammonia synthesis, gamma is essentially = 29.4 and beta is approximately 6 into 10 power – 5. And the thiele modulus typically used is about 1.2.

And for this case the thiele modulus that is used is approximately = 0.22. So, if you look at the numbers, if you stare at the numbers, there are some interesting aspects that one can observe from here. So, the maximum temperature rise that is actually achieved at this value of beta would likely to be very small. Because, delta T max is essentially the maximum temperature inside the pellet, – the surface temperature.

So, if that value is very small, then we can expect that the maximum temperature that is reached inside the pellet, is not going very different from that of the surface temperature. If it is 6 into 10 power – 5, it is even more smaller. So, the fractional difference in terms of the

maximum temperature difference which is possible is clearly a function of the value of beta that is actually chosen.

So, let us summarise what we have learnt today. So, what we have seen is that, we looked at the possibility of effectiveness thiele modulus relationship for the case where is the reaction might be exothermic or endothermic reaction. And the most important aspect we observed is that, the effectiveness factor can actually be larger than 1, owing to the fact that, the rate at which the reaction happens inside the pellet, which is, which depends upon the local temperature can be much larger than that of the rate, if the reaction is actually happening or conducted at the surface conditions.

That is the concentration at the surface and temperature at the surface. In the next class, we will extend all the aspects we have learnt in, to look at what is called as falsification of kinetics. Thank you.