Advanced chemical Reaction Engineering

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Lecture - 12
Catalyst Deactivation - II

We go on with advanced reaction engineering time dependent operations. We said last time when we met that there are several situations where we have to deal with time dependent operations. Of course, the classic example would be a batch reaction where we are concerned with how long it takes by to the process to get completed the level that you and I require. The other situation would be that you know you have a process which would not start up in the continuous process will take some time for it to stabilize. So, start up of a process also is a time dependent operation. A third situation which you also looked at is a case where this process running under steady state, but it becomes time dependent, because the catalyst tends to deactivate. And the deactivation brings the time dependent element which we must appropriately take in to account. So, the process runs as per our requirements we did speak about this briefly by this 1 to run through this once again just to emphasize a ((Refer Time: 01:23)).

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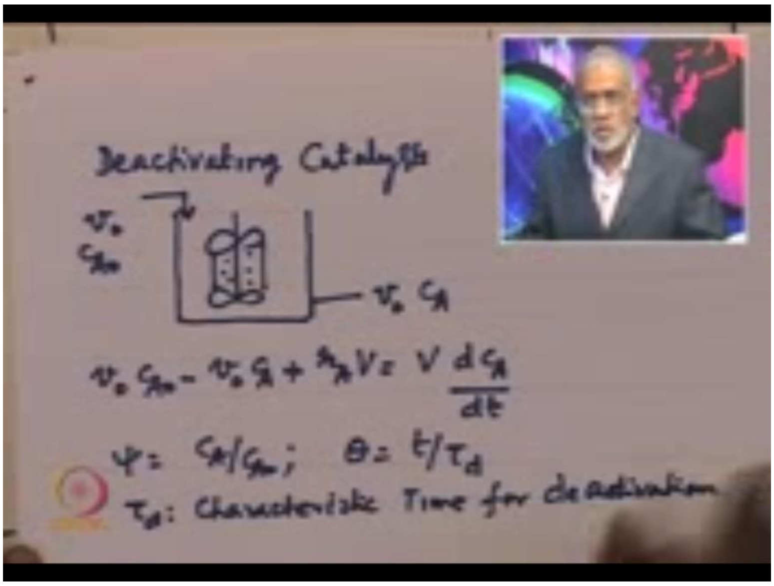

Deactivating Catalysts

$v_0 C_{A0} - v_0 C_A + r_A V = V \frac{dC_A}{dt}$

$\psi = C_A/C_{A0}$; $\theta = t/\tau_d$

τ_d: Characteristic Time for deactivation

So, we are looking at deactivating catalyst. So, we are looking at deactivating catalyst and what do you like to do is quickly get a view for how we handle the deactivate catalyst for which we require some understanding of what we call is deactivation kinetics. How do we get some information on deactivation kinetics? Other example there are many ways it can be done example is let us say we have a catalyst which is sitting on a spinning basket. And to which let say you have material coming in at some and material going out at some, so it under going some reaction. You want to understand what is the kinetics of this deactivation. So, to just to understand this and just writing the material balance input output then you have generation equal to accumulation. This is something that you and i have been writing for a very long time, so it is nothing very new.

Suppose I say that this c A by c A naught on the if I also say that time theta divided by tau d where the tau d is the characteristic time for deactivation what this meant by characteristic time we can understand it like this. Let us say catalyst has the life of let say 1 year then it is characteristic time is 1 year. So, essentially it is a time which is characteristic of the process and I take it as tau d. So that we try to understand this whole thing with respect to the characteristic time of the process let us see what it gives us. So, let me simplify and write this as is finally, elementary, so we will not go through all the steps.

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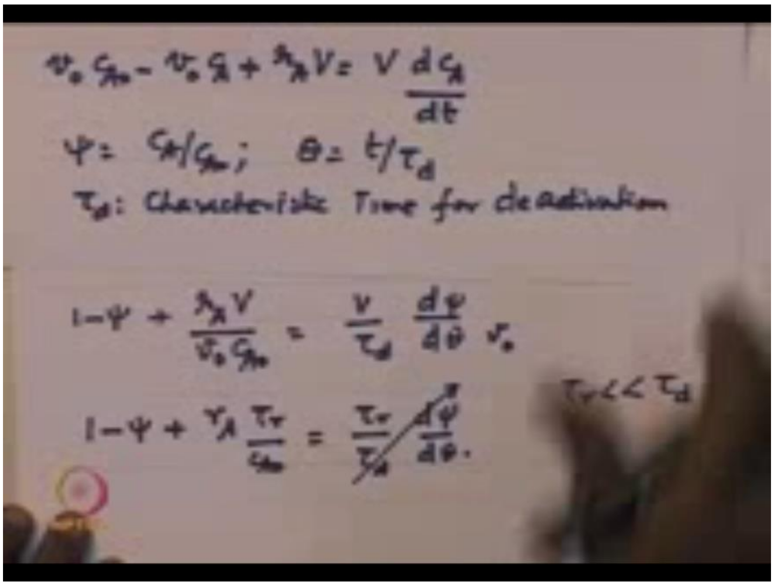

$$v_0 C_{A0} - v_0 C_A + r_A V = V \frac{dC_A}{dt}$$

$$\psi = C_A/C_{A0}; \quad \theta = t/\tau_d$$

τ_d: Characteristic Time for deactivation

$$1 - \psi + \frac{r_A V}{v_0 C_{A0}} = \frac{V}{\tau_d} \frac{d\psi}{d\theta} v_0$$

$\tau_r << \tau_d$

$$1 - \psi + r_A \frac{\tau_r}{C_{A0}} = \cancel{\frac{\tau_r}{\tau_d}} \frac{d\psi}{d\theta}.$$

So, you can same just write this as 1 minus and just simplify this and write this plus r A divided by v divided by v naught c A naught equal to v divided by tau d d psi by d theta times v naught. So, we can we written in this form plus r A times tau r divided by c A 0 equal to tau r divided by tau d d psi by d theta. So, a catalytic reaction in which the deactivation is important. This is the kind of material balance which describes what happen during the process of deactivation. Now, if it, so happen the tau r is less ten tau d on other words what we are saying is that the reaction time typically for 1 or 2 seconds.

In most of these catalysts the reaction time in the equipment is not more than few seconds. So, if the reaction time is few seconds while the deactivation time or the characteristic time deactivation are on the order of the months or years then this tau r by tau d is quiet small, so that we can neglect this. On other words when we do experiments on trying to understand deactivation we must recognize that the right hand side is not important than this, because it is 0. Therefore, we can understand the left hand side and then simply look at what happens to psi as function of time. Let just take this forward this whole idea forward

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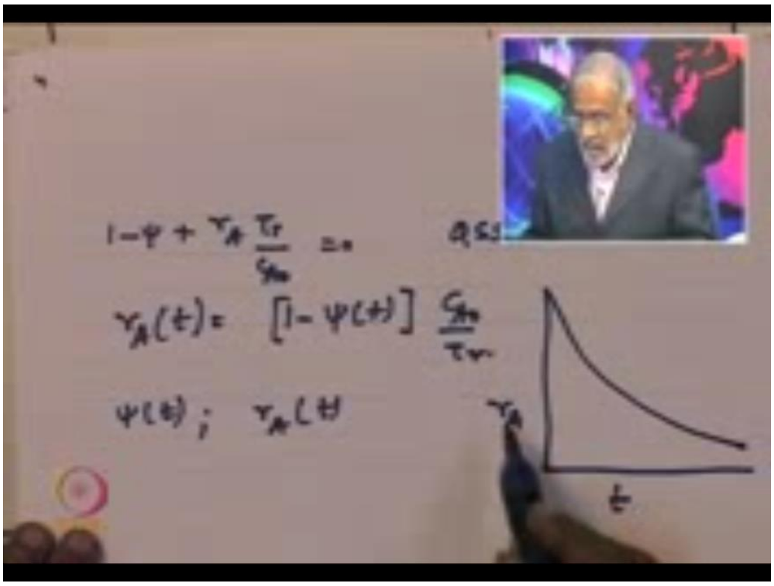

So, what it means is that 1 minus of psi plus r A by tau r divided by c A 0 equal to 0 this what is called as quasi steady state approximation. So that r A as a function of time is 1 minus of psi as a function of time divided by multiplied by c A 0 divided by tau r. On other words what we are saying is that simply by measuring psi t by the function of time we can get reaction rate of function of time. On other words we are able to plot reaction rate as a function of time and we find that this reaction rate does this over a period of time. What we are trying to say and we want to know how activity of the catalyst changes as the reaction takes place.

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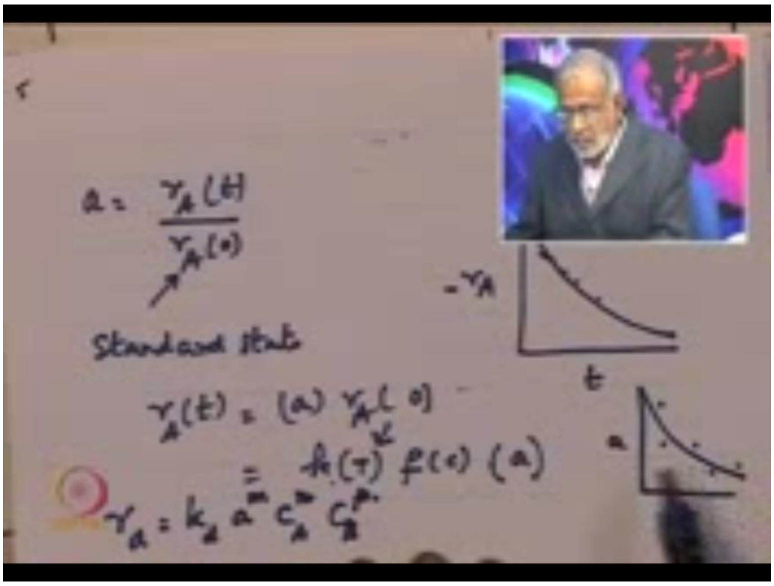

We pointed out is that we can understand this simply by trying to look at activity of the catalyst which is reaction rate at any time divided by reaction rate at 0 time. We mention this yesterday that by zero time what we mean is some standard state this is some standard state the standard state. And therefore, we can understand the activity with respect to the standard state. Therefore, what we are saying is that the reaction rate at any time is an activity multiplied by a standard state. Therefore, we can say if this standard states this is some function of concentration multiplied by an activity.

So, essentially what we need from our experiments from our experiments is that we need reaction rate we need reaction rate as a function of time I will put a minus sign here even here also I put a minus sign. Because our reaction may be a going to product therefore, we expect that I will put a minus here. So, we find that this decreases and therefore, if you want to find activity at any point if you want activity at any point how do you find activity? You simplified reaction rate at this point where reaction rate is 0 time. Therefore, reaction rate at any time divided by reaction rate 0 time gives you the activity. On other words our experiments can give you an activity as a function of time.

On other words from this data we can generate what is called as a versus time which source this kind of data. This is the kind of data we can generate from our experiments we point it out yesterday how to ah collect this data from the equipment like a CSTR and so on. But for the moment we know how to do it. So, all we have got now is that activity as a function of time. Now, what is required for us is to be able to find a function r d which tells us what is the rate at which the deactivation occurs. So, a to the power of m some function of I will say c to the power of n some concentration a to the power of n concentration b to the power of some p and so on. On other words just like we are talking about reaction rate function reaction rate similarly, we are talk about deactivation rate function. Therefore, all these parameters k d m n p are all parameters which we can determine by this kind of data which comes from the experiments. On other words we can generate this data a versus time of under different kinds of condition different temperature and different composition and so on therefore, we can generate this function. So, this we have said already, so what we did point out yesterday and the something that is interest to us.

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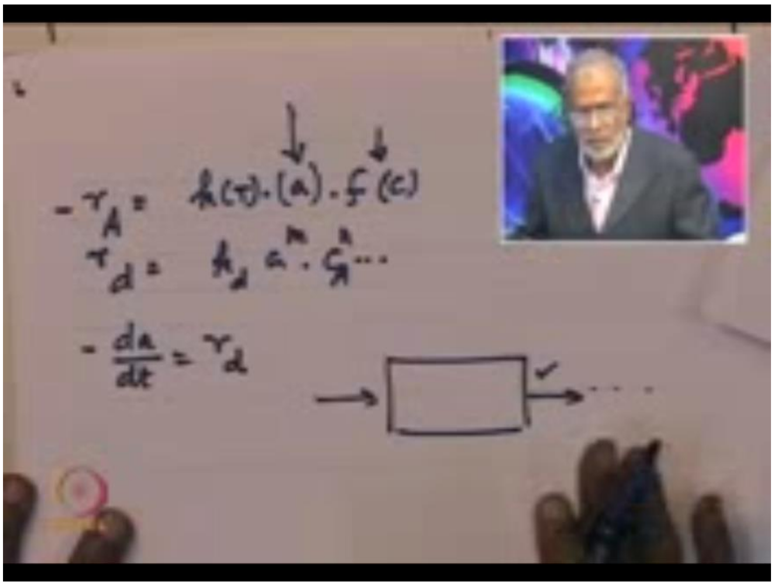

When we trying to understand process is that if we have a rate function a rate function A I will put a minus sign here to say that there it is a some function of time A and then some function of A and then some function of concentration where our r d is some function this is some function a to the power of m c A to the power of n and so on. On other words we have from our experiment the parameters of deactivation of models are known therefore, we know how activity d a d t changes as time changes. And therefore, we know from this data we know how a changes with time. Now, frequently our concern is that you want to run a process let us say we have a process and then we want to run. This process feed coming in and going out this process should run, so that the composition in the exit does not change much with time. Because that is useful because all the downstream equipment would have been design for certain capacities. And if these compositions keep changing with time then there are problems with downstream equipment. So, on other words that means you d o not want this function f c to change much during a process which would done for several months several years sometimes.

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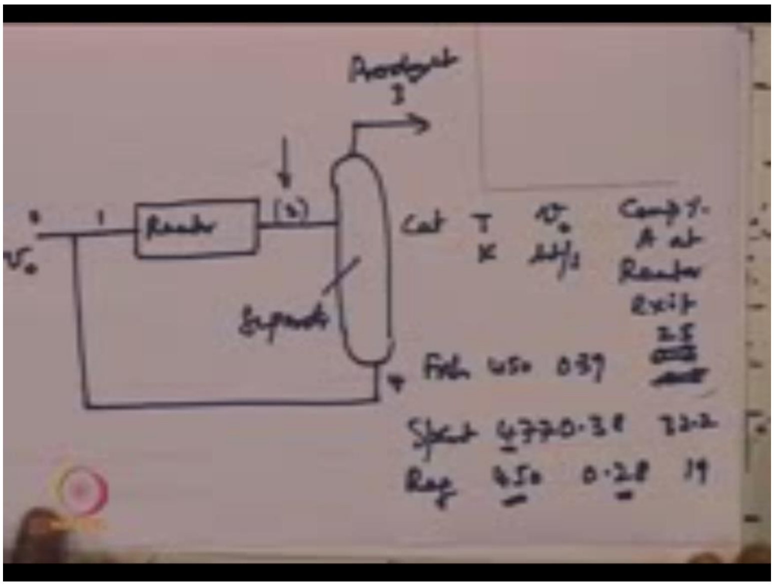

What I want to draw you attention is an interesting result that you and I will see when we go to a process ((refer time 10:47)). Draw this and then perhaps explain to you and something that you all know it is not that it is new to you. But I want to attention to some results which would be very useful for all of us. So, let me write here catalyst temperature v naught composition percent a at reactor exit. So, you have fresh catalyst fresh temperature is 450k this is Kelvin 0.39 litres per second is litres per second composition is point is 25 percent. And spent catalyst spent catalyst temperature is 477.38 and composition is 32.2 regenerated catalyst temperature 450 0.28 and 19 percent. So, what I what I have got here is the behaviour of A reactor separator it is behaviour of A reactor in which there is a deactivating catalyst. And the composition at reactor exit that is position 2 is given here notice here that when you run the reactor at 450 k v 0 coming in at 0.39 litres per second we were getting 25 percent at position 2 that is when the catalyst was fresh.

Now, when the reactors are operating for months and months we find that catalyst is deactivating. So, in order to a null the effect of deactivation what the operators are done is to increase the temperature to 477 there we increase the temperature to 477 and you can see that they have adjusted the v 0 what were 0.39 they reduced to 0.38. And in spite of that the composition at exit is 32.2 what is 25 that means the conversion 75 percent here that is become much less. Even though the temperature is increased the flow has come down and the composition are also come down, so what do we conclude from here? We have to conclude from here is that, but in to arrest the effect of catalyst deactivation the operator has increase the temperature. But in spite of that this performance is not very satisfactory you know in the sense that the catalyst deactivation is quiet large as you can see here. So, I mean that is an alternative process that the operator is looking at is that there is a regenerated catalyst whose performance is like this which says that 450 the flow rate is 0.28.

And then the composition at reactor exit is 19 means what? 25 this is 25 let me write it properly this is 25 percent 19 means what we are getting 81 percent conversion here. So, you might like to see I mean in fact our major interest would be in reactions engineering and evaluating performance process and so on. To see how the performance of A fresh catalyst, performance of the spent catalyst, performance of A regenerated catalyst compare on some common basis. And what could be a common basis for a catalyst the activity of the catalyst. In fact, therefore, when we look at problems like this we need to be able to look at what is the catalyst activity? Something that we would like to calculate for which of course, we set out procedures. This is the kind of problem that we are trying to understand trying to solve and for which we want to set a procedures. So, what is the procedures I mean we have said this before.

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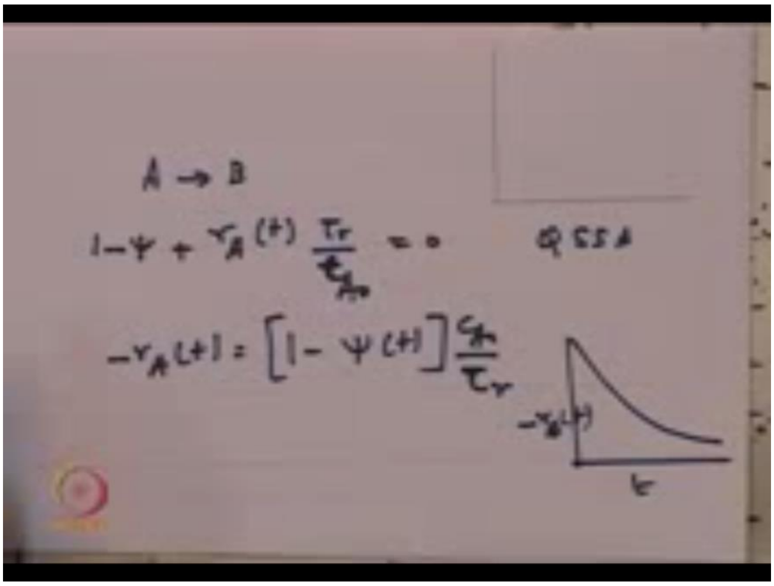

$A \rightarrow B$

$1 - \psi + r_A(t)\frac{\tau_r}{C_{A0}} = 0$ QSSA

$-r_A(t) = [1 - \psi(t)]\frac{C_{A0}}{\tau_r}$

But you know, so we have this reaction A going to let say B. Now, we said under quasi steady state approximation our equations look like this. If the experiments were done in a stirred tank looks like this equal to 0 under quasi steady state approximation. So that our reaction rate will look like this. And therefore, we are able to you know conduct this kind of experiments and find out how the reaction rate changes with time?

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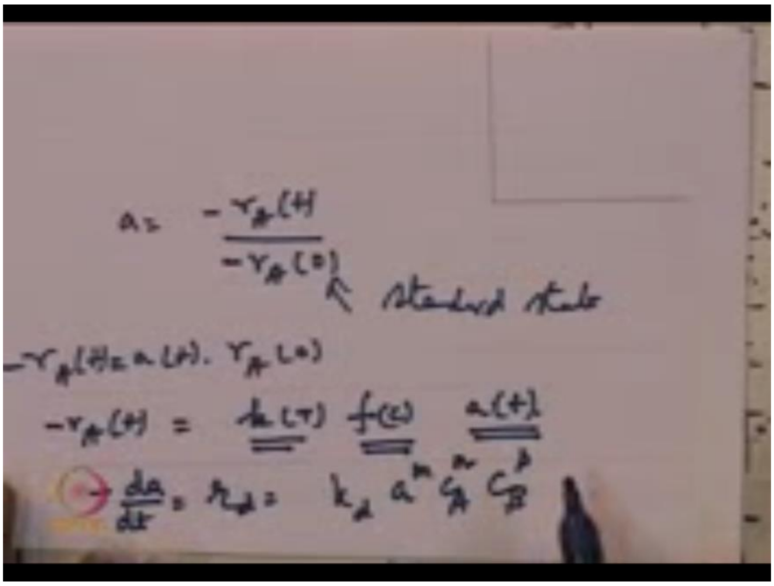

$a = \frac{-r_A(t)}{-r_A(0)}$ ↖ standard state

$-r_A(t) = a(t) \cdot r_A(0)$

$-r_A(t) = \underline{\underline{k(T)}}\ \underline{\underline{f(C)}}\ \underline{\underline{a(t)}}$

$-\frac{da}{dt} = r_d = k_d a^m C_A^n C_B^p$

That something you already said have said that what we also said is the activity of the catalyst which is given like this at 0 time or standard state can be found out. On other words what we are saying is that the rate at which the catalyst is reaction rate of rate of chemical reaction any time is r A at t time r A at 0. Or we can also say it as some function of temperature, some function of concentration and a some function of Activity. On other words the rate at which chemical reaction occurs depends up on temperature, depends up on activity depends up on the composition to which the catalyst is exposed. And we also said that we will be able to determine the deactivation function by doing the deactivation kind experiments which we already talked about which we already talked about.

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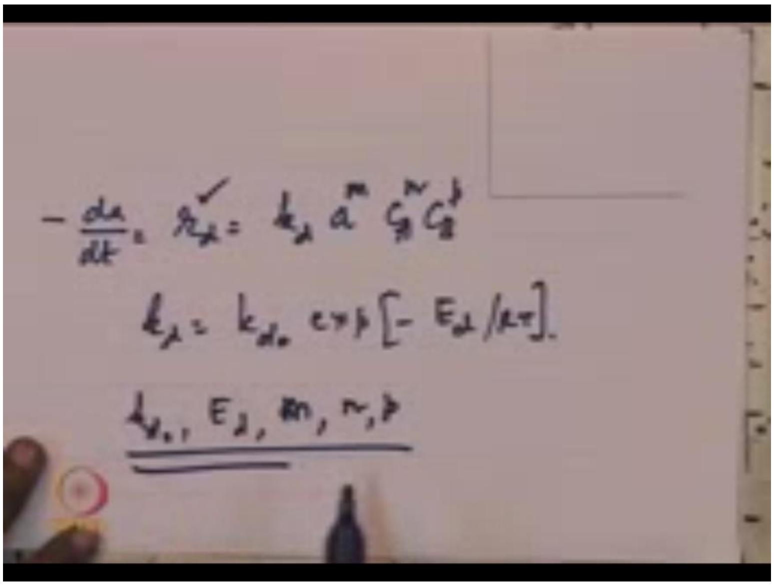

$$-\frac{da}{dt} = r_d = k_d a^m C_A^n C_B^p$$

$$k_d = k_{d0} \exp[-E_d/RT].$$

$$\underline{\underline{k_{d0}, E_d, m, n, p}}$$

So, that we know what are these parameter, because this k d we said this k d equal to minus of d a d t equal to r d equal to k d times a to the power of m c A to the power of n c B to the power of p where k d is here deactivation at last the constant which comes from. So, we have the parameters of the deactivation velocity which is k d E d a m n and p and so on. So, all these unknown therefore, r d is known therefore, a at any time is known and therefore, what is the reaction rate? Because reaction velocity constant this is something that is known from our reaction kinetics experiments at using standard statement and so on. Therefore, k t is known a function is known f function is known, because it comes from our reaction kinetics experiment. Therefore, our reaction rate at any time is known fully the point. I was trying to put across to you the point I was trying put across to you is that here is an instance of the catalyst which is deactivated.

And the operators are try to a null a null this effect by changing this temperature and in spite of that it was not satisfaction On other words what we find is that the composition at position 2 it is changing, because the composition at position 2 is changing it is not as per design. Therefore, what is coming out as product at position 3 is also not as per your design. And therefore, this separator is not be used to the capacity that you would like to use it to. On other words you are you are having a sub optimal kind of performance. Now, what is that you and I can do to see that this problem can be overcome? Now, the our friends in catalyst deactivation have a nice suggestion what is that suggestion? The suggestion is that if look at this function.

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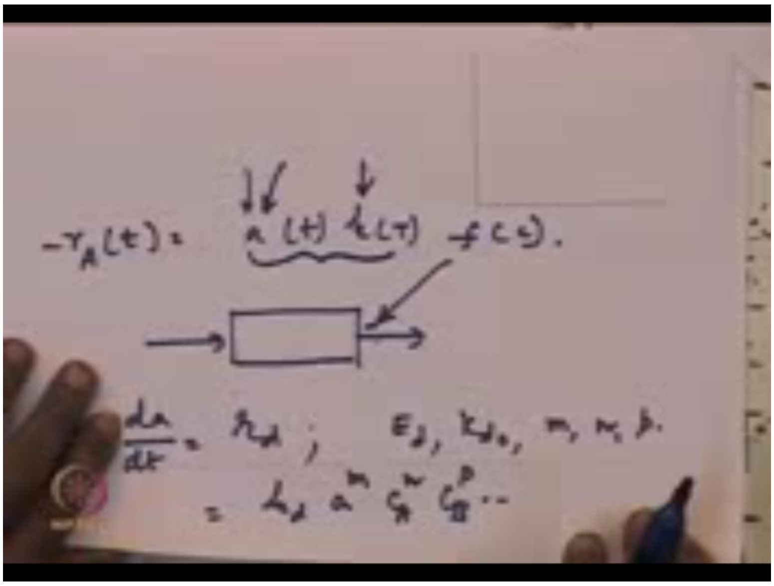

If you look at this function r A at any time t which is a as function of time and that k A function of time and that f c which is the function of composition. Now, what is that your this reactor this reactor why does this change composition here change? The composition here chance is, because this activity keeps decreasing how does this activity decrease? We said this activity decreases as per this deactivation rate function and the parameters of the deactivation rate functions are E d k d 0 m n p where r d is equal to k d times a to the power of m c A to the power of n c B to the power of p and so on. All these are known now; the question is that if I want to keep this concentration here the same at all times how do I achieve that? Which means I want this function f c here not to change now, to ensure that what I do if that if I can keep this product constant then what I am seeing here is that whatever the reaction rate at 0 time I will see that reaction rate at our times? So, this strategy for managing catalyst deactivation in a process is essentially to see that the product of this reaction velocity and this activity is held constant. Now, if we of course, something that we all know we have done in our reaction kinetics experiments how the reaction the rate constant k?

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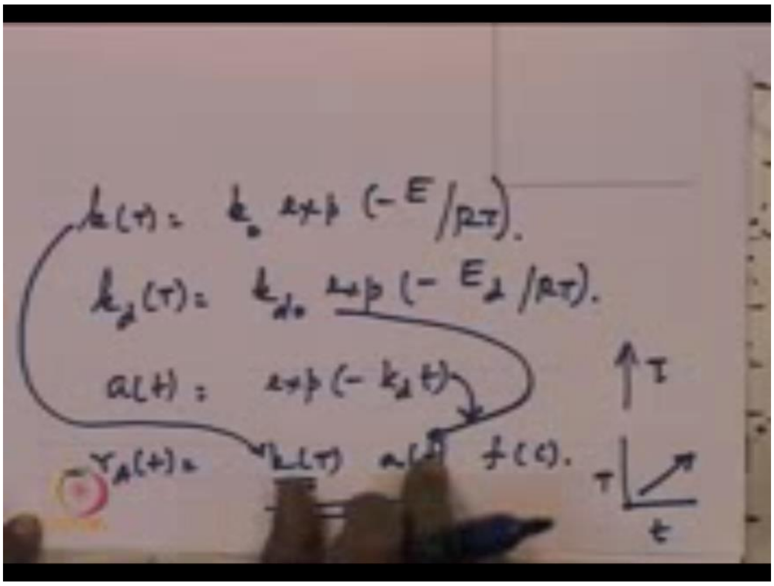

This rate constant k which is ((refer time 20:50)) k 0 exponential of minus of E by R T this is how the rate constant which decaying with temperature. Our k d which is changing like this exponential of minus of E d by R T where and this a the activity a itself is changing with time. Suppose I say it is an exp1ntial decay when I say that it is exponential of minus of k d of t, because it is an exp1ntial decay. Therefore, our rate function r A which is a function which is k t a t and some function of c you find that this changes temperature dependence of this is given by this the temperature dependence of this is taken care through this expression. Therefore, as a result of this you are able to maintain r at any times same as r at 0 time by simply increasing the temperature t. You increase t you increase t that means time you increase temperature and idea of increasing temperature is that the reaction velocity will go up and the deactivation velocity also goes up. But experience says that the increase in deactivation velocity constant is not as large as increasing the reaction velocity that is the experience of reaction velocity constant in the process. And as a result it is possible to find temperature time projector that will give you constant value of this function this product.

Therefore, in process industry we try and maintain such the reaction velocity to remain reasonably constant by ensuring that this product is held constant this is the strategy. Now, under this strategy under this strategy if you look at this data if you look at this data what is this data say? This data say that when you conduct the experiment at 477 spent catalyst which is getting deactivated we find that unit 477. It is giving at velocity at volumetric flow 0.38 only 32.2 showing that the spent catalyst has not been performing as well therefore, we should gone to higher temperature to higher temperature. So that you would have gotten results similar to what we except with fresh catalyst. Now, you point is that this kind of variations of temperature on a catalyst may not always be possible in an industry. The reasons are many most important reason could be there is an specification on the catalyst which will tell us that you know the temperature more than this is not permissible. And therefore this particular catalyst is sort of done its work and done it is like regenerated or discarded. This kind of Answers may be there in process industry.

But what we are trying to say here is that there is a strategy to manage this and to the extent that you know your catalyst permits you to change temperature in that direction to that level and so on. You will be able to handle this deactivation if it not possible you have to stop and then use fresh catalyst. I mean discard the old and get the fresh catalyst or look at a regeneration process which may give you a regenerated catalyst of reasonably a good activity. As you can see here that the regenerated catalyst 450 is able to give you 81 percent conversion of 19 percent exit here that, but it is able to process less it is able to process less.

On other words what we are trying to say here is that in when you have a deactivating catalyst you have to content. The fact you know the downstream equipment may have to be utilised at capacity lower then what we may have design for alternatively you may have to factor this in your design. So, the some of these problems can be adequately taking care in your design and in your operations. So, we want to illustrate this through an example we started last time, but now, we did not get for enough I though you know we should sort of look at this very effectively, because it is an important example from process industry point of view.

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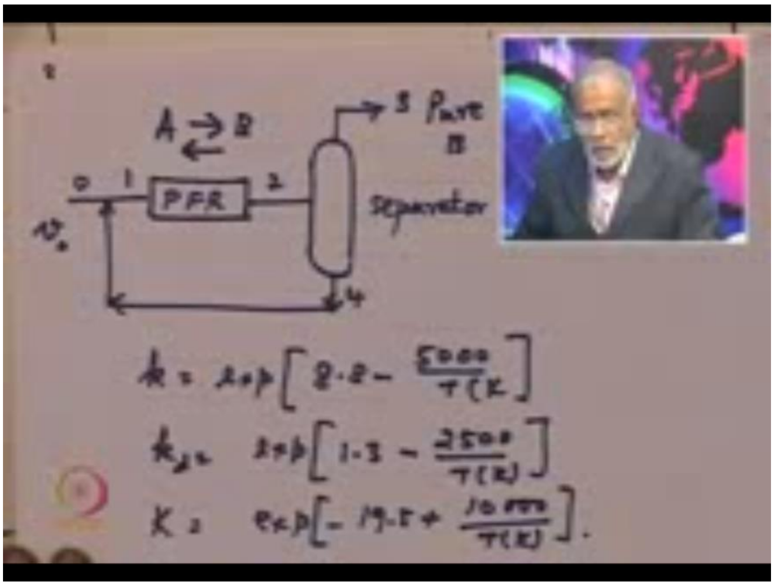

$$k = \exp\left[8.8 - \frac{5000}{T(K)}\right]$$

$$k_d = \exp\left[1.3 - \frac{2500}{T(K)}\right]$$

$$K = \exp\left[-19.5 + \frac{10000}{T(K)}\right].$$

So, here is an example of process this is the process. This is the PFR this is separator and now, we have this is position 0 position 1, 2 let us say its 3 and 4. All right and your feed coming in v not and then pure this pure product pure b. Let say the reaction taking place A going to B and B going to A the data are given is as follows rate constant k is exponential 8.8 5000 by t which is in Kelvin. And then deactivation velocity constant is exponential 1.3 minus 2500 divided by t function of k. And then you have equilibrium constant k which is exponential minus 19.5 minus 10000 divided by t which is also in Kelvin this whole exercise the context whole exercise is as follows. There are instances in which you will be running a process where this catalyst which is inside this PFR is used to produce this product B. Because this catalyst deactivates you would have to take care of this catalyst periodically to see that you get the product at the capacity rate that you have designed for. So, in this exercise in this exercise what is mean said by the manufacturer is the following says that this reaction A goes to B.

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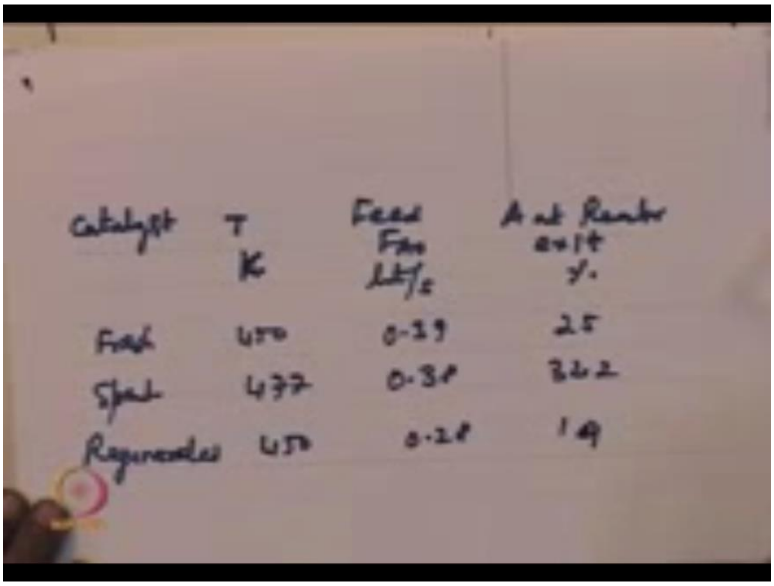

Catalyst	T K	Feed F_{A0} Lit/s	A at Reactor exit %
Fresh	450	0.39	25
Spent	477	0.38	32.2
Regenerated	450	0.28	19

Let me just write down the data I mean come back to catalyst temperature feed and a at reactor exit percent this is litres per second f A 0 this is t in sorry t in Kelvin. So, its fresh catalyst, spent catalyst, regenerated catalyst says 450 0.39 25 percent 477 0.38 32.2 percent 450 0.28 19 percent. Now, what is being said is the following that here is a process which is being running when it runs its fresh catalyst when it runs its spent catalyst when it runs with regenerated catalyst data is given for 3 situation. Three situations when you run this fresh catalyst process runs at 450 c And then f A 0 means feed at position 0 turns out to be 0.39 litres per second and exit composition of A is 25 percent you understand what it says when you run this process at using PFR v naught is given as 0.39 litres per second.

And then the composition at reactor at exit which is at position 2 is 25 percent now, when the catalyst get spent in the sense after few months I do not know how long let us say few months. Then it is found the catalyst is sort of its activity has become low at that time what is observed is that at 477 c the composition the composition here is that 32.2 here and the flow is 0.38. Now, what is being said is that when you run a process let us come back to this when you run a process with a deactivating catalyst we said just now, that you have to increase temperature with respect to time. So, that this product remains constant and in fact, if you look at this data here what they have said is that if they stared the process at 450. But continue to increase the temperature at 477 at that time when catalyst has become a little low in activity. The composition at A at the exit has increase from 25 to 32 you can see that the catalyst performing poorly as therefore; we have increase the temperature and so on.

And despite this increase in temperature we performing poorly, because 25 have become 32 problem statement says is that a spent this is a spent catalyst that means this catalyst should have been discarded. Now, the question is now, whether you discard the catalyst and then buy a new catalyst or alternatively in this problem the suggestion is that there is a nice process is available in the industry by which you can regenerate this catalyst. And then what has been done here is that the regenerated catalyst has this kind of performance that is at 450 c, but flow is only 0.28 the composition at reactor a exit is 19. On other words what is being said is that we have some data on catalytic reactor and asked to evaluate. They ask you to evaluate whether this regeneration process this regeneration process is good enough.

Now, how do you judge whether it is good enough or not they give a criteria. The criterion is the activity of this regenerated catalyst. The activity of regenerated catalyst should be 90 percent of the activity of fresh catalyst or it should be 2.25 times of this spent catalyst. Let me repeat what is being said in this problem statement is this we will accept the regeneration process. If the activity of the regenerated catalyst is the 90 percent of the activity of fresh catalyst or alternatively it is 2.25 times the activity of spent catalyst is that case we will accept the regeneration process. So, what is being asked of you is we left evaluate the data given to see whether the regeneration process is satisfactory with respect to the 2 criteria that is specified. So, what in essence expected of us is to be able to set up the equations and find out what is the activity of the catalyst. And so that you have to find the activity of the spent catalyst activity of the regenerated catalyst with respect to activity of fresh catalyst. And then see how the regeneration process is performing with respect to criteria that are specified. So, this is the exercise that we want to do and let us go through this exercise.

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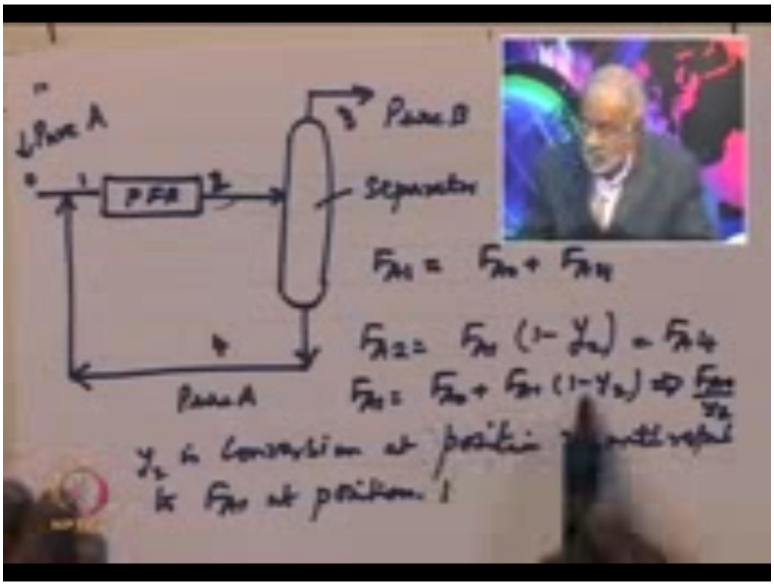

$F_{A1} = F_{A0} + F_{A4}$

$F_{A2} = F_{A1}(1 - Y_2) = F_{A4}$

$F_{A1} = F_{A0} + F_{A1}(1 - Y_2) \Rightarrow \frac{F_{A0}}{Y_2}$

Y_2 is Conversion at position [illegible] with respect to F_{A1} at position 1

This is not very difficult, but you know some of these things once some procedures are required I am just trying to do that I did do that to some extend last time. But I was not satisfied I am just doing it again does not mean that what I done last time we are not satisfied. But you know I am just sort of doing it again, so that i am satisfied with the procedure I have done 0 1, so 0 1 2 3 and 4. The problem statement say that this PFR the catalyst and then it goes to a separator and the separator is able to recover pure B. So, here what we have pure A and then you request pure therefore, what comes here is pure A?

This is, so let us go through this whole exercise, so what 1 by 1 what is f A 1? f A 1 equal to f A 0 plus f A 2 this is f A 1 equal to f A 0 plus f A 4 sorry f A 4 we know this. Now, let us say that f A 2 equal to f A 1 multiplied by 1 minus of y 2 where y 2 is conversion at position 2 with respect to with respect to f A 1 at position 1 what are we saying? See in order to define conversion we have said this before we have said this many times before. Then we need a reference conversions are always with respect to a reference what is a reference that we have taken? We have taken position with respect to position 1 that f A 1 at position 1 position 1 is our reference.

So, we can define conversion with respect to position 1 that is what we have done. All right, so in that case now, that we know this I can substitute it here. Therefore, f A 1 equal to f A 0 plus f A 1 times 1 minus of y 2 why is that whatever is a here will be the a here. Because all the b recovered in this process therefore, I have written f A 2 this is f A 2 is f A 1 this is also equal to f A 4 we know this therefore, I have written this, so this implies what? This implies f A 1 equal to f A 0 by y 2 is it correct? It is comes directly from here therefore, implies f A 1 f A 0 by y 2.

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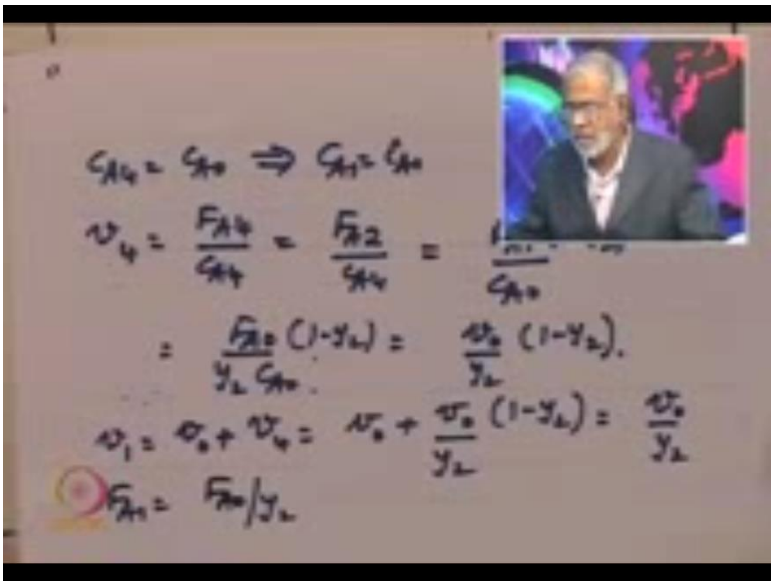

$$C_{A4} = C_{A0} \Rightarrow C_{A1} = C_{A0}$$

$$v_4 = \frac{F_{A4}}{C_{A4}} = \frac{F_{A2}}{C_{A4}} = \frac{\text{[illegible]}}{C_{A0}}$$

$$= \frac{F_{A0}}{y_2 C_{A0}}(1-y_2) = \frac{v_0}{y_2}(1-y_2).$$

$$v_1 = v_0 + v_4 = v_0 + \frac{v_0}{y_2}(1-y_2) = \frac{v_0}{y_2}$$

$$F_{A1} = F_{A0}/y_2$$

We know that c A 4 is c A 0 we agree with this why c A 4 equal to c A 0? The reason is that at 2 we have both A and B and reactor A and reactor A and recovering completely B here therefore, here it should be pure A. Therefore, the composition c A 4 here should be equal to c A 0 that is what I am saying c A 4 should be equal to pure a equal to c A 0 c A 0 component c A 1 is equal to c A 0 that is point I am trying to make. So, implies c A 1 equal to c A 0 I hope this is clear to all of you that, because c A 4 is c A 0 and then what is coming is c A 0 pure A. Therefore, at position 1 the concentration is c A 0 that is commonsense. So, let us see what else we can do what is v 4 by our definition is f A 4 divided by c A 4. f A 4 we said is f A f A 2 by c A 4 this we have said this is equal to f A 2 is what? f A 1 times 1 minus of y 2 divided by c A 4 which is c A 0, so that is equal to f A 1 is what f A 0 by y 2 c A 0 in to 1 minus of y 2. So, that is equal to v 0 by y 2 in to 1 minus of y 2 is it all right what we are saying? What we are saying is that the flow at position 4 flow at position 4 what is flow at position 4? By definition it is f A 4 by c A 4 now, c A 4 c A I mean c A 4 is c A 0 you already proved that saying.

Because B is completely recovered therefore, this must be c A 0 then we said that f A 2 f A 2 is what? f A 2 is component 2 at position 2 by definition f A 2 is f A 1 times of 1 minus y 2 by definition, so that is what i have been putting here. Now, what is v 1? v 1 is v 0 plus v 4 that is v 0 v 0 y 2 multiplies by 1 minus of y 2 which is equal to v 0 by y 2. So, what we have done? We have found out that f A 1 equal to f A 0 by y 2 already proved that similarly, v 1 is v 0 by y 2. So, we have got some information about what are the flow rates at position 1 what are the compositions at position 1. Therefore, we are now in a position to write the reactor design equation for PFR, so that we can understand what is happening in this PFR and address all the question that is being raised by the by the problem. Let us do 1 by 1 let us address this 1 by 1. So, what we want to do now is we want to write the design equation for PFR and then understand and then use the data to be able to give proper explanation for the data. So, this is what we are trying to do? What we are trying to do is we will write the design equations for PFR I am making use of this relationship that we have already established. And then look at the data to see how we can explain what is going on. Let us see how to do this.

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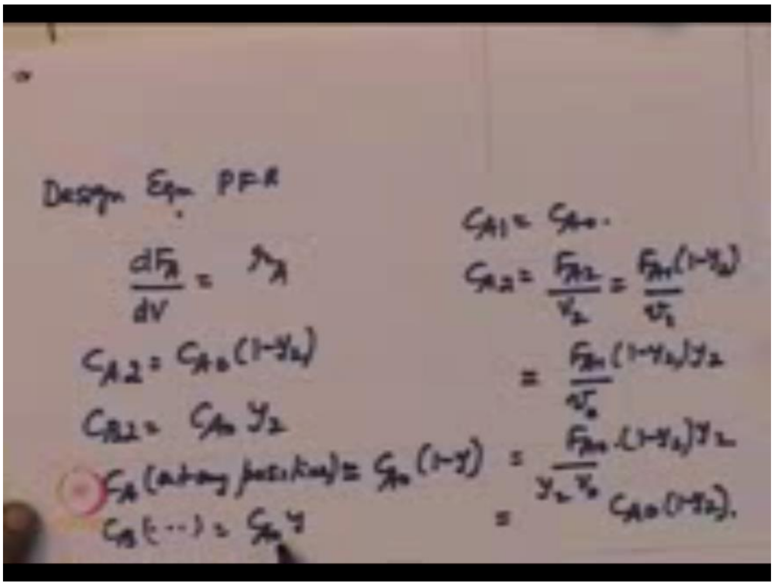

Design Eqn PFR

$$\frac{dF_A}{dV} = r_A$$

$$C_{A2} = C_{A0}(1-y_2)$$

$$C_{B2} = C_{A0}\,y_2$$

$$C_A(\text{at any position}) = C_{A0}(1-y)$$

$$C_B(\ldots) = C_{A0}\,y$$

$$C_{A1} = C_{A0}.$$

$$C_{A2} = \frac{F_{A2}}{v_2} = \frac{F_{A1}(1-y_2)}{v_1} = \frac{F_{A0}(1-y_2)y_2}{v_0} = \frac{F_{A0}(1-y_2)y_2}{y_2 v_0} = C_{A0}(1-y_2).$$

So, design equation for PFR what is the design equation for PFR we have done this many times. So, I say there it is d F A by d v equal to r a this is well known design equation that we written for a long time. Now, we know that c A 1 equal to c A 0 what is c A 2? By definition f A 2 by v 2 what is f A 2? It is f A 1 multiplied by 1 minus of y 2 and what is v 2? We said is v 1 v 2 is v 1, because there is no volume change that is v 1 equal to f A 1 in to 1 minus of y 2 v 1 is what v 0 divided by y 2 i put it on what is f A 1? f A 1 is f A 0 divided by y 2 v 0 in to 1 minus of y 2 in to y 2 therefore, if this becomes c A 0 times 1 minus of y 2. So, what we have is that c A 1 c A 2 equal to c A 0 1 minus of y 2 similarly, c B 2 equal to c A 0 in to y 2 similarly what we are saying. This is this coming from basic sticheeometric we are not saying anything new here.

So, we just calculate what is concentration at position 2 which is c A 0 1 minus of y 2 concentration of B at position 2 c A 0 1 minus of, so this is at the exit from the PFR. Therefore, if I ask you what is c A 2 what is c A at any position inside reactor then we will say it is c A 0 in to 1 minus of y, so y goes from y goes from 0 here to y 2 here is that clear? Similarly, what is c B at any position we say it is equal to c A 0 times y where y is a variable that goes from 0 at this point to y 2 at the end and y is defined as conversion with respect to position 1. So, if I want to substitute if I want to take r A now, the rest is value straight forward in you have done this many times before, so this is not new.

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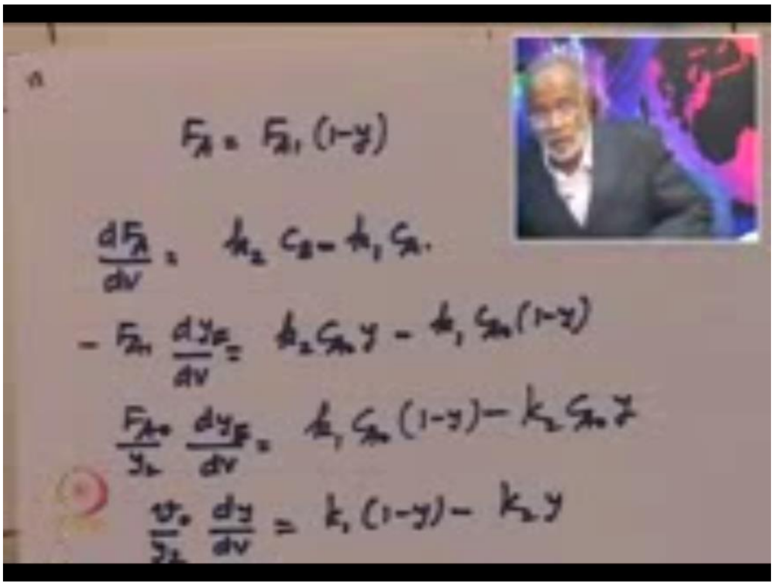

$$F_A = F_{A1}(1-y)$$

$$\frac{dF_A}{dV} = k_2 C_B - k_1 C_A$$

$$-F_{A1}\frac{dy_F}{dV} = k_2 C_{A0}\, y - k_1 C_{A0}(1-y)$$

$$\frac{F_{A0}}{y_2}\frac{dy_F}{dV} = k_1 C_{A0}(1-y) - k_2 C_{A0}\, y$$

$$\frac{v_0}{y_2}\frac{dy}{dV} = k_1(1-y) - k_2 y$$

Let us go through this d F A d v equal to r A what is r A? r a by definition is k 2 time c b minus of k 1 times c A where c A and c b are concentrations in the equipment. All right now, we can put we know that f A by definition is f A 1 times 1 minus of y, y is the conversion at any position in the reaction equipment. And that y is defined with respect to position 1. So, y is the conversion in the in our nomenclature but, this time the conversion is defined with respect to position 1 that is the only difference. All right now, let us put all these things here left hand side becomes F A 1 times d y 1 by d v equal to the right hand side is k 2 times c A 0 times y minus of k 1 times c A 0 times 1 minus of y is this all right. Now, what is f A 1 by definition f A 0 by y 2 d y 1 d y no d y 1 d y d y d y sorry d v equal to k 1 c A 0 1 minus of y minus k 2 c A 0 y. Now, we can cancel off the c A 0 which will give you v 0 d y d v y 2 equal to k 1 1 minus of y k 2 y. Now, what we have done? What we have done is in order to be able to explain this data which we have to explain this data and using the data calculate what is the activity of the catalyst here and here?

So, that we can judge whether the appropriately the criteria is satisfied or not, so to be able to do that we will have to use this process data for which we need to do a process analysis. We have done the process analysis and based on the process analysis we find that the differential equation governance. The performance of this reactor is given by this is the differential equation which governs the performance of this reactor. Now, once you know the differential equation performance equation to an equipment. The rest is very straight forward let us integrate this and then, so when you integrate this please notice here that this k 1 it is important here this k 1 I will put a bracket here just to indicate that this are reactions 1 and 2. These are reactions A goes to B is reaction 1 this is reaction 2 and this is not be confused with the positions this is not be confused with positions 1 2 3 etcetera in the equipment that is important one. That, so I put a bracket here, so say that this is reaction 1 this is reaction 2.

Now, can we integrate this answer is yes let us integrate this and then find out what is the integral I have done this integration fairly straight forward, so I will not show you the details now. The one more point that we must bare in our mind right here that is this representation of this equation we must take in to account the fact that the catalyst that is now, being used activity seems to be changed. And it does change depending up on the operating conditions. Therefore, we recognize that there is catalyst activity we must account for in our analysis. So, I am putting that alpha here, so that we take in to account the catalyst activity that is. On other words what we are trying to say here is that if you operate the process in 1 condition and change the conditions then the catalyst activity also change, because of the conditions I have changed. Therefore, I have put the catalyst activity of Alpha is activity. I put the effect, so that we are in a position to see how the activity is contributing to our process.

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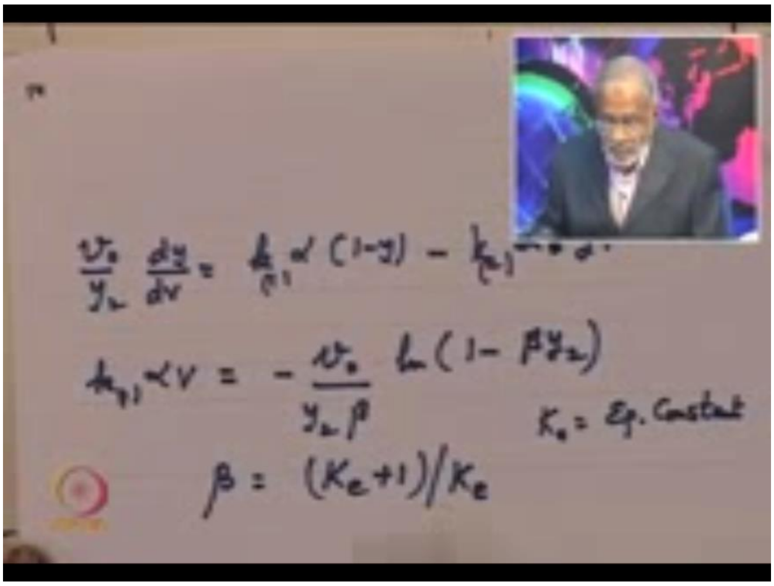

$$\frac{v_0}{y_2}\frac{dy}{dV} = k_{r,1}\alpha(1-y) - k_{r,2}$$

$$k_{r,1}\alpha V = -\frac{v_0}{y_2\beta}\ln(1-\beta y_2)$$

K_e = Eq. Constant

$$\beta = (K_e+1)/K_e$$

So, let us quickly write down once again of the difference the differential equation that governs our process is this is y k 2 alpha y. So, we can integrate this, so I have the integrated form let me integrated form looks like this. Now, you might ask how I got this integrated form? Now, this is the first order differential equation is very simple to integrate nothing new about this it is alpha multiplied by y there is no term like this is not there. Now, beta is k e plus 1 by k e where k e is equilibrium constant. Now, most important thing is now, try to understand how we can understand the data now, we know that the performance equation. Now, what is performance equation tell us? It tells us that k 1 alpha v what is k 1 reaction velocity constant what is alpha catalyst activity? What is v reactor volume what is v naught?? It is inlet flow rate and then what is y 2? y 2 is the mole fraction in percentage at position 2. So, on other words we have express the performance of the reactor to make good use of the data that is our data is in this form only. You can see here our data is given, so nicely our data temperatures are given flow rate, so this is actually certain f A 0.

But it is given in terms of flow v 0, so we have got v 0 here and similarly, we have composition, so the reactor exit which is y 2 which is given what is beta? Beta is the equilibrium constant and we have data all the data is also here we can calculate equilibrium constant at any temperature. On other words what we are saying is that we have using the fundamental of the reactor design equation that we have? We have generated a performance equation which is now, in a position to tell us how to evaluate the data that in front of us. Now, it is a question of us quickly doing some calculations to find out what is the value of k alpha for the different situation for which data is available in front of us. So, let us do that that, because that would give us a way of I mean evaluating whether the, our regeneration process is good enough or not. So, let met let me do the calculations.

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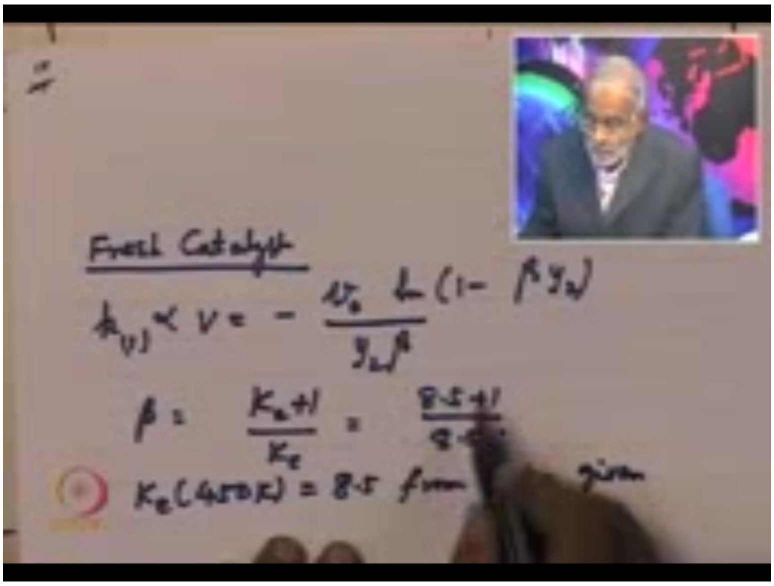

Fresh Catalyst

$k_{v1}\alpha v = -\frac{v_0}{y_2\beta}\ln(1-\beta y_2)$

$\beta = \frac{K_e+1}{K_e} = \frac{8.5+1}{8.}$

$K_e(450K) = 8.5$ from given

So, let us do fresh catalyst what I am doing now? I am trying to find the value of k 1 alpha v for fresh catalyst fresh k 1 alpha v. What is now that is equal to we have said v naught l n 1 minus of beta y 2 divided by y 2 times beta what is beta? Beta is k e plus 1 divided by k e and fresh catalyst data is given at 450 c. So, we have to do k e at 450 I have calculated k e at 450, so it is 8.5 plus 1 divided by 8.5. The reason is k e at 450 k equal to 8.5 from data this comes from data given. So, beta is known let us put all the numbers and then find out let me put all the numbers please help me fresh catalyst continued.

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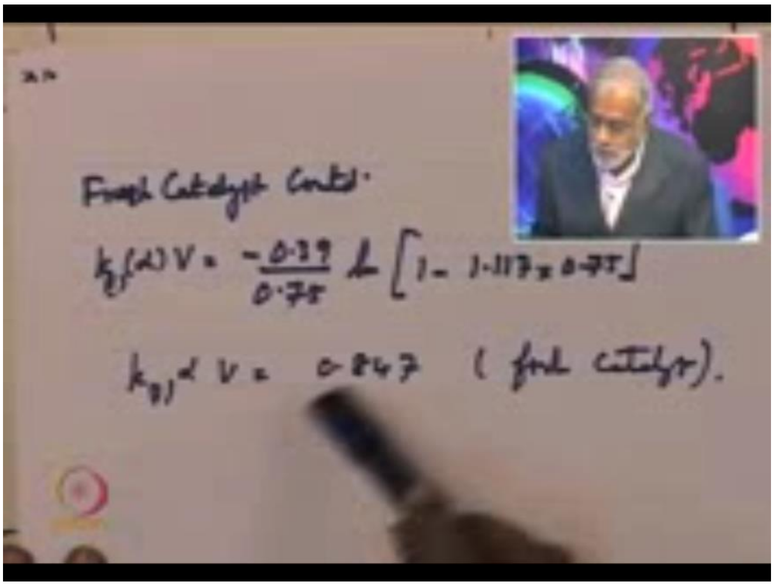

Fresh Catalyst Contd.

$$k_1(\alpha) V = -\frac{0.39}{0.75} \ln\left[1 - 1.117 \times 0.75\right]$$

$k_1 \alpha\, V = 0.847$ (fresh catalyst).

Fresh catalyst continued, so we have k 1 alpha v equal to I have written 0.39 help me please 0.75 l n 1 minus 1.117 multiplied by 0.75 that k 1 alpha v equal to 0.847. This is fresh catalyst what I have done? Of course, I have not done the calculation in front of you, but I am sure this is anybody can do this? So, I putting the number by putting the numbers v naught which is given notice here y 2 I have taken y 2 as 0.75 look at the data y 2 is 0.75 is it correct? I have taken y 2 as 0.75 why is it 0.75 where is it 0.75? It is the way to the way to handle this is it is data says the composition here is 25 percent. So, that means the mole fraction here is 25 percent let me just say what is mole fraction? Let me just quickly calculate what is mole fraction then you can tell.

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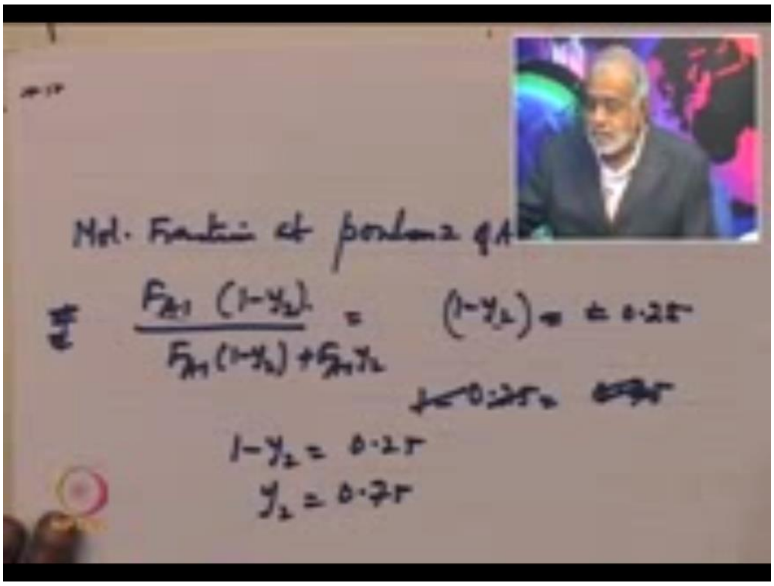

Mol. Fraction at position 2 of A

$$= \frac{F_{A1}(1-y_2)}{F_{A1}(1-y_2)+F_{A1}y_2} = (1-y_2) = 0.25$$

~~1-0.25 = 0.75~~

$1-y_2 = 0.25$

$y_2 = 0.75$

So, mole fraction at position 2 what is it? f A 1 1 minus of y 2 divided by f A 1 that is mole fraction of A position 2 of A. This is moles of A coming out total moles f A 1 1 minus of y 2 plus f A 1 y 2 that is 1 minus of y 2 is a 1 minus of 0.25 is 0.75 that is how we have substitute at the value of y 2 what is given? So, please understand what is given is I have done properly. So, this is this whole this is given as 0.25 I hope you understand this what is given is that mole fraction at position 2 is given as 0.25. By definition mole fraction is 1 of y 2 therefore, 1 minus of y 2 is 0.25 therefore, y 2 is 0.75. So, what we are saying is that in our process in the data that is given 25 percent means at this position 2 the mole fraction of A is 25 percent means conversion y 2 is 75 percent that is why y 2 is taken as 0.75 percent.

So, you put all the numbers here you get k 1 alpha v equal to 0.847 all right let us go forward how do you find out? So, the important thing is to find out activity means we need a reference we can take 450 data fresh catalyst as a reference. Therefore, essentially we must compare with respect to this data. On other words since we do not know the volume of the equipment given to us therefore, and then therefore, the best would be to use this as the reference fresh catalyst and evaluate the other catalyst let us do that. So, let us do that for the case of let us look at our spent catalyst. For spent catalyst some spent data is given let me write it down once again spent catalyst; what is spent catalyst? Spent catalyst data here you are spent catalyst here 477.38 and 32.2 let us do that.

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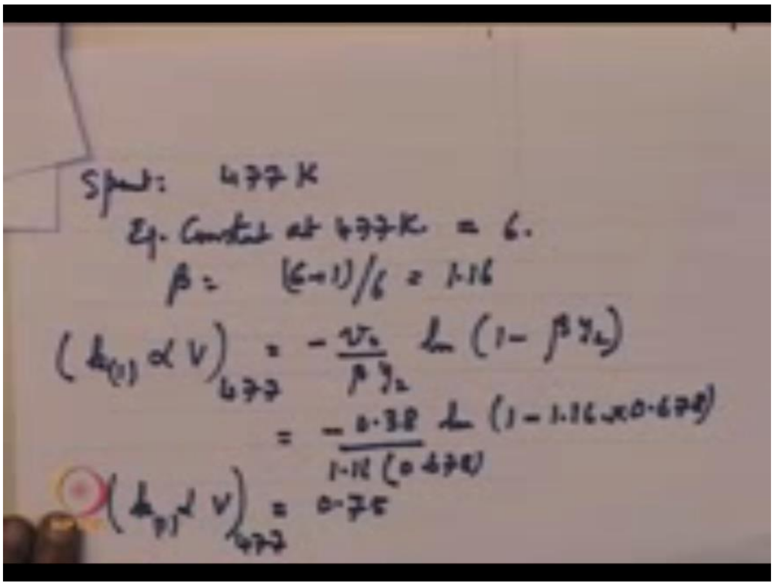

Spent: 477 K

Eq. Constant at 477 K = 6.

$\beta = (6+1)/6 = 1.16$

$$(k_{(1)} \alpha V)_{477} = -\frac{v_0}{\beta y_2} \ln (1-\beta y_2)$$

$$= -\frac{0.38}{1.16 (0.678)} \ln (1-1.16 \times 0.678)$$

$$(k_{(1)} \alpha V)_{477} = 0.75$$

So, spent catalyst is spent catalyst data is given at 477 k and then equilibrium constant equilibrium constant at 477 k equilibrium constant see I showed you the this 1. Let us come back here it is you said equilibrium constant is described by this equation this equation. So, you can calculate at 477 what is the equilibrium constant I have done? That I have done that, so that number turns out to be equilibrium constant for 477 turns out to be it is 6 therefore, beta turns out to be 6 plus 1 divided by 6 that is equal to 1.16. And now k 1 alpha at 477 I we have look at our design equation where is our design equation somewhere I wrote down somewhere.

Equation is v naught beta y 2 l n of 1 minus of beta y 2 now, how to substitute for these numbers from this data here from this, so y 2 is what is the 32.2 means y 2 minus of 32.2, so it is 0.678. I will put all the numbers here right now in front of you, so this you notice here this v not is 0.38. So, I will substitute this, so it is looks like minus sign is there minus 0.38 divided by 1.16 which is beta and then what else then you have y 2 0.678 ln 1 minus 1.16 and then multiplied by point 678. So, when you do all this calculations k 1 alpha v turns out to be 0.75 what are we saying? We go through this once again what we are saying is that the data given please let us look at process once again.

So, when you are implying fresh catalyst, so you are running the process at 450. As the catalyst deactivates you are increasing the temperature slowly over a period of time and what is the program of increasing the temperature? We have talked about that also we said that we would increase the temperature as per this program. And as per this time temperature program is given by this equation. And when you do that and it has become 477 at 477 our data says that this is the data and for that data we have done the calculation using the numbers given and it turns out that our results are something like this.

The k 1 alpha v at 477 is 477 is 0.75 now if I ask you now, what is the activity of this spent catalyst with respect to the fresh catalyst what will you say? You will say that we have done the calculation for fresh catalyst we have done this just now. I hope I have find it here it is, so we have we have said this is fresh catalyst correct this is fresh catalyst 0.847. Suppose I ask you what is the activity of spent catalyst with respect to the fresh catalyst then fresh catalyst is at 477 for 450. So, the activity with respect to fresh catalyst, because it is standard state is 477.

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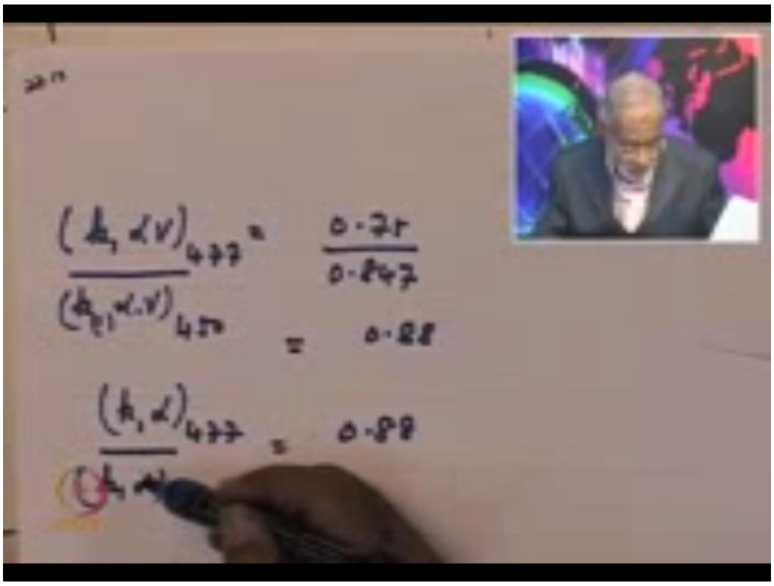

$$\frac{(k_1 \alpha v)_{477}}{(k_1 \alpha v)_{450}} = \frac{0.75}{0.847} = 0.88$$

$$\frac{(k_1 \alpha)_{477}}{(k_1 \alpha)} = 0.88$$

So, we should say that k 1 alpha v at 477 this is 0.75 we have done this calculation here. Now, we want it with respect to fresh catalyst what is fresh catalyst? k 1 alpha v is 0.847, so it is point divided by k 1 alpha v 450 this is 0.847. So, this ratio comes out to be 0.88 is this clear, so what are we getting out of this? We are getting that k 1 alpha at 477 divided by k 1 alpha at 450 equal to 0.88, but what is that we want? We want activity alpha at 477 in relation we need to find out. So, what in other words we should activity of spent catalyst at 477 you have to calculate that is important. So, we will come to that in a minute what is the activity of the spent catalyst? So, I will write here straight forward.

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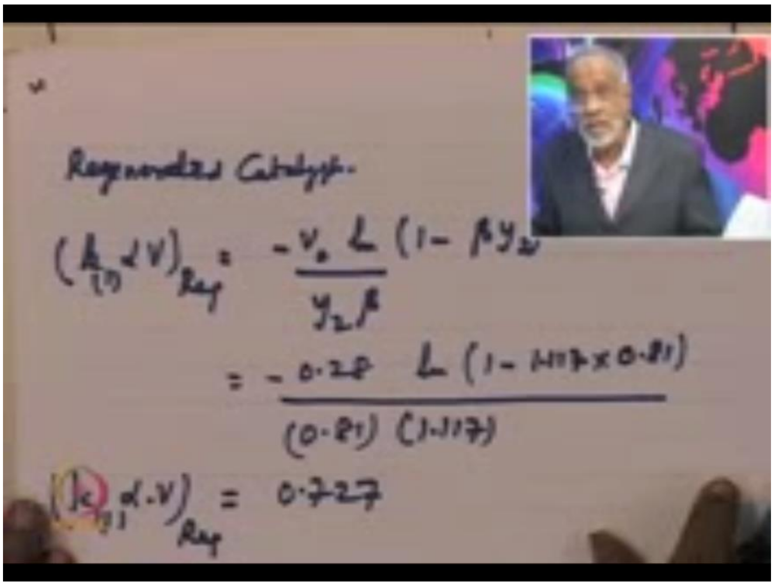

Regenerated Catalyst.

$$(k_1 \alpha V)_{Reg} = -\frac{v_0 \ln(1-\beta y_2)}{y_2 \beta}$$

$$= -\frac{0.28 \ln(1-1.117\times 0.81)}{(0.81)(1.117)}$$

$$(k_1 \alpha . V)_{Reg} = 0.727$$

So, we would not spent too much time activity of spent catalyst at 477 k what is it equal to what shall we say? Based on this what shall we say activity of spent catalyst at 477 divided by activity that mean what we are asking for the ratio of Alpha at 450 477 to alpha at 450. So, what we have to do? You simply have to multiply 0.488 by value of k 1 at 450 and divided by value of k 1 at 477.

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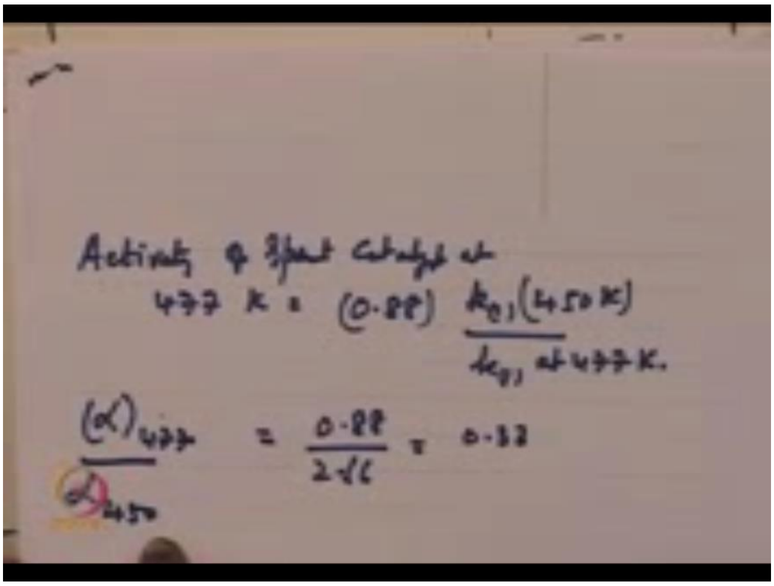

Activity of spent catalyst at

$$477\ K = (0.88)\ \frac{k_{01}(450\ K)}{k_{01}\ \text{at}\ 477\ K.}$$

$$\frac{(\alpha)_{477}}{(\alpha)_{450}} = \frac{0.88}{2.66} = 0.33$$

So, activity of spent catalyst at 477 is equal to 0.88 I will write here its already calculated, so its 0.88 multiplied by k 1 at 450 k divided by k 1 at 477 k. Now, we can calculate all these things, because the data is given, so I have done all that. So, it turns out that this ratio becomes 0.88 divided by 2.6 I have done this calculation this ratio that turns out to be 0.33. So, what we are saying now is that the activity of spent catalyst at 477 in relation to activity. So, I will write this as alpha at 477 divided by alpha at 450. So, what we have done? So, what we have done is that the activity is calculated with respect to standard condition which is 450 that is important. So, this ratio turns out to be 0.33 now, let us quickly look at what is the regenerated catalyst?

Now, what is our regenerated catalyst k 1 alpha v regenerated that is equal to once again v naught l n 1 minus beta y 2 divided by y 2 beta we can put all the numbers, so please our data is in front of us. So, we can put all the numbers I have done that here, so it becomes minus of 0.28 and then l n of 1 minus of beta value is this is at 450, so that beta value is known which is 1.117 1.17 then y 2 y 2 value please note here this 19, so 1 minus 0.19 is 0.81 correct 0.81. So, its 0.81 divided by divided by y 2 is 0.81 and then beta is 1.117, so you calculate this its comes out to be 0.727. So, k 1 alpha v regenerated is 0.727 what we are saying now what we want is what is the activity with respect to fresh catalyst? So, let us calculate what is the activity with respect to fresh catalyst? The activity with respect to fresh catalyst is simply how do you do that?

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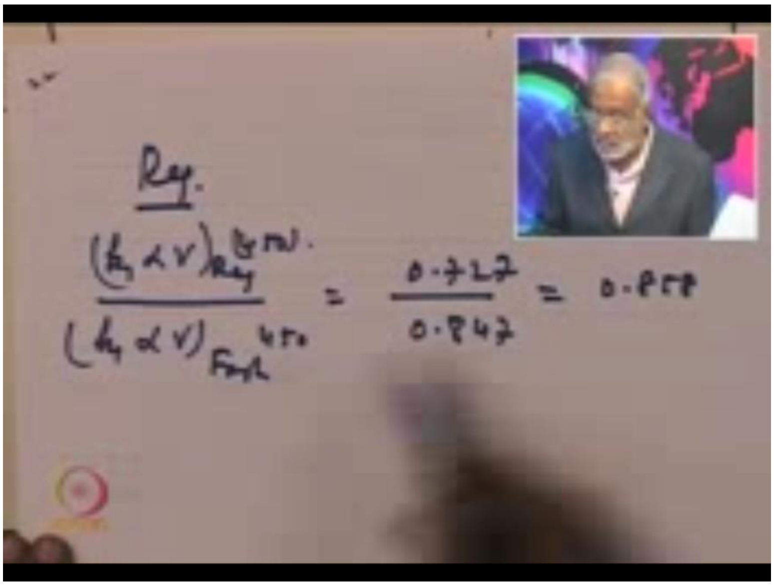

Reg.

$$\frac{(k_1 \alpha v)_{Reg}^{450}}{(k_1 \alpha v)_{Fresh}^{450}} = \frac{0.727}{0.847} = 0.858$$

So, you have k 1 alpha v regenerated now, this is at 450. So, this is this is actually at 450 data is given at 450 then we have k 1 alpha v fresh catalyst which is also at 450 unfortunately. So, this is 0.727 and if you re call you are calculated for the case of fresh catalyst turned out to be 0.847 sorry 0.84 we have calculated that is equal to 0.858. So, what we are saying now is that that there are 2 situations. We are considered situation 1 in which we find that the regenerated catalyst this is regenerated catalyst the activity with respect to fresh catalyst is 0.858. The other situation we have found out is that the regenerated catalyst the spent catalyst this is spent catalyst. The spent catalyst activity with respect to fresh catalyst this is fresh that is 0.33. And the data say please let us look at the data is says as long as 2.25 5 times at is 2.25 times 0.33 should be 2.25 times of fresh catalyst what we are saying? Re generated catalyst is 0.727 if you just multiply by 2.25 you finding that it is 2.25. So, let us say 2.25 multiplied by 0.33 this comes to approximately 0.7 0.71. So, it is on other words this is more 0.727 is more than 2.25 times 0.33 showing that the regenerated catalyst has activity more than 2.25 times the activity of the regenerated spent catalyst and that criteria satisfied. So, what we are saying is that the criteria let me just write down what we are saying is the criteria.

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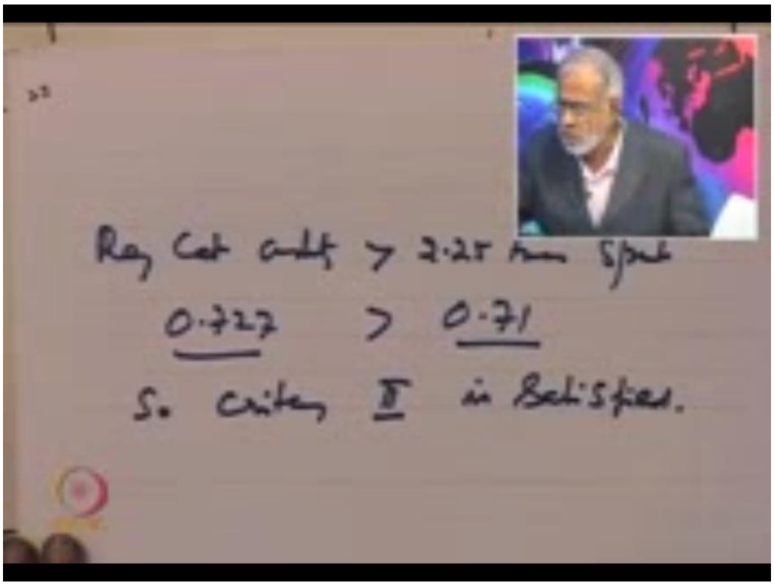

Reg Cat actvt > 2.25 time Spent

0.727 > 0.71

So criteria II is Satisfied.

What is the criteria? Regenerated catalyst activity should be greater than 2.25 times spent catalyst. So, this activity is 0.727 this is 0.71 therefore, this is greater than 0.71. So, criteria in this particular criteria 2 are satisfied. Now, the point of going through this exercise let us not forget the whole thought though is important the details some times and so on. In a process in you will always find a situations where the catalyst is deactivated. And therefore, you will have to change the conditions and those conditions have to be changed as per a program which is pointed out to you. The program is given by this is the program which you have done now, but more important in many situation is that you may have to change the catalyst and because of the cost implications here. Therefore, there are criteria that you might like look at. So, what we have done in this exercise we have set up an equation which describes the process how it performance. And we have related the process performance to measurable quantities. And therefore, by doing that we are able to evaluate how the decision that we have taken with respect to spent catalyst regenerated catalyst and fresh catalyst how they all come together.

Thank you.