Advanced Chemical Reaction Engineering

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Lecture - 10

Semi Continuous Reactor Operation

We are going to be looking at a time dependent operations in this lecture. Of course, the need for a time dependence, of course, is quite obvious, when we are looking at batch operations, you know, time is the essence; how long you take to complete the process and so on.

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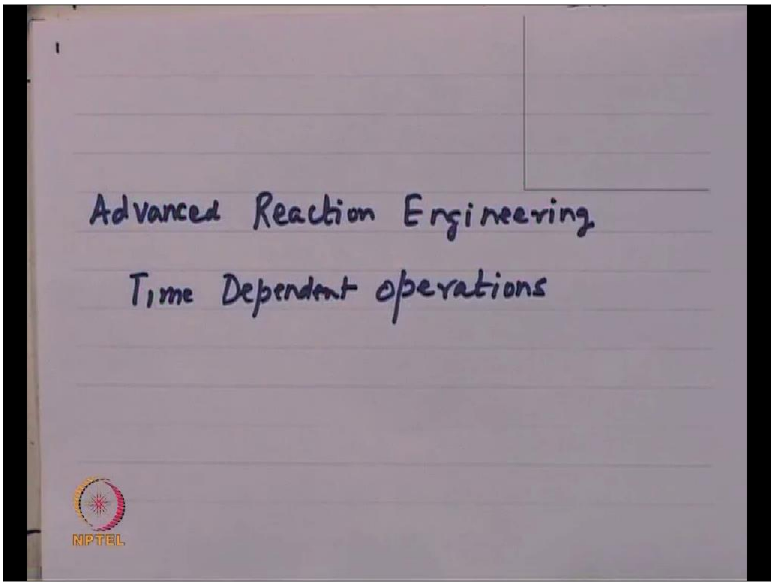

Advanced Reaction Engineering
Time Dependent operations

There are several other cases in which, your time dependence becomes important. For example, if you are starting up a process, how long does it take to reach steady state and what are the conditions that you could make use of to see that this time that is required to reach steady state is a as quickly as possible, there could be a semi batch operation in which you have to remove a material from a process and so on, and how long it takes; there where, time is a crucial element in several operations where, we talking about batch or semi batch kind of operations. So, here, we will look at some examples to illustrate how we can deal with such situations, and come to a way by which, we can formulate our equations to take care of these kind of situations.

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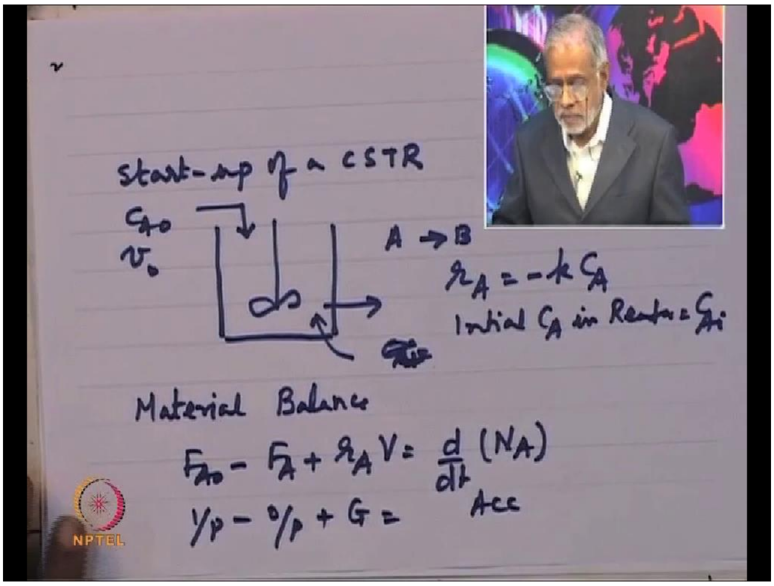

start-up of a CSTR

C_{A0}

v_0

$A \rightarrow B$

$r_A = -k C_A$

Initial C_A in Reactor $= C_{Ai}$

Material Balance

$$F_{A0} - F_A + r_A V = \frac{d}{dt}(N_A)$$

$$I/p - O/p + G = \underset{Acc}{}$$

So, first exercise, we would like to look at is for example, start up; I will just take the example of start up. So, start up of a CSTR. What do we have? We have a CSTR, let us say, to which, material is coming in and material is going out; it is well stirred; say, it is C a 0 coming in at v 0. As an example, we will say that there is a reaction, A going to B taking place, and these rate functions are a; let us say, k times C a as an example. Let us say that initially, this is the material here; the initial C a in reactor, equal to C a I, let us say. This is the initial condition which, we want. So, we want to see how long it takes for this process to reach steady state; number one, and what else that we can do to see that you know, the steady state is attained, as quickly as possible. It is something that is a great interest to us if you are starting up a CSTR on a daily basis for some process. So, how do we deal with this? Let us say we write our material balance, which is what input, output, plus generation, equal to accumulation. This is our statement of material balance. Input; I will say input. This is output; this is generation; this is the accumulation, all right.

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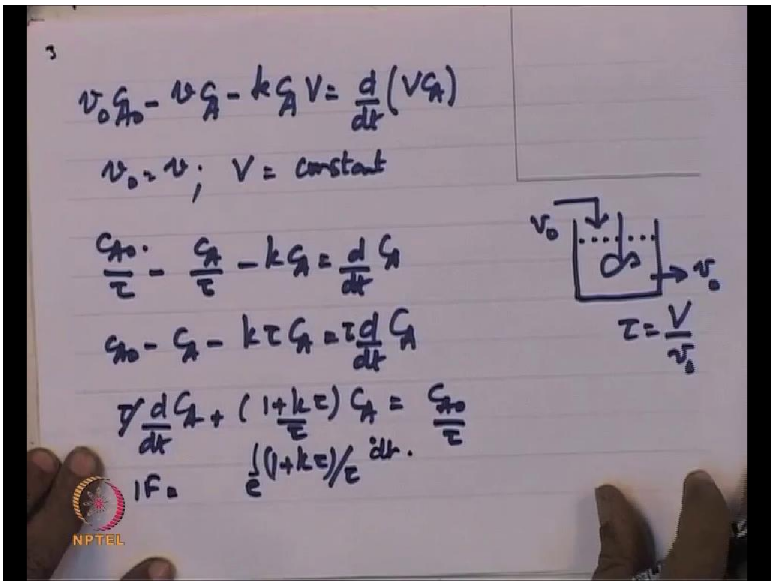

$v_0 C_{A0} - v C_A - k C_A V = \frac{d}{dt}(V C_A)$

$v_0 = v$; V = constant

$\frac{C_{A0}}{\tau} - \frac{C_A}{\tau} - k C_A = \frac{d}{dt} C_A$

$C_{A0} - C_A - k\tau C_A = \tau \frac{d}{dt} C_A$

$\cancel{\tau}\frac{d}{dt} C_A + \left(\frac{1+k\tau}{\tau}\right) C_A = \frac{C_{A0}}{\tau}$

$IF = e^{\int (1+k\tau)/\tau \, dt}$

$\tau = \frac{V}{v_0}$

Let us see how, what we can do with this. I will write this as v naught, C a naught; that is input, and then see, v C a; that is output. Then, say our reaction is k times C a equal to d by d t of what is n a, which is v times C a. So, we can say that v naught equal to v, which means that there the flow or the inlet; I will draw it once again here; what we are saying here is that if this is v naught, we are saying that this is also v naught. This typically, what we might expect; v equal to v naught, and then we assume that capital V is constant, which means that the amount of fluid in the equipment, remains constant; that is what we saying. So, this can come out of the derivative and so on.

Therefore, we can write this as C a naught. So, if I say tau, the residence time as V by v naught; therefore, this becomes minus tau, and then C a by tau, minus of k times C a, equal to d by dt of C a, or write this as C a naught, minus of C a, minus of k tau C a, equal to d by d t of C a. I just forgot to multiply by tau. Therefore, let me write this as tau times d by d t of C a, plus 1 plus k tau times C a, equal to C a 0. So, this is the equation that describes the stirred tank during the unsteady state. So, what is the integrating factor? Integrating infector is e raise to the power of 1 plus k tau, multiplied by; I will put this tau here; there, I will put this tau here. So, it is tau integral d t. So, this is the integrating factor. So, we can integrate this and I will write the solutions, so that, we do not spend too much time in trying to do what we know, quite well.

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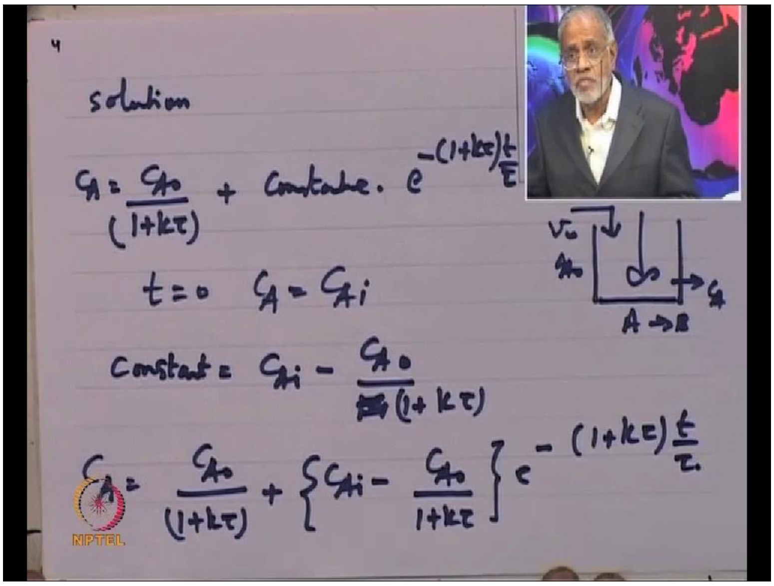

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solution

$$C_A = \frac{C_{A0}}{(1+k\tau)} + \text{Constant} \cdot e^{-(1+k\tau)\frac{t}{\tau}}$$

$$t = 0 \quad C_A = C_{Ai}$$

$$\text{Constant} = C_{Ai} - \frac{C_{A0}}{(1+k\tau)}$$

$$C_A = \frac{C_{A0}}{(1+k\tau)} + \left\{ C_{Ai} - \frac{C_{A0}}{1+k\tau} \right\} e^{-(1+k\tau)\frac{t}{\tau}}$$

So, I will write the solution. As the solution, I mean, we can solve that by the integration factor and all that. So, solution looks like this. Solution is C a equal to C a 0 by 1 plus k tau, plus constant of integration, multiplied by e raise to the power of minus 1, plus k tau t by tau. So, solution to the C s; what we are saying once again, let us just not forget the physics in this situation; we have stirred tank materials, coming in and going out. The reaction is taking place. This is v naught and C a naught and C a and so on. So, this is the solution. We want to find the constant of integration. At t equal to 0, we have said that C a equal to C a i; this is the assumption.

So, if you put this here, you get the constant of integration becomes, we required obvious constant of integration; you can just see very easily that is C a i minus of C a naught, divided by 1 plus k tau. So, this is the constant of integration. You can substitute here. Therefore, solution becomes C a equal to C a naught, divided by 1 plus k tau, plus C a i minus of C a naught by 1 plus k tau; this is the constant of integration, multiplied by e raise to power of 1 plus k tau, multiplied by t by tau. So, this is the solution to the case of a start up of a stirred tank. So, what is that we are saying; that if you have a stirred tank and you started up with c equal to C a; this is initially C a i. So, this is the unsteady state behavior of the stirred tank.

Now, let us see what happens at t equal to infinity; this becomes 0. So, what happens at t equal to infinity? C a equal to what shall we say? At t equal to infinity, if this whole terms appear; therefore, C a becomes C a naught by 1 plus k tau; this is something that we know from our understanding of stirred tanks, but what is more important is if I ask you how long does it take if we appropriately, choose C a I; the question is if we choose C a i equal to C a naught, divided by 1 plus k tau, then the time to reach steady state is nil, or in other words, the process operates at steady state from time t equal to 0. On other words, by appropriate choice of the initial state in the CSTR, in the equipment, you can actually avoid that time that you will lose in breathing steady state. This is the point that is to be remembered that this time required to reach steady state. So, let me just put it down in this.

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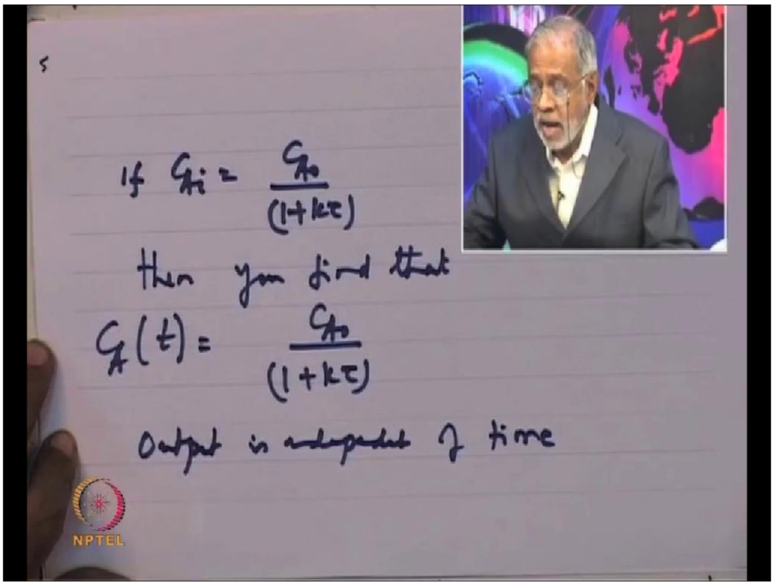

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If $C_{Ai} = \frac{C_{A0}}{(1+k\tau)}$

then you find that

$C_A(t) = \frac{C_{A0}}{(1+k\tau)}$

Output is independent of time

If C a i equal to C a naught, divided by 1 plus k tau, if C a i is so chosen, that it is equal to C a naught, then you find that C a, at any time t of becomes equal to 1 plus k tau. On other words, the output is independent of time. So, this CSTR is able to reach steady state, immediately, so that, you are able to avoid that time that is lost in reaching steady state. So, to cut the long story short, what we are trying to say is that start up of a CSTR, you can actually, achieve practically, the final endpoint by appropriate choice of C a i. If you choose C a i properly, your steady state is obtained very quickly, and therefore, your process is able to run at steady state, without losing too much time. So, this is the most important aspect of this unsteady state that we should recognize by an appropriate choice of the initial state.

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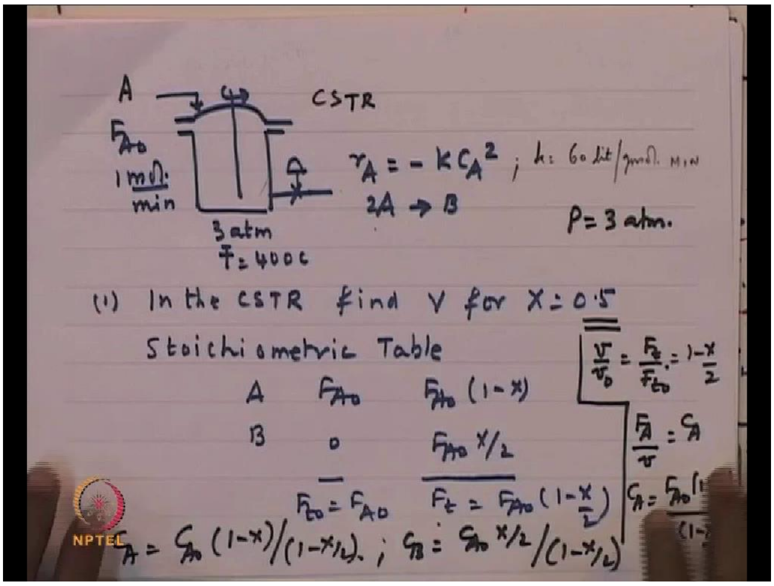

A

F_{A0}

1 mol/min

CSTR

3 atm

T = 400 C

$r_A = -kC_A^2$; k = 60 lit/gmol. min

$2A \rightarrow B$

P = 3 atm.

(1) In the CSTR find V for X = 0.5

Stoichiometric Table

A	F_{A0}	$F_{A0}(1-x)$
B	0	$F_{A0}\, x/2$
	$F_{t0} = F_{A0}$	$F_t = F_{A0}(1-\frac{x}{2})$

$\frac{v}{v_0} = \frac{F_t}{F_{t0}} = 1-\frac{x}{2}$

$\frac{F_A}{v} = C_A$

$C_A = \frac{F_{A0}(1}{(1-}$

$C_A = C_{A0}(1-x)/(1-x/2)$. ; $C_B = C_{A0}\, x/2/(1-x/2)$

We are looking at an illustrative exercise to understand how we can apply the design equations we have derived. The problem is we have a stirred tank, CSTR to which, a component A enters and goes out. A reaction 2A going to B, is taking place; a dimidiation reaction. The rate function r a is given as minus of k times C a squared. The rate constant k is 60 liters per gram mole per minute. The reactor works in three atmospheres and temperature of 400 c. The problem is in two parts. First part; we have to find out what is the volume of this equipment for a conversion of 0.5. We will do that first, and then we look at the second part, a little later. Now, to be able to handle a problem like this where, there is a change in volume, because of chemical reaction; we have to write the stoichiometric table and take into account how the volume change can be appropriately, taken into account.

So, you have component A and component B. Component A comes in at F a 0. There is no component B at the inlet. At the outlet, if conversion is defined with respect to component A, we know that the outlet flow will be F a 0 times 1 minus of x as statement of material balance, and component B; nothing is coming in at the inlet and it reacts as per this twice A, going to B or A going to half B. Therefore, the amount of B form, will be F a 0 x by 2. So, if you add the inputs and the outputs; input, if you add, it is F t 0; it is the total moles of component A coming in, which is same as F a 0 and the total moles of what goes out as if you can add A and B together, you find that is F a 0 times 1 minus of x by 2. So, that you know that F t 0, which is F a 0 and it becomes F a 0 times 1 minus of x by 2, and you can see there is a change in the number of moles, because of chemical reaction.

Now, to be able to account for the effect of this what we do is that we apply what is called as called as gas law, because this reaction twice A going to B, is a gas phase reaction. Now, we know from our gas law that v by v 0 is F t by F t 0, t by t 0, p 0 by p and so on, and since, gas is taken as ideal, we have simply, it is F t by F t 0. Why is that, because there is no change in pressure; there is no in temperature and therefore, those effects are removed. Therefore, you have v by v 0 is simply, F t by F t 0. What is v? v is a volumetric flow at the outlet and v 0 is the volumetric flow at the inlet. So, v by v 0 tells us the change in volume, because of chemical reaction. Now, F t by F t 0; you can see from here, F t divided by F t 0 is simply, 1 minus of x by 2. Therefore, we get v by v 0 is 1 minus of x by 2. So, essentially, we are now taken into account, the fact that there is a change in volume, and that effect of change in volume is now expressed, in terms of extent of reaction on conversion with respect to component A as reference.

Now, if you have to calculate what is C a and C b, because we require C a in our rate expression. We now want to calculate what is C a. Now, C a by definition, F a divided by v where, F a is the molar flow rate at the exit and v is the volumetric flow rate at the exit. Now, F a from here, we find it is F a 0 times 1 minus of x and volumetric flow is v is v 0 times 1 minus of x by 2. Therefore, we find C a at the exit is F a 0 times 1 minus of x, divided by v 0 times 1 minus x by 2. So, that we get C a as C a 0 times 1 minus of x, divided by 1 minus of x by 2. So, we are now able to substitute for this C a in the rate expression, so that, now we can use that result effectively. Now, what is C b? C b by definition, is F b by v and that becomes C a 0 x by 2, divided by 1 minus of x by 2. So, what we have done is that using the fact that there is volume change, we have been able to express concentrations in terms of conversion. We have done all this. Now, what is important is we have to calculate what are the values of these numbers?

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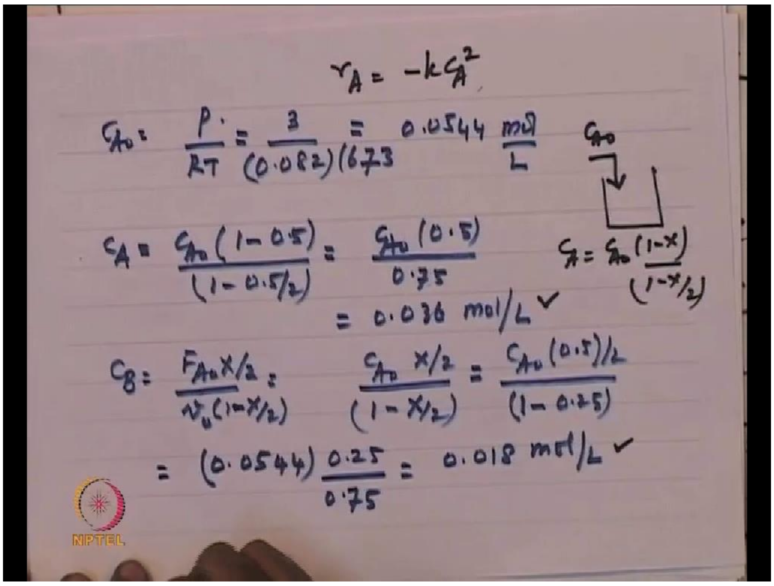

$$r_A = -kC_A^2$$

$$C_{A0} = \frac{P}{RT} = \frac{3}{(0.082)(673} = 0.0544\ \frac{mol}{L}$$

C_{A0}

$$C_A = \frac{C_{A0}(1-0.5)}{(1-0.5/2)} = \frac{C_{A0}(0.5)}{0.75}$$

$$= 0.036\ mol/L\ ✓$$

$$C_A = C_{A0}\frac{(1-x)}{(1-x/2)}$$

$$C_B = \frac{F_{A0}x/2}{v_0(1-x/2)} = \frac{C_{A0}\ x/2}{(1-x/2)} = \frac{C_{A0}(0.5)/2}{(1-0.25)}$$

$$= (0.0544)\frac{0.25}{0.75} = 0.018\ mol/L\ ✓$$

For example, what is C a 0? C a 0 by definition, is P by RT; this is gas law. What is pressure is given as 3 atmospheres; the gas constant is 0.082 liter atmosphere per gram mole at degree k and the temperature is 673, which is 400 c. So, that you find that C a 0 is 0.0544. Now, what is C a? We have just now said C a is C a 0, 1 minus of x, divided by 1 minus of x by 2. Therefore, we can now put all the numbers and find out that C a at the exit is equal to 0.03 c at the exit. This is the exit; exit C a. C a at the exit is 0.036 moles per liter and what is C b is F a 0 x by 2, divided by v 0, 1 minus of x by 2, which you have already said, and if you put all the numbers, it becomes 0.018 mole per liter. So, we have calculated what is C a and what is C b, as soon as we also calculated what is C a 0. Now, we are in position to put these things in our design equation to find out what is the volume of the equipment that is required to obtain a conversion of 0.5. Let us do that now.

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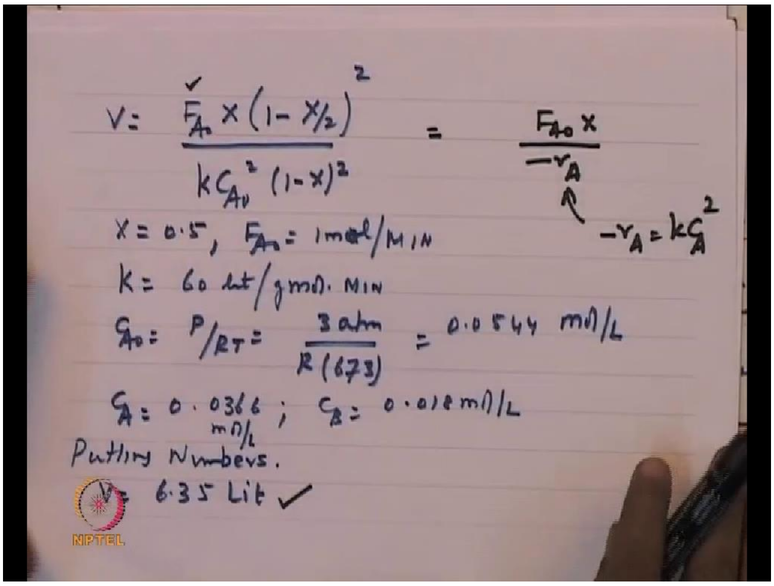

$$V = \frac{\checkmark{F_{A0}}\, x \left(1 - x/2\right)^2}{k C_{A0}^2 (1-x)^2} = \frac{F_{A0}\, x}{-r_A}$$

$$-r_A = k C_A^2$$

$X = 0.5$, $F_{A0} = 1$ mol/MIN

$k = 60$ lit/gmol. MIN

$C_{A0} = P/RT = \frac{3\text{ atm}}{R(673)} = 0.0544$ mol/L

$C_A = 0.0366$ mol/L ; $C_B = 0.018$ mol/L

Putting Numbers.

$V = 6.35$ Lit ✓

What we have done now? We said v equal to F a 0 x divided by minus of r a and this substituting of minus of r a, which is; what is minus of r a? Minus of r a is k times C a squared and therefore, I am putting k is here and what is C a, which this C a 0 squared, multiplied by 1 minus of x, divided by 1 minus of x by 2, which have derived all these. Therefore, now we know the volume of the equipment is given by the right hand side. Now, we know what is F a 0; we know what is x; we know all the numbers here. If you put all the numbers, you can get the volume of the equipment to be 6.35 liters; putting all the numbers; k is 60; C a 0 is known. So, everything is known here, and therefore, we can calculate what is the volume of the equipment, which turns out to be 6.35 liters. Now, the second part of the exercise is quite interesting.

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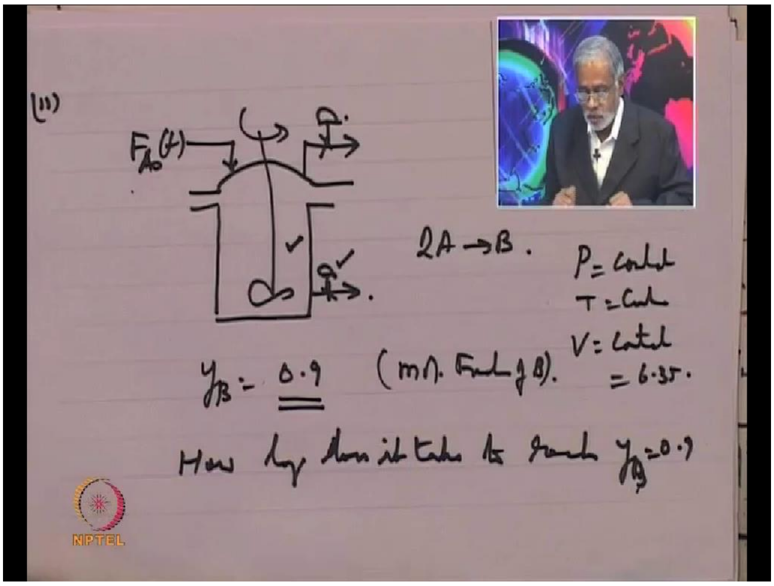

$2A \rightarrow B$.

P = Constant

T = Const

V = Constant = 6.35.

$y_B = \underline{\underline{0.9}}$ (mol. Fraction of B).

How long does it take to reach $y_B = 0.9$

Second part of the exercise; what is this in the second part of the exercise. What it says is now, as this CSTR, which is running at steady state at an instant of time, when the steady state is achieved, and the process is running at x is equal to 0.5; we close the outlet valve. All the outlet valves are closed and the inlet flow F a 0 is adjusted. So, that the pressure remains constant; temperature remains constant. Temperature remains constant, because we maintain temperature constant. So, question is how long would it take for the outlet mole fraction here, sorry, how long the mole fraction inside the equipment to become 0.9? Let me repeat; the question is when the process is running at steady state, we close the outlet valves and we adjust the flow entering the equipment. So, that pressure remains constant and we want to find out how long it would take for the equipment, for the composition inside the equipment, to reach y b or mole fraction of y, component b is 0.9. So, this is what we would like to do now.

Now, clearly, this is an instance of an unsteady process. Therefore, we have to set up our balances to take into account the fact that it is an unsteady state process. Now, let us see how to address this.

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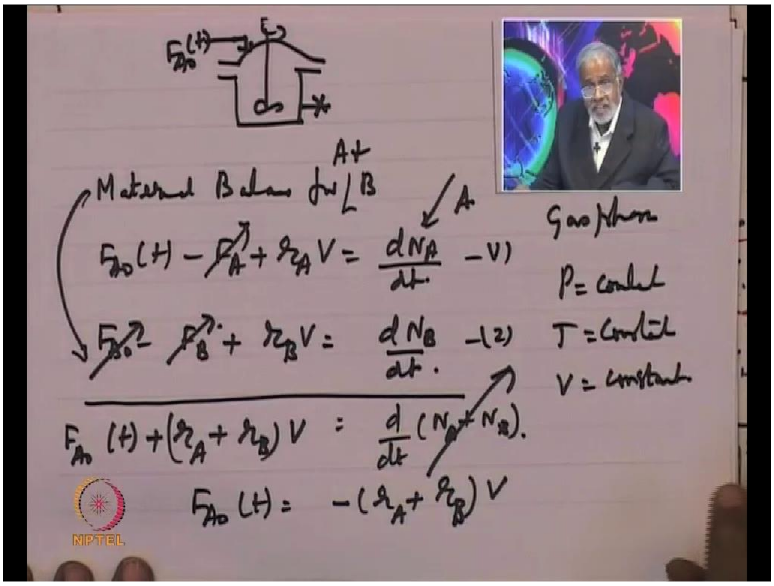

Material Balance for A + B

$F_{A0}(t) - \cancel{F_A} + r_A V = \frac{dN_A}{dt}$ -(1)

$\cancel{F_{B0}} - \cancel{F_B} + r_B V = \frac{dN_B}{dt}$ -(2)

Gas phase

P = constant

T = constant

V = constant

$F_{A0}(t) + (r_A + r_B) V = \frac{d}{dt}\cancel{(N_A + N_B)}$

$F_{A0}(t) = -(r_A + r_B) V$

Now, what we said is that we are adjusting; let me just draw it once again; we are adjusting; we have this feed is coming in, but there is no output. This is all F a 0 and it is a function of time. So, if you write a material balance for A and B, you have material balance for A and material balance for B. Let us see what it is. Input F a 0 of t, which is function of time; output, there is no output, plus generation equal to accumulation. Input of B, output of B, generation of B, equal to accumulation of B. We know that there is no output of A, because the valves are closed. Therefore, F a disappears. Similarly, if you look at component B, there is no input of component B; there is no output of component B and therefore, rate of generation of component B equal to accumulation of component B. So, the material balance for A and B gives us these equations 1 and equations 2

Now, let us recognize that this is a gas phase reaction where, pressure is constant; temperature is constant; volume is constant. Volume is constant, because the equipment volume does not change. Now, here is an instance of a gas phase reaction where, temperature is constant; pressure is constant; volume is constant. Therefore, we should expect that the number of moles inside the equipment from the time, we start this process, would not have changed. On other words, if you add equation 1 and 2, d by d t of n a plus n b; the right hand side should go to 0. That is the requirement of problem statement, because pressure is constant; temperature is constant; volume is constant. Therefore, we have the right hand side is 0. Therefore, if you add the left hand side F a of; it is a function of time, plus r a, plus r b, multiplied by v become 0. Therefore, F a of time, F a 0 at any time t, t equal to minus of r a, plus r b, times v. On other words, the material balance taking into account, the fact that gas law gives us the condition that d by d t of n a plus n b is 0, gives us a result, which tells us how we should regulate this process to be able to achieve constancy of pressure, which says, we must regulate the flow of F a 0, so that it becomes always equal to minus of r a plus r b times v. So, this is the condition that we will impose on the control system that will regulate the flow of component A into the system.

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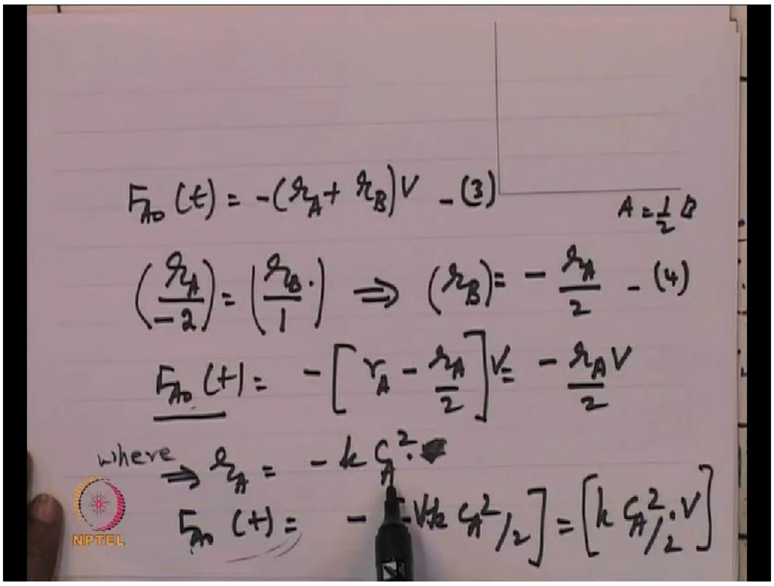

$$F_{A0}(t) = -(r_A + r_B)V \quad -(3)$$

$$A = \frac{1}{2} B$$

$$\left(\frac{r_A}{-2}\right) = \left(\frac{r_B}{1}\right) \Rightarrow (r_B) = -\frac{r_A}{2} \quad -(4)$$

$$\underline{F_{A0}(t)} = -\left[r_A - \frac{r_A}{2}\right]V = -\frac{r_A V}{2}$$

where $\Rightarrow r_A = -k C_A^2$

$$F_{A0}(t) = -\left[V k C_A^2/2\right] = \left[k C_A^2/2 \cdot V\right]$$

Once we know this, the rest is fairly, straight forward. Let us just look at all that, once again. Now, what we have said? We have said that the material balance tells us that we must regulate F a 0, coming into the equipment as minus of r a, plus r b times v. We also know from the statement of a stoichiometry that the rate at which, chemical reaction occurs r a by minus 2, must be equal to r b by plus 1, because A is reacting; B is getting formed, and as a result, we should have the rate of formation of B, equal to minus of r a by 2, follows by from the fact that stoichiometry tells us that A equal to half of B; it follows from that. That means, if you can say, we can substitute this result that r b is minus of r a by 2 in our equation 3 here, so that, now we get F a 0 of t equal to minus of r a, and then r b is minus r a by 2; I will just call this as equation 4. So, you get r b as minus of r a by 2. So, that F a 0 of t becomes minus of r a by 2, multiplied by v. This is clear. Notice here, that r a is minus of k ca square, is already given in the problem statement, which is what is mentioned here where, r a is minus of k ca square.

Now, we can substitute for r a here.

So, that now we get the rate at which, the material is entering the equipment, F a 0 of t; how it must change its time is now given, which is r a which is k times ca square v, divided by 2 minus; there are two minus signs here. So, that now, we get F a 0, which is the function of time, must be k times C a squared by 2 times v. On other words, what is being said in the problem statement is that we must adjust F a 0 of t, so that, it is always equal to k times C a squared by v, C a squared by 2 v. So, we must adjust F a 0 of t, so that, it satisfies this equality always. This is the control system that we must implement. Having said this, now, the rest is even, fairly straight forward. Now, what does it mean? It means that if you look at the material balance for component A, What is the material balance for component A; input, output, generation equal to accumulation.

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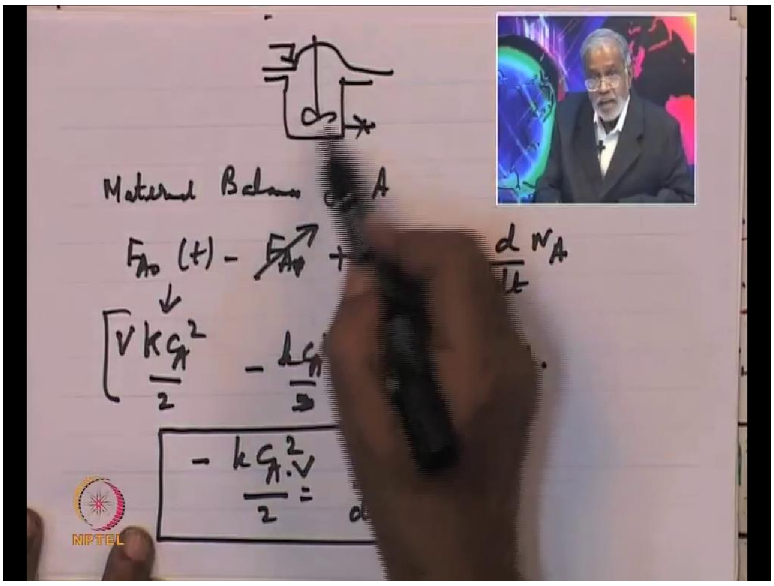

There is no output, because the equipment is closed. There is nothing coming out of the equipment now. So, this valve is closed. So, whatever comes in, it can only accumulate. Therefore, we have output is 0. So, input F a zero of t is already shown in the previous description as v times k Ca squared by 2, and r a is what; k C a square. This also, we know, because r a is given as k C a squared in the problem statement, with a minus sign. So, we have F a 0 of t, which is v times k C a squared by 2 and r a is minus of k C a squared by two times v. So, that we get d by d t of n a is minus of k C a squared by 2, multiplied by v. So, what we have been able to do by utilizing the material balance in the problem statement is to show that the d by d t of n a is now, equal to k times C a square v by 2.

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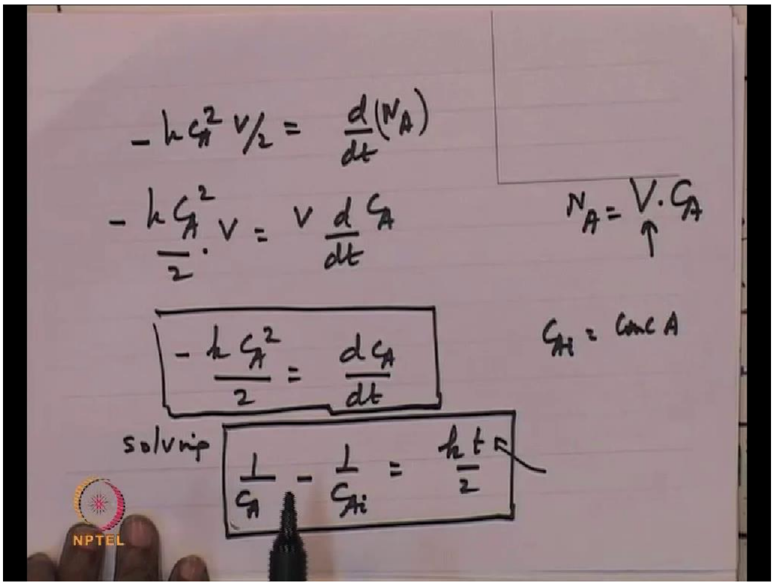

$$-kC_A^2 V/2 = \frac{d}{dt}(N_A)$$

$$-\frac{kC_A^2}{2}\cdot V = V\frac{d}{dt}C_A$$

$$N_A = \underset{\uparrow}{V}\cdot C_A$$

C_A = Conc A

$$\boxed{-\frac{kC_A^2}{2} = \frac{dC_A}{dt}}$$

solving $\boxed{\frac{1}{C_A} - \frac{1}{C_{Ai}} = \frac{kt}{2}}$

Now, having said this, we can go forward and carry out the integration. Now, left hand side is minus k C a squared v by 2. The right hand side n a is by definition, n a, you know of this; n a is always v times C a and v is constant. Therefore, v can come out of the derivative which cancels off. So, that we get now that the differential equation, which governs the variation of C a with time inside the equipment is given by minus of k C a squared by 2, equal to d by d t of C a, which on integration, gives us the result 1 by C a minus of 1 by C a, equal to k t by 2. So, what we are saying now, is that we are now in a position to tell how long we must run the process. So, that we get concentration of C a as might be specified in the problem. What is specified in the problem? What is specified in the problem is the following.

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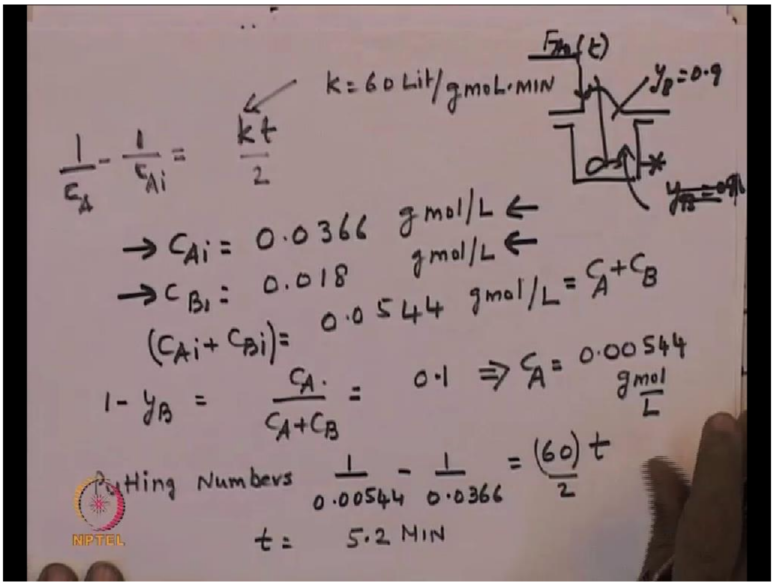

$k = 60$ Lit/gmol·MIN

$$\frac{1}{C_A} - \frac{1}{C_{Ai}} = \frac{kt}{2}$$

$\rightarrow C_{Ai} = 0.0366$ gmol/L $\leftarrow$

$\rightarrow C_{Bi} = 0.018$ gmol/L $\leftarrow$

$(C_{Ai} + C_{Bi}) = 0.0544$ gmol/L $= C_A + C_B$

$$1 - y_B = \frac{C_A}{C_A + C_B} = 0.1 \Rightarrow C_A = 0.00544 \ \frac{\text{gmol}}{\text{L}}$$

Putting Numbers $\frac{1}{0.00544} - \frac{1}{0.0366} = \frac{(60)}{2} t$

$t = 5.2$ MIN

Problem statement says that; let me draw it once again; it says this is closed; we want this y b here, to be equal to 0.1. This is what it says. Problem statement says that how long does it take for the contents of this equipment to reach y b equal to 0.9 or y a equal to; let me write this here; we want y b equal to 0.9. Now, this one point, we must remember is that at the instant of time when we close this valve, the processes running at steady state at that time composition of A and B; I have written at C a i and C b i; the compositional A and B at the instant when we close the valve, were the values corresponding to the steady state, achieved corresponding to x equal to 0.5 in the first part of the problem. On other words, at the time when we close these valves, so that, it ran as a semi batch operation; C a i and C b i was a steady state values that we have achieved in part 1 of the problem. We have already found that values to be 0.0366 gram moles per liter and C b as 0.018 gram moles per liter. So, that C a plus C b i, at the time we close the valve, was 0.0544 gram moles per liter.

Now, we have also said when we looked at the material balance, that p equal to constant; t equal to constant; volume equal to constant, and therefore, the total number of moles cannot change. Therefore, the concentration inside this equipment, C a i plus C b i must always be equal to C a plus C b, because that is the statement of the problem. On other words, what we are saying is that C a i plus C b i, which is 0.0544 when we close this valve, that total cannot change as this reaction proceeds, because that is the problem statement. So, what we are saying now, therefore, is that if you want y b equal to 0.9 or y a equal to 0.1, C a by C a plus C b is 0.1 where, C a plus C b is specified as 0.0544. On other words, what we are saying is that the value of C a at which we want to stop the process, is given by this number; C a must stop at 0.00544.

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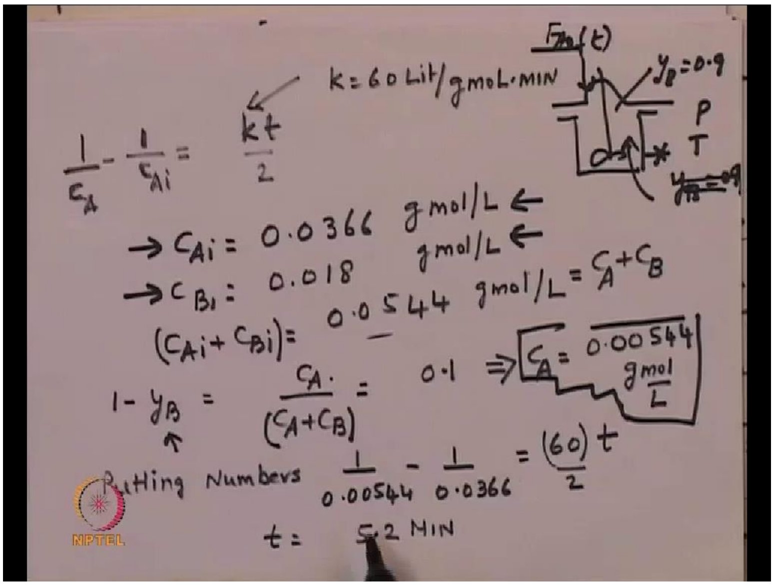

k = 60 Lit/gmoL·MIN

$$\frac{1}{C_A} - \frac{1}{C_{Ai}} = \frac{kt}{2}$$

$\rightarrow C_{Ai} = 0.0366$ gmol/L $\leftarrow$

$\rightarrow C_{Bi} = 0.018$ gmol/L $\leftarrow$

$(C_{Ai} + C_{Bi}) = 0.0544$ gmol/L $= C_A + C_B$

$$1 - y_B = \frac{C_A}{(C_A + C_B)} = 0.1 \Rightarrow \boxed{C_A = 0.00544 \ \frac{\text{gmol}}{\text{L}}}$$

Putting Numbers $\frac{1}{0.00544} - \frac{1}{0.0366} = \frac{(60)t}{2}$

t = 5.2 MIN

We started at C a i as 0.0366. We want to stop at 0.00544. On other words, C a, we want the time required to reach y b equal to 0.9 or y a equal to 0.1; we must substitute C a value of 0.00544 and C a i value of 0.0366. That will be the time that is required to reach y b equal to 0.9. If you put all these numbers, you will find that the time required to reach y b equal to 0.9 is 5.2 minutes. On other words, this whole exercise that we have tried to illustrate the use of design equations is essentially, tell how we can use the design equations for unsteady state process, like a stirred tank, to understand how a semi batch process can be understood, can be modeled, can be regulated, depending upon the statements of the process or depending on the requirements of the process we are dealing with.

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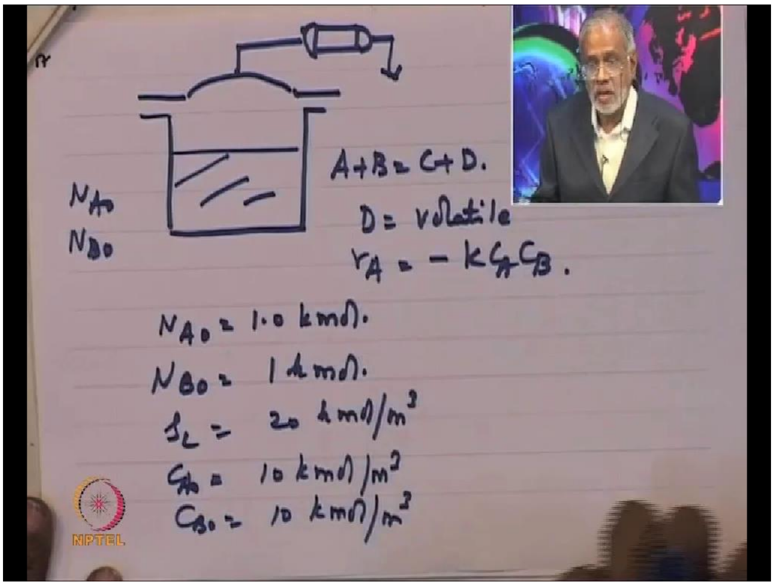

N_{A0}

N_{B0}

$A+B = C+D.$

$D =$ volatile

$r_A = -k C_A C_B.$

$N_{A0} = 1.0$ kmol.

$N_{B0} = 1$ kmol.

$\rho_L = 20$ kmol/m^3

$C_{A0} = 10$ kmol/m^3

$C_{B0} = 10$ kmol/m^3

The third exercise, we want to look at is the following that you have a chemical reactor. Now, the output goes to a condenser, and then you have the reaction taking place is A plus B going to C plus D. D is volatile, and the reaction is minus of k to C a and C b. You have a batch, starting with n a 0 and n b 0. So, this is the exercise in front of us. You have a reaction A plus B going to C plus D and the product D is volatile. Therefore, we are able to boil it off, and then condense it. Now, the question in front of us is how the volume of fluid in this equipment will change with time. Of course, this is relevant event in a commercial practical situation, because if you are having this in a practical situation, you will have to find out, I mean, what is the volume that is left unreacted, so that, you know, you can start the next batch. See, you must you know whether, it is to what extent, the fluids have been consumed. So, this has got very practical significance. The data given is N a 0 equal to 1 kilo mole; N b 0 is given as 1 kilo mole. Then, density is given as 20 kilo mole per cubic meter; this is for the fluid. C a 0 is given as 10 kilo mole per cubic meter and C b 0 is also given as 10 kilo mole per cubic meter. The problem statement is that you have a batch equipment in which, you have N a 0 moles of A and N b 0 moles of B, and then the fluid density mixture is given as 20 kilo moles per cubic meter; C a 0 and C b 0s are given and this reaction, A plus B going to C plus D, and the rate function is minus of k C a C b; second order reaction.

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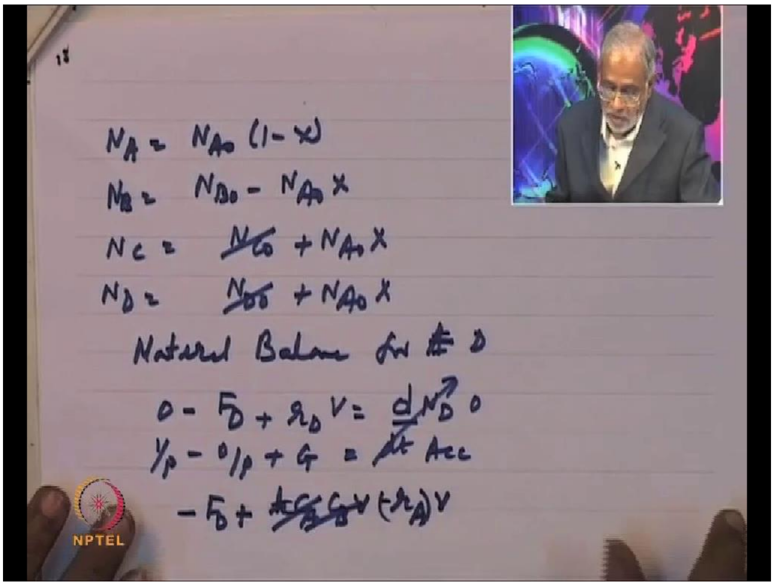

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$N_A = N_{A0}(1-x)$

$N_B = N_{B0} - N_{A0}x$

$N_C = \cancel{N_{C0}} + N_{A0}x$

$N_D = \cancel{N_{D0}} + N_{A0}x$

Material Balance for ~~A~~ D

$0 - F_D + r_D V = \cancel{\frac{dN_D}{dt}}\ 0$

$I/p - O/p + G = Acc$

$-F_D + \cancel{kC_AC_B}V\ (-r_A)V$

Question is what is the volume of fluid left in the equipment, after a given extent of time? Let us see how to understand this. Our stoichiometry is what; N a equal to N a 0 times 1 minus of the x; we know this. N b is equal to N b 0 times N a 0 x; we know this. N c is N c 0, which is plus N a 0 x and N d is N d 0 plus N a 0 x; I have canceled this off, because it is not there, initially. Now, if you write a material balance for A, what do we get? Input and, sorry, I am writing material balance for D, sorry, not D. There is no input of D here. Output, you notice here is that this D, is going out here; this D is coming out here. So, F d plus R d times v equal to 0. Why is it 0? It is 0, because N d does not accumulate. What is the question? Question, we are having in front of us is that as the reaction occurs, the D formed being volatile; it is rapidly removed. Therefore, there is no accumulation of D in the equipment. That is why we have this input. This is input; this is output; this is generation of component D; this is accumulation of component D, all right. So, there is no input. What is R d? R d by definition, what we have said is that R d is k C a C b times v. On other words, R d is same as, I mean, we can even say this R d is same as R a V with the minus sign; is it all right, because whatever is the; what should I say; whatever is with the minus sign, whatever is the D a formed; a consumed is in D formed, all right.

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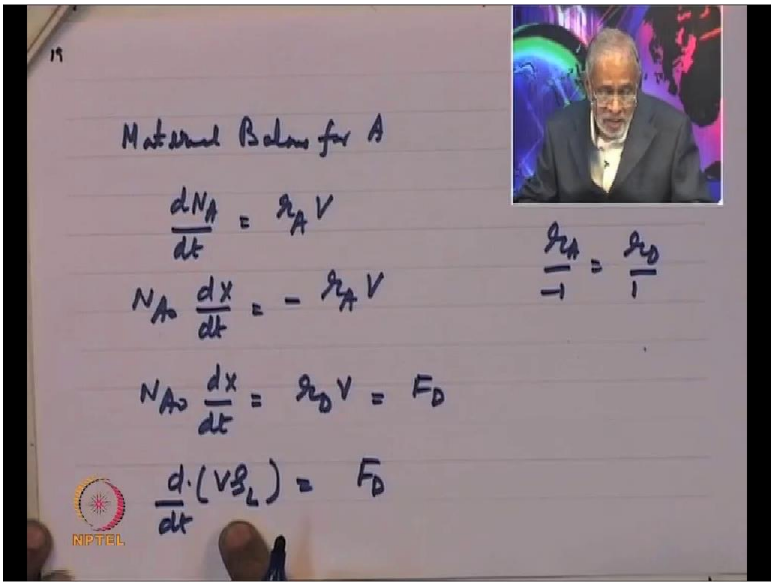

19

Material Balance for A

$$\frac{dN_A}{dt} = r_A V$$

$$N_{A0}\frac{dx}{dt} = -r_A V$$

$$N_{A0}\frac{dx}{dt} = r_D V = F_D$$

$$\frac{d}{dt}(V\rho_L) = F_D$$

$$\frac{r_A}{-1} = \frac{r_D}{1}$$

Essentially, what we are saying is suppose, you write a material balance for A. We get d N a by d t; there is no input, no output; there must be equal to R a V. Now, N a is what? N a 0 times d x d t; that we know, equal to minus of R a V; this also we know. N a 0 d x d t equal to what is this R d; we know from our stoichiometry, R a by minus 1 is equal to R d by plus 1. So, R a R d; this is minus R a V is equal to plus R d. So, this is simply equal to R d V; is that clear? What we are saying? What we are saying is that, F d, you can see here; no need to write this; F d equal to R d V.

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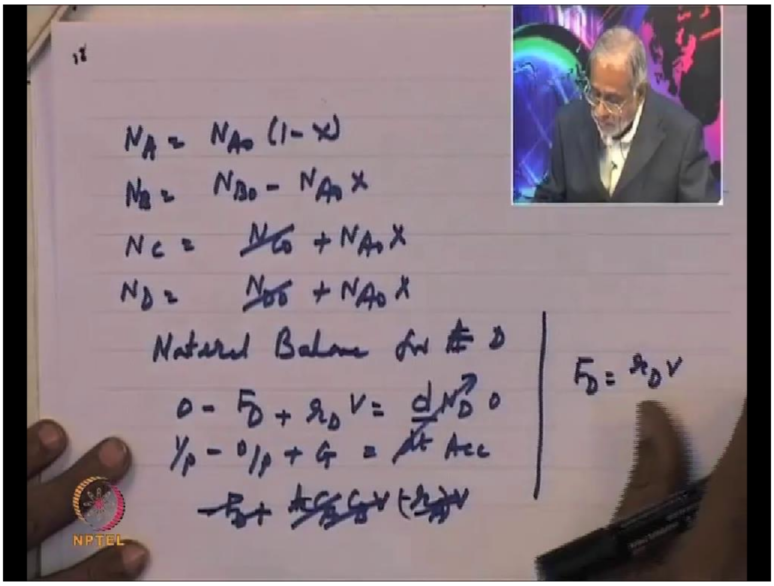

18

$$N_A = N_{A0}(1-x)$$

$$N_B = N_{B0} - N_{A0}x$$

$$N_C = \cancel{N_{C0}} + N_{A0}x$$

$$N_D = \cancel{N_{D0}} + N_{A0}x$$

Material Balance for ~~A~~ D

$$0 - F_D + r_D V = \cancel{\frac{dN_D}{dt}}\ 0$$

$$I/p - O/p + G = Acc$$

[illegible]

$$F_D = r_D V$$

So, this actually, gives you; let me just write it here; F d equal to R d V; this will come from the material balance for D. Now, R a equal to minus of R d; therefore, this is equal to F d. That is what we are saying. So, what we are saying is that this is equal to F d. Now, we also know the rate at which, volume must be equal to F d. Whatever is the change in mass of the fluid in the equipment, must be equal to the rate of change of F d; is it clear; where, royal refers to molar density of the mixture and so on. So, we can look at these two equations. You can see this equation and this equation. We can see here since, they are both equal to F d; therefore, N a 0 d x d t must be equal to d by d t. Let me write this for you, and then let us look at it, once again. So, what we are saying is that N a 0 d x d t; please note here; N a 0 d x d t equal to F d; d by d t of v l is also equal to F d. So, you notice here; d by d t of v l; here, v l is, this is decreasing; therefore, there must be a minus sign here. That is why I put a minus sign here. So, what do we get?

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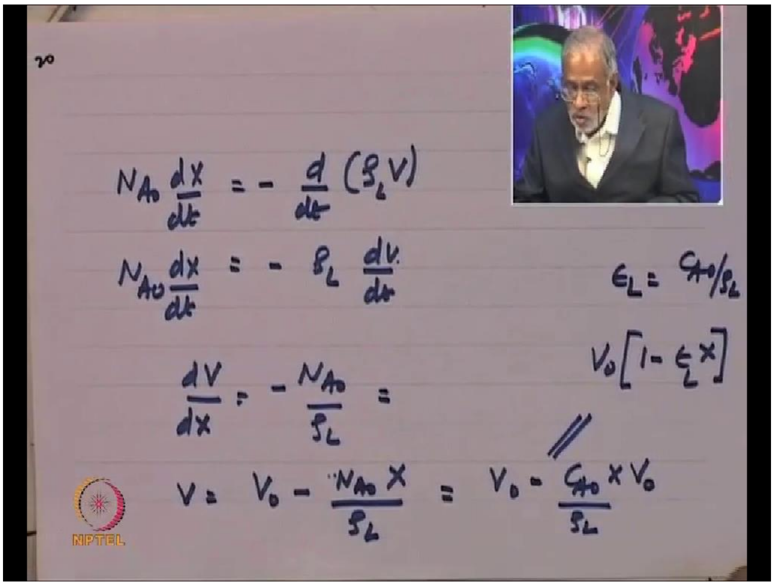

20

$$N_{A0}\frac{dx}{dt} = -\frac{d}{dt}(\rho_L V)$$

$$N_{A0}\frac{dx}{dt} = -\rho_L\frac{dV}{dt}$$

$$\epsilon_L = C_{A0}/\rho_L$$

$$V_0\left[1-\epsilon_L x\right]$$

$$\frac{dV}{dx} = -\frac{N_{A0}}{\rho_L} =$$

$$V = V_0 - \frac{N_{A0}x}{\rho_L} = V_0 - \frac{C_{A0}}{\rho_L}x V_0$$

So, what we get here is that N a zero d x d t must be equal to minus of d by d t of rho l times V. That is equal to minus of rho l times d V d t, equal to N a 0 d x d t or we can write N a 0, sorry, d V d x equal to N a 0, divided by rho l with the minus sign; is that right? What we are saying; that means, rate at which, volume changes with respect to extent of reaction, is a N a 0 by rho l. So, I have written this as; we can integrate this and so on. So, let me integrate this. I will get V equal to V 0 minus of N a 0 x, divided by rho l. I will write this as V 0 minus of C a 0 x by rho l; is it all right? C a 0 x by into V; N a 0 is C a 0 times v, x by rho l. So, I can write V 0. So, I will just write this here. So, V 0 multiplied by 1 minus of epsilon l times x. What is epsilon l? Epsilon l equal to C a 0 by rho l; this is what we are saying.

What we achieved? What we have achieved is that we have an instance of a chemical reaction. Let me just go back to this chemical reaction that we have.

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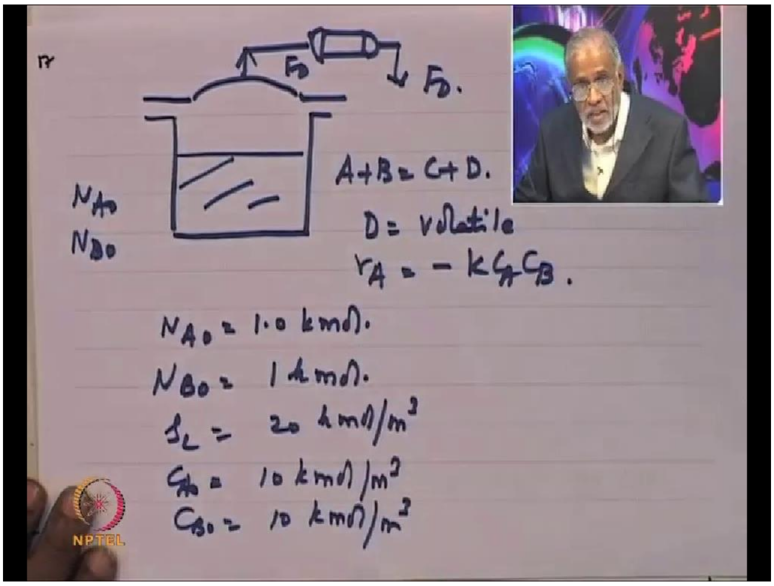

17

F_D

F_D.

N_{A0}

N_{B0}

$A + B = C + D$.

$D =$ volatile

$r_A = -k C_A C_B$.

$N_{A0} = 1.0$ kmol.

$N_{B0} = 1$ kmol.

$\rho_L = 20$ kmol/m^3

$C_{A0} = 10$ kmol/m^3

$C_{B0} = 10$ kmol/m^3

We have this chemical reaction, A plus B goes to C plus D; D is volatile. So, that as this reaction proceeds, the D being volatile, it can be boiled off; therefore, the volume keeps on decreasing, because D is going away. So, that is a question that we have in front of us.

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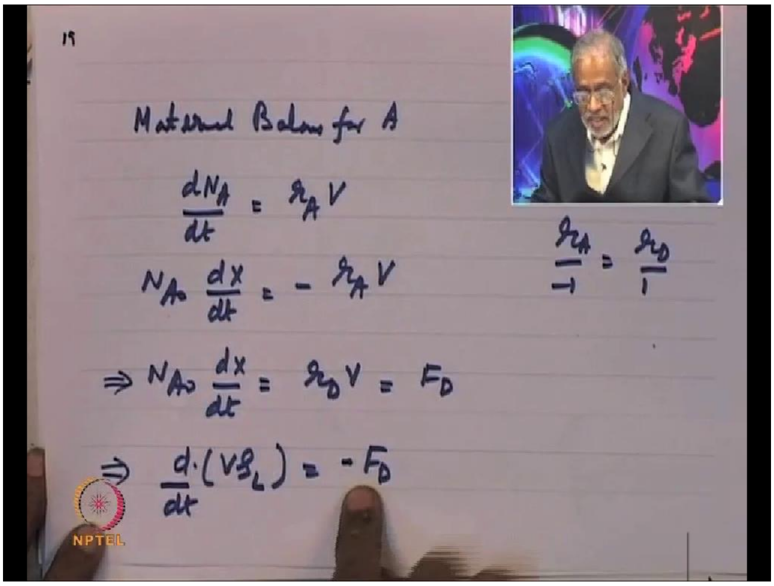

19

Material Balance for A

$$\frac{dN_A}{dt} = r_A V$$

$$N_{A0} \frac{dx}{dt} = -r_A V$$

$$\frac{r_A}{-1} = \frac{r_D}{1}$$

$$\Rightarrow N_{A0} \frac{dx}{dt} = r_D V = F_D$$

$$\Rightarrow \frac{d}{dt} \cdot (V \rho_L) = -F_D$$

We have shown from our material balance that N a 0 d x d t is F d and similarly, d by d t V is also minus of F d; therefore, we can equate these two. That is what we have done and found that the rate at the volume change is related to conversion like this.

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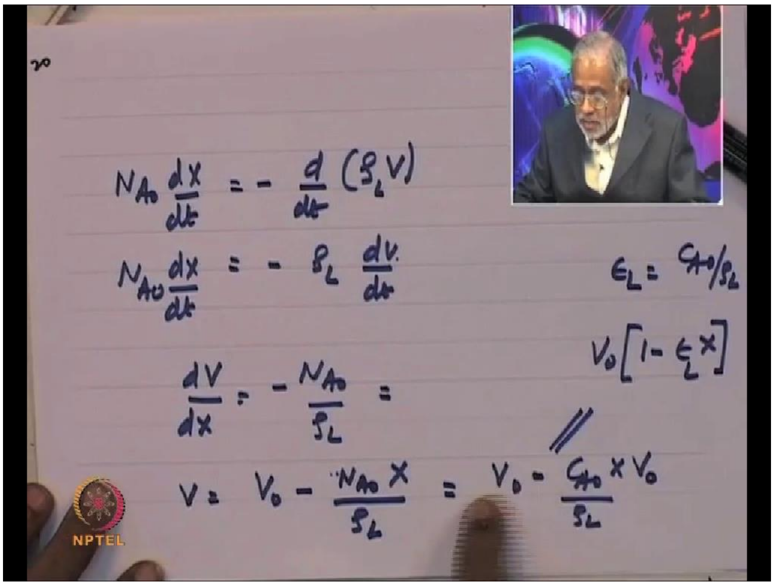

$$N_{A0}\frac{dx}{dt} = -\frac{d}{dt}(\rho_L V)$$

$$N_{A0}\frac{dx}{dt} = -\rho_L \frac{dV}{dt}$$

$$\epsilon_L = C_{A0}/\rho_L$$

$$\frac{dV}{dx} = -\frac{N_{A0}}{\rho_L} =$$

$$V_0\left[1 - \epsilon_L x\right]$$

$$V = V_0 - \frac{N_{A0}x}{\rho_L} = V_0 - \frac{C_{A0}xV_0}{\rho_L}$$

So, V 0 and conversion are related like this. So, this is the relationship we will keep with us. Let me write that once again. We say that V equal to V 0 minus, sorry, V 0, 1 minus epsilon l by x, all right.

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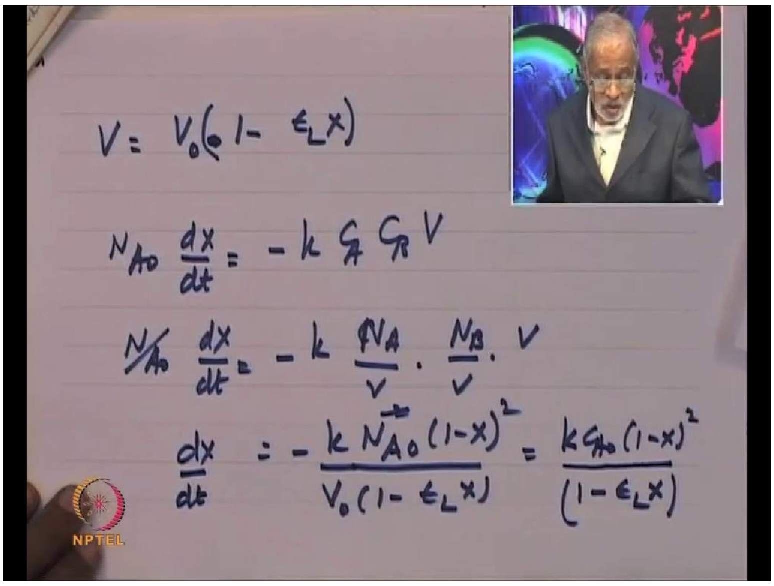

$$V = V_0(1 - \epsilon_L x)$$

$$N_{A0}\frac{dx}{dt} = -k C_A C_B V$$

$$\cancel{N_{A0}}\frac{dx}{dt} = -k \frac{N_A}{V}\cdot\frac{N_B}{V}\cdot V$$

$$\frac{dx}{dt} = -\frac{k N_{A0}(1-x)^2}{V_0(1-\epsilon_L x)} = \frac{k C_{A0}(1-x)^2}{(1-\epsilon_L x)}$$

Now, let us go back to our equations, N a 0 times d x d t; see, this is our equation, which is minus of k C a times C b times V. Now, this V, we can substitute from here. That was the idea. So, we have N a 0 d x d t, equal to minus of k C a. What is C a, which is N a by V and what is C b, is N b by V, and this is V are equal to minus of k. N a 0, 1 minus of x; they are both equal; therefore, I will put like this. It is V, which is V 0 times 1 minus of epsilon l x. So, it is equal to; one N a 0 gets canceled off. So, it is k C a 0, 1 minus of x whole square, divided by 1 minus of epsilon l x, equal to d x and d t; is that clear? We can solve this now. It is a fairly simple thing to solve this.

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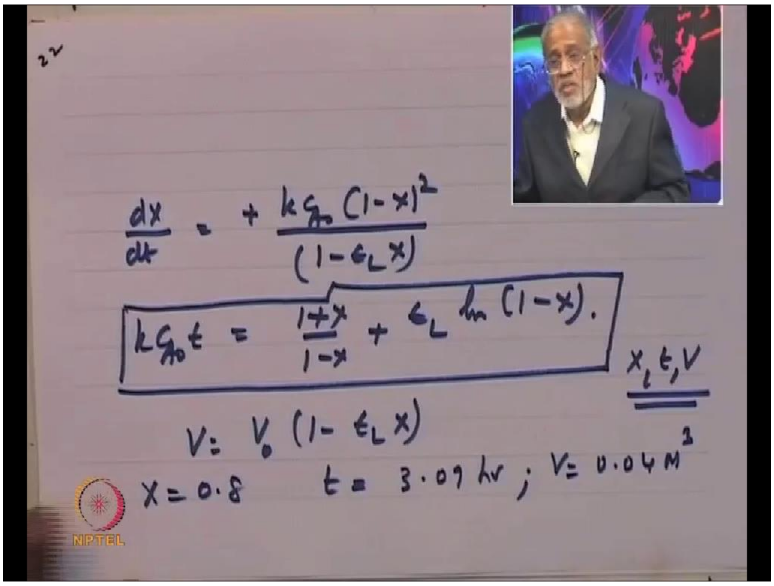

$$\frac{dx}{dt} = + \frac{k C_{a0} (1-x)^2}{(1-\epsilon_L x)}$$

$$\boxed{k C_{a0} t = \frac{1+x}{1-x} + \epsilon_L \ln (1-x).}$$

x, t, V

$$V = V_0 (1 - \epsilon_L x)$$

$x = 0.8$ $t = 3.09$ hr ; $V = 0.04 M^3$

We have now, our equation is d x d t, equal to minus, sorry, plus k both sides, sorry, N a 0; this will be a minus sign here; will be a minus here; I forgot the minus sign here, the minus sign here. So, d x d t becomes k C a 0, 1 minus of x whole square, divided by 1 minus of epsilon l x. So, we can solve this, and then the solution is fairly, simple; k 0 t equal to 1 plus x, divided by 1 minus of x, plus epsilon l, l in 1 minus of x; all right. Now, basically, what it means is that once you are given what is the m extent to which, you want to remove; once x is given, you can find t or when t is given, x can be found out.

Basically, this is the equation, which determines what happens to the process, and V equal to V 0 into 1 minus of epsilon l times x. So, all the data is given; therefore, you can calculate what is the, I mean, basically, x, t, V; there are three things here. So, if you want to calculate, if two are given, the third can be found out. So, essentially, depending upon what is specified in the exercise, in this particular exercise, what is specified is 80 percent; x is given as. If you put x equal to 0.8, you can find t. Once you put x equal to 0.8, you can find V. Here, for x equal to 0.8, you will find t equal to; I have found t equal to 3.09 hours and V equal to 0.04 cubic meters. So, what we have tried to do in this exercise is the following; that we have taken three examples of unsteady processes. First exercise was to find out how long it will take for a steady state to be achieved to a CSTR. Second exercise, we took is look at the chemical reaction in which, we want to hold volume pressure constant over a period of time. We said how it can be done. Third exercise is that we are looking at process in which, continuously removing the liquid and how long it takes for you to reach a certain extent of reaction and so on. All three cases, essentially, we set up the equations and found out how the different things are related.

Thank you