Advanced Chemical Reaction Engineering

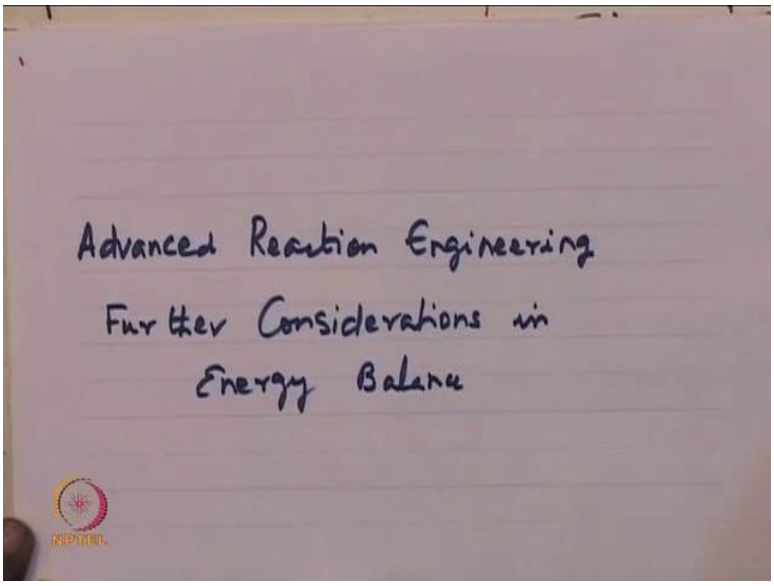
Prof. H. S. Shankar
Department of Chemical Engineering
Indian Institute of Technology, Bombay

Lecture - 24

Illustrative Example:
1) Further Considerations in Energy Balance
2) Multiple Reactions

Welcome in this advanced reaction engineering.

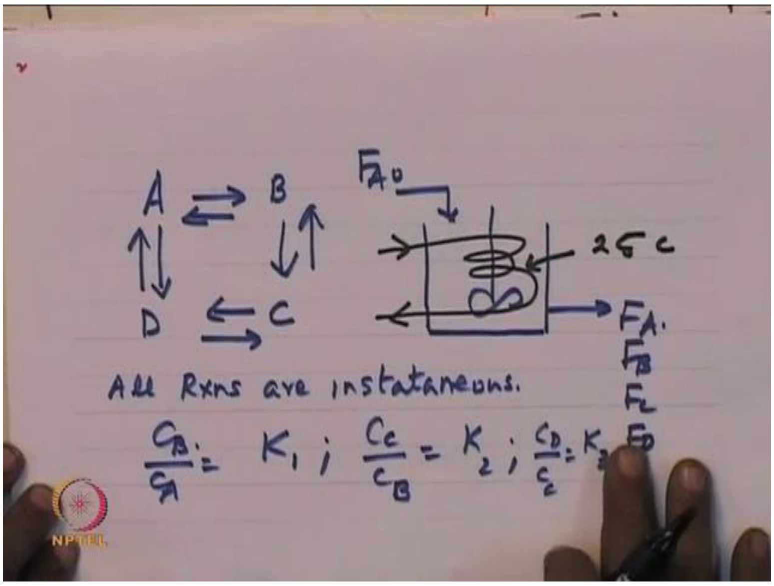
(Refer Slide Time: 00:26)



Advanced Reaction Engineering
Further Considerations in
Energy Balance

Today we look at further considerations in energy balance. Now, what we would like to do is a look at what you have already learned. And, then and apply them situations that we might encounter in real life situations; which I mean selected situations which are more involved. So that can we really see how equations apply ok.

(Refer Slide Time: 01:22)

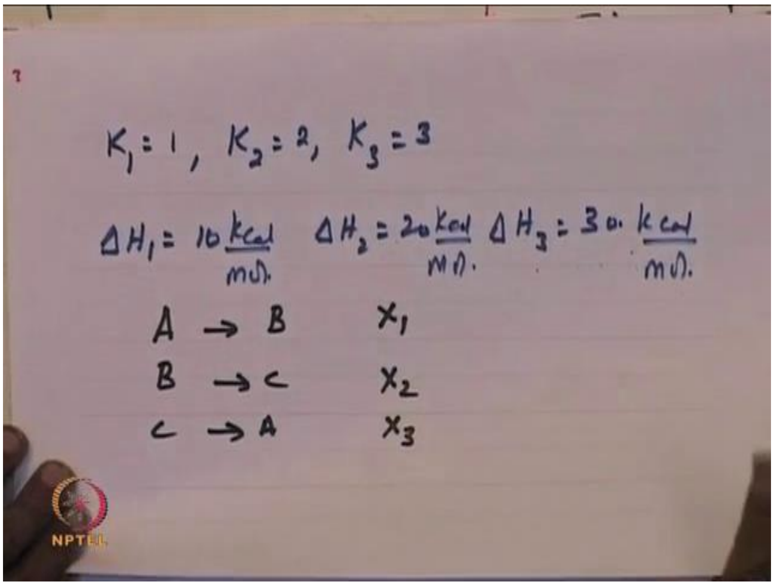


All Rxns are instataneous.

$\frac{C_B}{C_A} = K_1$; $\frac{C_C}{C_B} = K_2$; $\frac{C_D}{C_C} = K_3$

So, first example we would like to take is a multiple reactions; A goes to B, B goes to A then C goes to A, C goes to D. So, this is the reaction would like to look at. And, all reactions for the movement with considered that these reactions occur in a stirred tank, these are occurring in a stirred tank; you have A component a coming in and going out. And, we will assume all reactions are instantaneous; which means that they are all in equilibrium implying that C B by C A is K 1, C C by C B is K 2 and C D by C C is K 3 ok. So, it is instantaneous; therefore, the compositions are as per describe the equilibrium. And, K 1, K 2, K 3.

(Refer Slide Time: 02:57)



$K_1 = 1$, $K_2 = 2$, $K_3 = 3$

$\Delta H_1 = 10 \frac{kcal}{mol}$ $\Delta H_2 = 20 \frac{kcal}{mol}$ $\Delta H_3 = 30 \frac{kcal}{mol}$

$A \rightarrow B$ x_1

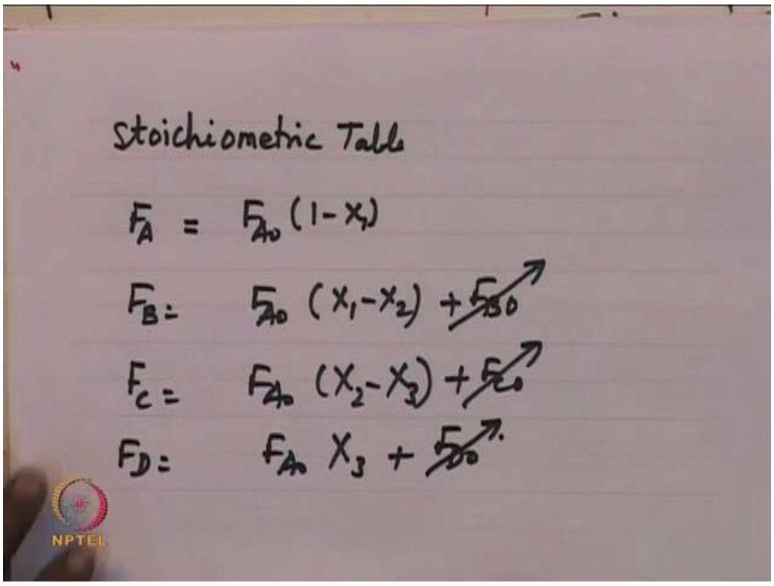
$B \rightarrow C$ x_2

$C \rightarrow A$ x_3

For example, take a situation where K 1, K 2, K 3 situation is something like this; K 1 equal to 1, K 2 equal to 2, K 3 equal to 3. And, delta H 1 equal to 10, delta H 2 equal to 20, delta H 3 equal to 30; these are all in units of k cal per mole, k cal per mole, k cal per mole. What do we have? We have a stirred tank in which A is coming in and going out. The stirred tank is maintained that 25 C this is the temperature maintained. So, I mean all these reactions are you can see from the delta H 1 values here; there are all endothermic. Therefore, you would expect that this reaction will proceed only if heat is added. So, we expect some amount of heat to be put in for this reaction to take place.

Therefore, the question of interest to us is that what is the amount of heat that is to you put in number 1? And, then what is the composition of the leaving stream assuming there is the temperature of C stirred is maintain with 25? So, it is obvious that to be able to maintain this temperature at 25 you would supply heat; because all the reactions are endothermic ok. So, this is what we would like to do all right. So, A goes to B, B goes to C, C goes to A; if there are 3 reactions if I call X 1, X 2, X 3 are the extends of reactions in each of these we can write this Stoichiometry.

(Refer Slide Time: 04:52)



Stoichiometric Table

$F_A = F_{A0}(1-X_1)$

$F_B = F_{A0}(X_1-X_2) + \cancel{F_{B0}}$

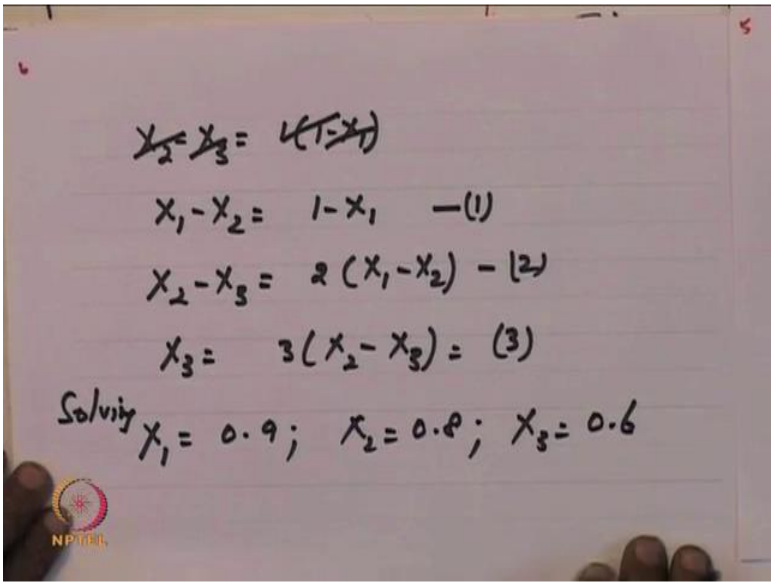
$F_C = F_{A0}(X_2-X_3) + \cancel{F_{C0}}$

$F_D = F_{A0}X_3 + \cancel{F_{D0}}$

So, let us write this Stoichiometry. Now, so we can write this Stoichiometry table; where, this F A is F A 0 into 1 minus of X 1 the first reaction. And, then F B is F A 0 times X 1 minus of X 2; of course, F B 0 is nothing is sated so with think it is 0. F C is F A 0 X 2 minus of X 3 plus F C 0; which is 0. F C is F A 0 times X 3 plus F D which is 0 this is Stoichiometry ok. And, we have said little earlier that all these reactions are instantaneous, reactions are all instantaneous. And, we said that there are all instantaneous that B with this C B by C A is K 1 and all that we said already.

So, we can now use these relationships to understand what does happen in the equipment. So, let us do that quickly; so, we have C B by C A which is C B is F A 0 times X 1 minus of X 2 divided by F A 0 times 1 minus of X 1; so this is K 1 which is 1 equal to 1. Similarly, you have a C C by C D is F A 0 times what is C C? Which is X 2 minus of X 3 divided by F A 0, C B by C S, B sorry into X 1 minus of X 2 that is equal to K 2 that is equal to 2. C D by C C, C D is what? F A 0 times X 3. And, then C C is F A 0 times X 2 minus of X 3 equal to K 3 equal to 3. So, you have to solve these 3 questions that is do that quickly.

(Refer Slide Time: 07:16)



6

5

$\cancel{X_2 - X_3} = \cancel{4(1-X_1)}$

$X_1 - X_2 = 1 - X_1 \quad -(1)$

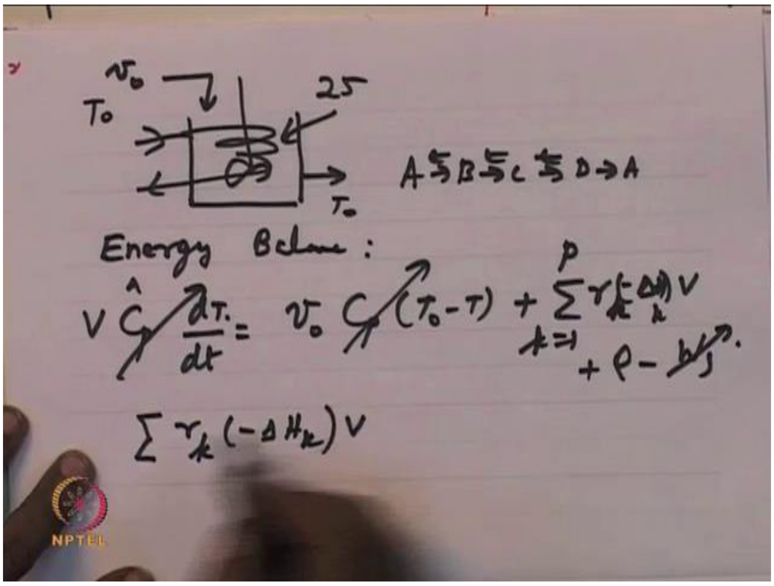
$X_2 - X_3 = 2(X_1 - X_2) \quad -(2)$

$X_3 = 3(X_2 - X_3) = (3)$

Solviy $X_1 = 0.9; \quad X_2 = 0.8; \quad X_3 = 0.6$

So, the questions in front of us; so, the equations there are the following I am just I am putting the same thing again just to make it easiest to solve. So, X 1 minus of X 2 equal to 1 minus of X 1; this is 1 equation when you have X 2 minus of X 3 equal to 2 times X 1 minus of X 2 that is another equation. Third equation is X 3 equal to 3 times X 2 minus of X 3 this is third equation. So, we have to solve these 3 equations. And, Foley elementary to solve we will find X 1 equal to 0.9, solving X 2 is 0.8, X 3 is 0.6 and this is Foley elementary; so, nothing much needs to be done. So, we can solve this and find what were X 1, X 2 and X 3.

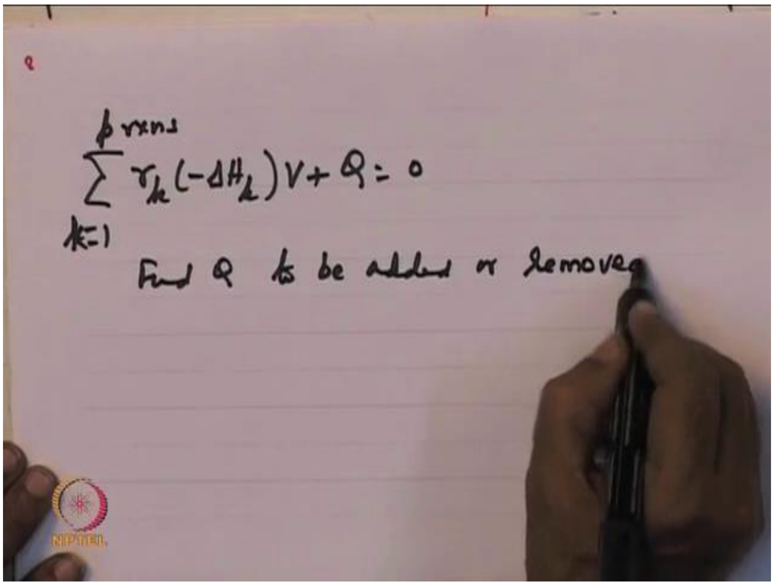
(Refer Slide Time: 08:19)



Now, what we need to do is to find out how much heat is to be added or removed correct. Because that is what we will ensure that our C S T r; so, what you got a C S T r in which you have this instantaneous reactions A goes to B, B goes to C, C goes D, D goes to A this is running here at 25. So, we have to put in heat to be able to ensure that this happens actually correct. So, we need to write the energy balance to find how much heat is to be put in etcetera. So, what is our energy balance equation? V C p d T, d t equal to V naught; C p T naught minus of T plus sigma i equal to 1 to all the p reactions r I will put k here, r k delta minus delta H k times V plus Q minus of W s which is not there.

So, now this is at steady state therefore, this is not there; this is V naught C p is volumetric specific heat volumetric we know all that inlet temperature, outlet temperature all the data is given. If the inlet temperature equal to outlet temperature as is the case here this is T naught here this is also T naught; so, this term is also not there. So, essentially what you have sigma r k times minus of delta H k V; i equal to 1 to p, k equal to 1 to p plus q equal to 0 all right. So, we can expand this essentially you know you have to substitute to put all these find out how we can relate r k times V to X 1, X 2 and X 3 which are the extent of reactions in the different reactions. Once, we do that our numbers are straight forward ok.

(Refer Slide Time: 10:14)

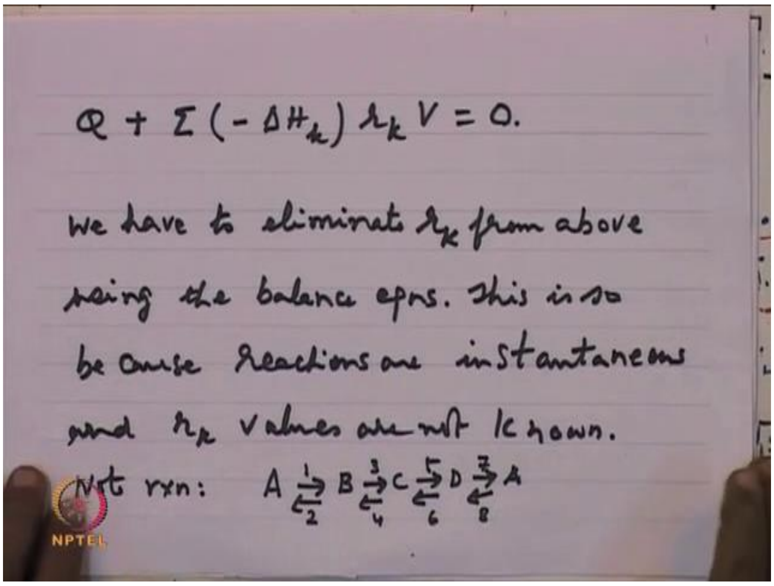


$$\sum_{k=1}^{p\ \text{rxns}} r_k(-\Delta H_k)V + Q = 0$$

Find Q to be added or remove

So, let us recognize here to we want to find out sigma r k times minus of delta H k times V plus Q equal to 0, i equal to sorry, k equal to 1 to p reactions find Q to be added this what we have to do r removed.

(Refer Slide Time: 10:40)



$$Q + \Sigma(-\Delta H_k)\, r_k V = 0.$$

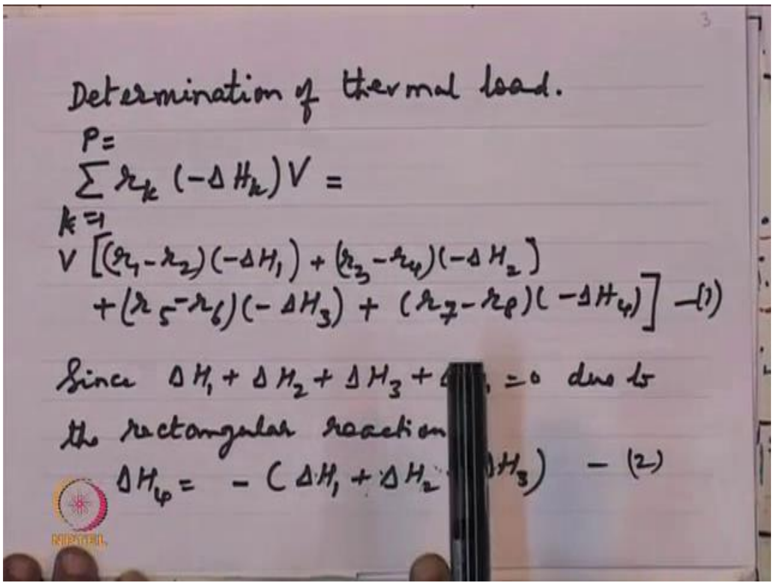
We have to eliminate r_k from above using the balance eqns. This is so because reactions are instantaneous and r_k values are not known.

Net rxn: $A \underset{2}{\overset{1}{\rightleftarrows}} B \underset{4}{\overset{3}{\rightleftarrows}} C \underset{6}{\overset{5}{\rightleftarrows}} D \underset{8}{\overset{7}{\rightleftarrows}} A$

Now, we have been looking at instantaneous reaction and we want to want calculate the value of Q which is coming from the energy balance. And, based on the energy balance we said that Q plus sigma of minus delta H k r k v equal to 0. So, we want to calculate what is Q, and, for that we must know; what is r k, so that we can substitute and find out the value of Q. Now, we know that r k being an instantaneous reaction; we did not know those numbers and therefore, we must find there other ways of finding out r k. So, recognizing that we have A going to B, B going to C, C going to D, D going A. So, rectangular reaction all of them are reversible there is a procedure by which we can eliminate r k using our material balance.

Let see how to do this. Now, let us recognize that is recognize that A going to B, B going to C, C going to D, D going to A and all that. And, we denoted this is reaction 1, reaction 2, it is reaction 3, reaction 4, reaction 5, reaction 6 and reaction 7, reaction 8. Now, we have noted for a convenience that delta H 1 as reaction going A going to B as the heat of reaction for A going to B. And, delta H 2 as the heat of reaction for A going to B, B going to C. And, delta H 3 for the heat of reaction C going to D and delta H 4 heat of reaction for D going to A ok.

(Refer Slide Time: 12:19)



Determination of thermal load.

$$P = \sum_{k=1} r_k(-\Delta H_k)V =$$

$$V[(r_1 - r_2)(-\Delta H_1) + (r_3 - r_4)(-\Delta H_2)$$
$$+ (r_5 - r_6)(-\Delta H_3) + (r_7 - r_8)(-\Delta H_4)] \quad -(1)$$

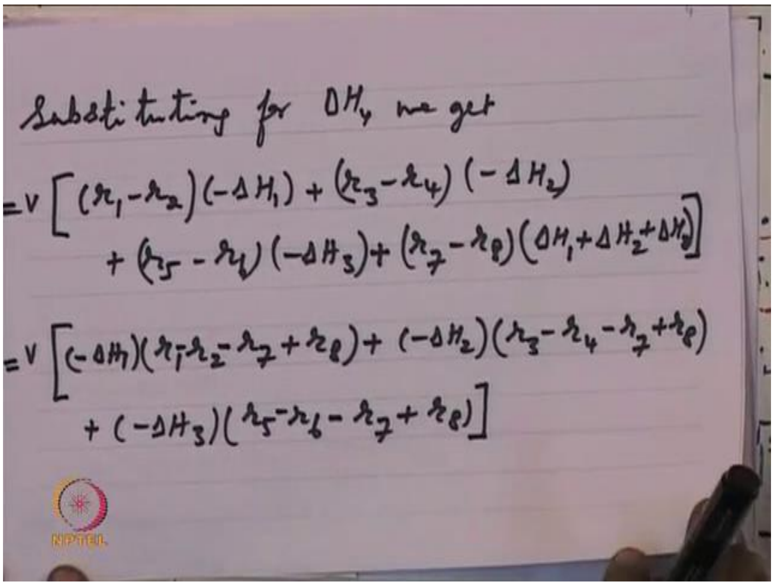
Since $\Delta H_1 + \Delta H_2 + \Delta H_3 +$ [illegible] $= 0$ due to the rectangular reaction

$$\Delta H_4 = -(\Delta H_1 + \Delta H_2 \text{ [illegible] } H_3) \quad -(2)$$

Now, I mean said this let us look at how we can determine the value of r k sigma delta H k V form our material balance. So, let us just expand r k minus of delta H k V what do we get? V times r k is r 1. If just expand this you will find there it is r 1 delta H 1, r 2 delta H 2, r 3 delta H 3, r 4 delta H 4 and so on up to r 8, delta H 8. But we know from our understanding that coming back this heat of reaction for A going to B and heat of reaction for B going A; just the reverse of each other keeping that in mind we have simplified this summation as r 1 minus of r 2 delta H 1, r 3 minus of r 4 delta H 2, r 5 minus of r 6 delta H 3, r 7 of r 8, delta H 4. This is something that we all know that for a reaction A going to B the heat of reaction for B going to A; simply the negative of reaction for A going to B something that we all know.

Now, let us look at this representation of sigma r k delta H minus delta H k V given on the right hand side equation 1. We notice that; because being a rectangular reaction as we have said here delta H 1 plus delta H 2 plus delta H 3 plus delta H 4 must equal to 0 that is come from our basic understanding from dynamic. Therefore, we can say that since delta H 1 plus delta H 2 plus delta H 3 plus delta H 4 equal to 0. We can write delta H 4 as minus of delta H 1 plus delta H 2 plus delta H 3 or on other words we are able to eliminate delta H 4 from equation 1; that make as certain advantages in terms of trying to eliminate r k from this equation.

(Refer Slide Time: 14:26)



Substituting for ΔH_4 we get

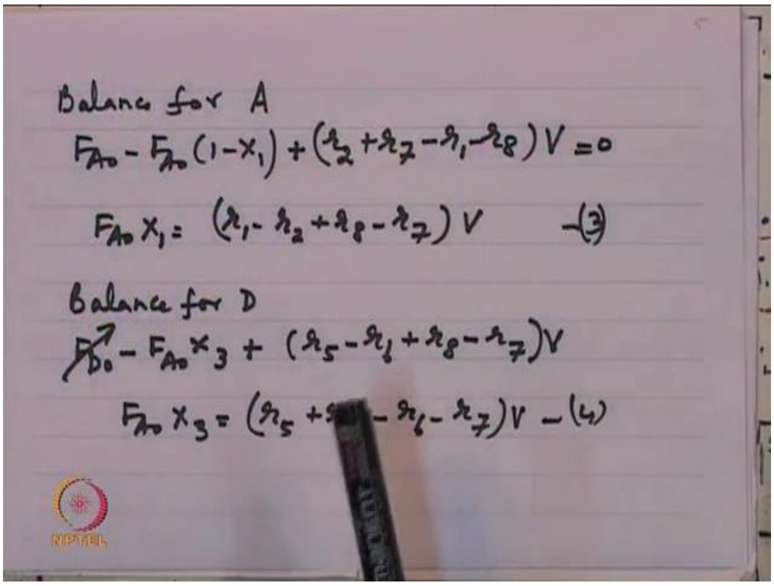
$$= V\left[(r_1 - r_2)(-\Delta H_1) + (r_3 - r_4)(-\Delta H_2) + (r_5 - r_6)(-\Delta H_3) + (r_7 - r_8)(\Delta H_1 + \Delta H_2 + \Delta H_3)\right]$$

$$= V\left[(-\Delta H_1)(r_1 - r_2 - r_7 + r_8) + (-\Delta H_2)(r_3 - r_4 - r_7 + r_8) + (-\Delta H_3)(r_5 - r_6 - r_7 + r_8)\right]$$

We will tell shortly how it can be done. Now, substituting just recalling what we have done we have just replacing delta H 4 in from equation 2. And, then simplifying that is what I am going to do? Now, we can see here that just summation being written once again r 1 minus of r 2 delta H 1 star, r 3 minus of r 4 delta H 2 star, r 5 minus of r 6 minus of delta H 3 star. And, then r 7 of r 8 the delta H 4 it is replace as delta H 1 plus delta H 2 plus delta H 3. Please, recognize that delta H 4 is minus of delta H 1 plus delta H 2 plus delta H 3. So, this delta H 4 is replaced in equation 2 ok.

Now, having done this; notice the delta H 1 and delta H 1 here, delta H 2 and delta H 2 here, delta H 3 and delta H 3 here. So, we can combine all that and make the whole thing look little simpler. So, I have done that here minus of delta H 1 multiplied by r 1minus of r 2, r 7 minus of r 8 with a negative sign; because this minus and this no minus here. So, it becomes minus r 7 plus r 8 multiplied by minus of delta H 1; then, delta H 2 minus delta H 2 multiplied by r 3 minus of r 4 you can see here. And, then minus of r 7 plus r 8. Similarly, delta H 3 here minus r 5 minus of r V, r 5 minus of r 6 and then minus of r 7 plus r 8.So, nothing new has been done it is simply you know assembling them together inform that we can deal with them conveniently.

(Refer Slide Time: 16:10)



Balance for A

$$F_{A0} - F_{A0}(1-X_1) + (r_2 + r_7 - r_1 - r_8)V = 0$$

$$F_{A0}X_1 = (r_1 - r_2 + r_8 - r_7)V \quad -(3)$$

Balance for D

$$\cancel{F_{D0}} - F_{A0}X_3 + (r_5 - r_6 + r_8 - r_7)V$$

$$F_{A0}X_3 = (r_5 + \text{[illegible]} - r_6 - r_7)V \quad -(4)$$

Now, what we recognize? Now, is that each of these terms multiplying delta H 1, multiplying delta H 2 and multiplying delta H 3; we can find what those numbers are using our material balance. Let us just do a material balance on component T A to recognize how simple it becomes. For example, if you write a material balance please which is recall our reactions; because it is important that recall our reaction I just putting it here just for the sake of understanding we have A going to B. So, I am writing the material balance for component A what is input, output, generation equal to 0; because there is no actual relation ok.

So, it is in a stirred tank that is what problem, So, input minus of output based on our Stoichiometry; we have said there F A is F A 0, 1 minus of X; that what we said here r 2 look at all the generations. Now, A is generate from reaction 2, A is generated from reaction 7 that is why I have written r 2 plus r 7 they are both positive and A is consumed in reaction 1. So, minus of r 1 A is consumed in reaction 8; so it is written minus. So, the signs are as we expect; so, you have r 2 plus r 7 minus of r 1minus of r 8 multiplied V equal to 0.

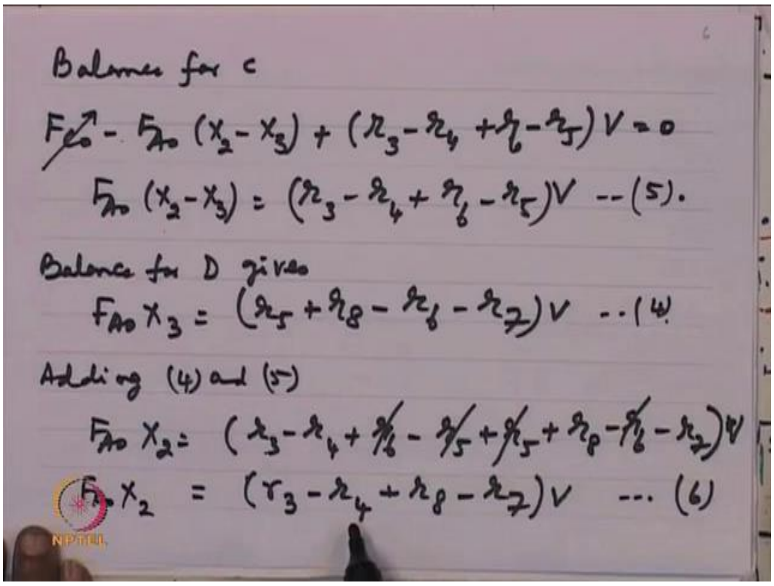
So, you get from this what you get is a following that F A 0 X left hand side plus I have just taken it to the other side. Therefore, r 1 minus of r 2 plus r 8 minus of r 7 multiplied by V. So, essentially material balance on A gives us F A 0 X 1 on the other side you get r 1, r 2, r 8, r 7. So, you notice here that even though we do not know what is r 1, r 2, r 8 and r 7; because reactions are instantaneous. Now, the right hand side becomes equal to F A 0 X 1. But F A 0 X 1 is measurable. So, this is the advantage of the formulation that even though we did not know the right hand side. Because these numbers are very large; I mean numbers r 1, r 2, r 8, r 7 may be large. But the totality of it may be something that it is not very large that is why we are able to measure.

So, essentially what we are done is that since our numbers are very large; we are able to replace in our equation by numbers that we can measure that is the advantage of writing the material balance. Now, just let just recognize what we have done; we have said that in A minus of delta H 1 multiplies r 1 minus of r 2 minus of r 7 plus r 8. We notice here that this term r 1 minus of r 2 plus r 8 minus of r 7 actually appears in the previous equation that we have done. So, we come back to that in a minute ok.

Now, similarly let us write a material balance for D input, output and what is the generation of component D? Let us see what is a generation of component D? So, what we are saying now is that component D is formed in reaction 5. So, it is plus r 5 and consumed in reactions 6 it minus of r 6. Now, component D is formed in reaction 8 plus r 8 it is consumed in reaction 7 is minus of r 7. On other words all these if generations are positive, all the consumptions are negative and that is the material balance of component D. So that you get F A 0 X 3 I have taken in to the right hand side; so that it becomes F A 0 X 3 becomes r 5 plus r 8; we can see here minus of r 6 minus of r 7 we have written material balance. For a material balance for A and found our F A 0 X 1 it a in terms of all the reaction rates function; similarly, F A 0 X 3 in terms of reaction rate functions.

Once, again we recognize that r 5, r 8, r 6, r 7 are large quantities; so, by themselves are not easy to measure. But the left hand side is measurable that is advantage of the procedure. Now, you have done material balance for A, material balance for B.

(Refer Slide Time: 20:10)



Balance for C

$$\cancel{F_{C0}} - F_{A0}(X_2 - X_3) + (r_3 - r_4 + r_6 - r_5)V = 0$$

$$F_{A0}(X_2 - X_3) = (r_3 - r_4 + r_6 - r_5)V \quad \text{--}(5).$$

Balance for D gives

$$F_{A0}X_3 = (r_5 + r_8 - r_6 - r_7)V \quad ..(4)$$

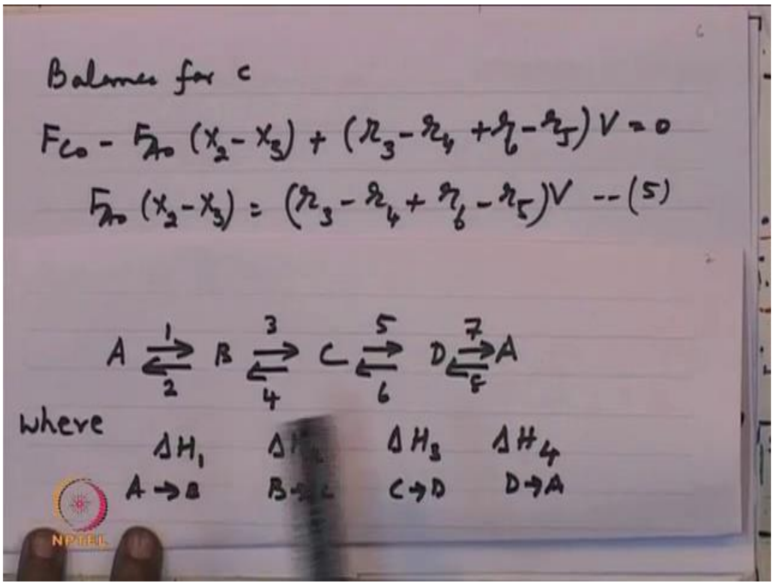
Adding (4) and (5)

$$F_{A0}X_2 = (r_3 - r_4 + \cancel{r_6} - \cancel{r_5} + \cancel{r_5} + r_8 - \cancel{r_6} - r_7)V$$

$$F_{A0}X_2 = (r_3 - r_4 + r_8 - r_7)V \quad ...(6)$$

Let us now see whether we can do something more that is material balance for C. So, what I done here is that I have written a material balance for C. Please, recognize that A going to B, going to C, going D going to A component C is formed in reaction 2 and consumed in reaction 3 that is why it is written X 2 minus of X 3 input minus of output plus generation. What are the generations of component?

(Refer Slide Time: 20:32)



Balance for C

$$F_{C0} - F_{A0}(X_2 - X_3) + (r_3 - r_4 + r_6 - r_5)V = 0$$

$$F_{A0}(X_2 - X_3) = (r_3 - r_4 + r_6 - r_5)V \quad --(5)$$

$$A \underset{2}{\overset{1}{\rightleftarrows}} B \underset{4}{\overset{3}{\rightleftarrows}} C \underset{6}{\overset{5}{\rightleftarrows}} D \underset{8}{\overset{7}{\rightleftarrows}} A$$

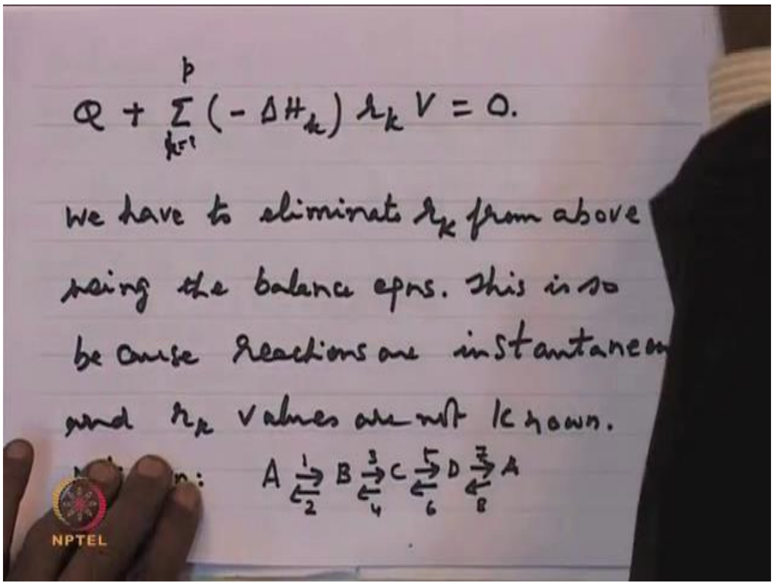
where ΔH_1 ΔH_2 ΔH_3 ΔH_4

A → B B → C C → D D → A

Let us just put here notice that component C is formed in reaction 3, r 3 is plus it is consumed in reaction 4, r 4 is minus. And, then component C is formed in reaction 6, r 6 is plus and it is consumed in reaction 5, r 5 is negative. So, we have taken generations is positive, consumption is negative; therefore, you have a material balance component C which since. So, we have here the material balance so this is 0. I have just simplified it and then it is written as F A 0 times X 2 minus of X 3 and it is taken and this is how it appears. So, since negative sign; therefore, I have written it in this form showing that F A 0 X 2 minus of X 3 is given by the right hand side that I have denoted it equations 5.

Now, we have just done in the little bit earlier what is F A 0 X 3. So, I have just put equation 4; once again, I have put the equation 4 which we have already derived. What does it says F A 0 X 3 is r 5 plus r 8 minus of r 6 minus of r 7; that is equation 4 which you have derived little earlier. Now, if you add equation 5 and equation 4 you notice here we adding equation 5 and equation 4 X 3 gets canceled; so, you get F A 0 X 2. Now, let us put all the numbers here; where, r 3, r 4, r 6, r 5 I have written down r plus r 5 plus r 8 minus of r 6 minus of r 7. Now, you notice carefully here r 6 cancels off r 5 cancels off; so that F A 0 X 2 becomes r 3 minus of r 4 plus r 8 plus r 8 minus of r 7 V.

(Refer Slide Time: 22:21)



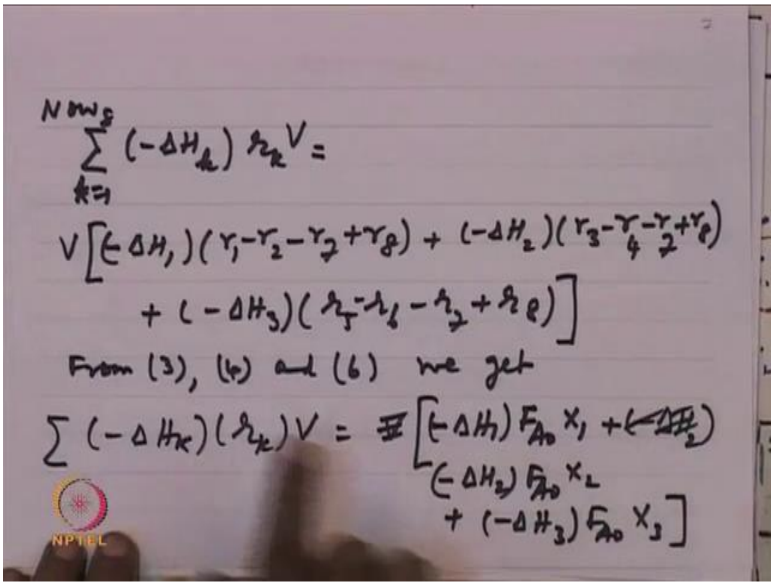
$$Q + \sum_{k=1}^{p} (-\Delta H_k)\, r_k V = 0.$$

We have to eliminate r_k from above using the balance eqns. This is so be cause Reactions are instantaneo and r_k values are not known.

n: $A \overset{1}{\underset{2}{\rightleftarrows}} B \overset{3}{\underset{4}{\rightleftarrows}} C \overset{5}{\underset{6}{\rightleftarrows}} D \overset{7}{\underset{8}{\rightleftarrows}} A$

So, what is it we have done? What we have done is that since what we are saying here is that we expand this function this sigma minus of delta H k, r k going from 1 to p; we find that right hand side r k is very large. Therefore, we are able to eliminate them using the material balance and that is what we are try to do So, what we have done is that we have found out F A 0 X 1, F A 0 X 2, F A 0 X 3 in terms of rate functions.

(Refer Slide Time: 22:58)



Now

$$\sum_{k=1}^{8} (-\Delta H_k)\, r_k V =$$

$$V\left[(-\Delta H_1)(r_1 - r_2 - r_7 + r_8) + (-\Delta H_2)(r_3 - r_4 - r_7 + r_8) + (-\Delta H_3)(r_5 - r_6 - r_7 + r_8)\right]$$

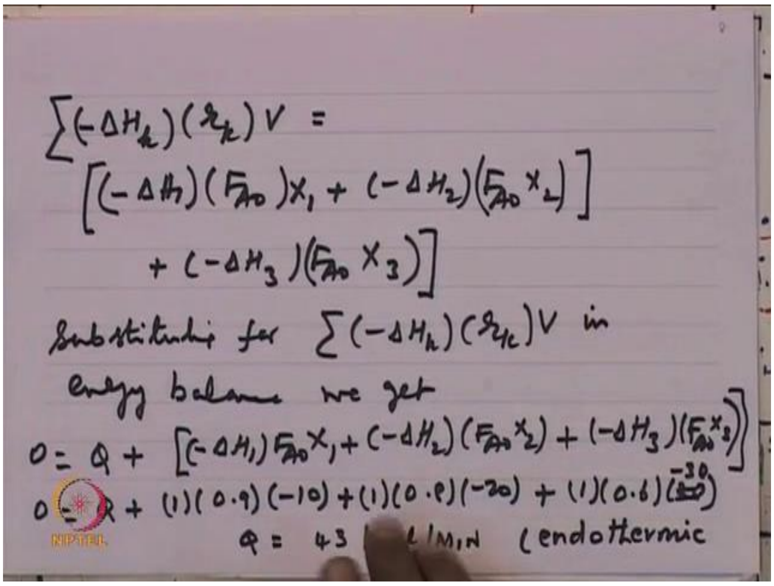
From (3), (4) and (6) we get

$$\sum (-\Delta H_k)(r_k)V = \cancel{F}\left[(-\Delta H_1) F_{A0} X_1 + \cancel{(-\Delta H_2)} (-\Delta H_2) F_{A0} X_2 + (-\Delta H_3) F_{A0} X_3\right]$$

Now, that we know them in terms of rate functions we can substitute in our equation and find out how they simplified. So, what I have done here is notice here that this is how we expanded delta H 1 I mean r k and put in terms of all the rate functions. Now, what we have done just now is that all these rate functions, all these r 1 minus of r 2, minus of r 7 minus of r 8; we have just now shown that this term. Please see here we just now shown that r 1 minus of r 2 plus r 8 minus of r 7 is F A 0 X 1 we are shown using our material balance this is what we done. So, I am able to replace this r 1 minus of r 2 minus of r 7 plus r 8 as F A 0 X 1. So, this is F A 0 X 1 that is what I have done.

Now, similarly we have shown material balance for this is delta H 3 r 5 minus plus r 8 minus of r 7 minus of r 6 this is F A 0 X 3 we have shown that. Similarly, we have shown from our material balance on component C; we have shown the following that F A 0 X 2 we have shown this. Similarly, we have shown that r 3 minus of r 4 minus of r 7 plus r 8 we shown it F A 0 X 2. In other words what we are trying to say here this is the point that we must recognize that if you recognize in number of independent reactions and then do all your stoichiometry table on the basis of independent reactions.

(Refer Slide Time: 24:51)



$$\sum(-\Delta H_k)(r_k)V = \left[(-\Delta H_1)(F_{A0})X_1 + (-\Delta H_2)(F_{A0}X_2)\right] + (-\Delta H_3)(F_{A0}X_3)\Big]$$

Substituting for $\sum(-\Delta H_k)(r_k)V$ in energy balance we get

$$0 = Q + \left[(-\Delta H_1)F_{A0}X_1 + (-\Delta H_2)(F_{A0}X_2) + (-\Delta H_3)(F_{A0}X_3)\right]$$

$$0 = Q + (1)(0.9)(-10) + (1)(0.8)(-20) + (1)(0.6)(\overset{-30}{\cancel{}})$$

$$Q = 43 \text{ [illegible] l/min (endothermic}$$

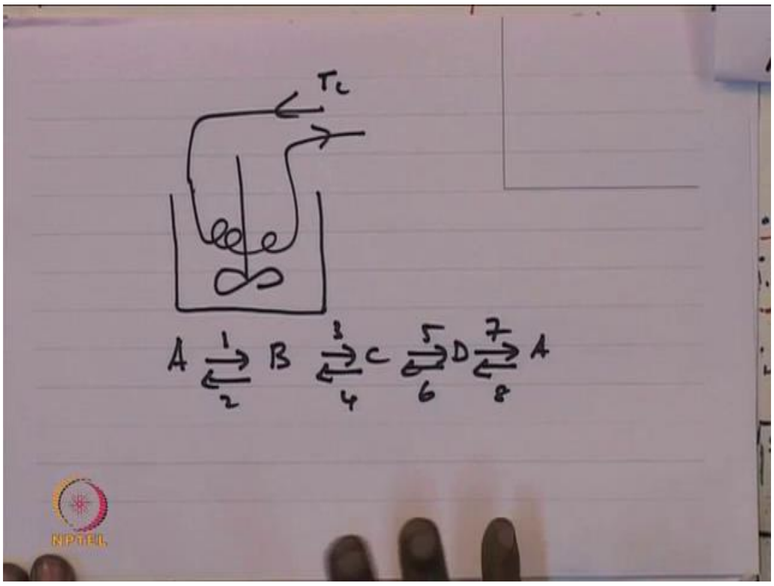
Then, the term that multiplies the rate function that multiplies delta H 1 will F A 0 X 1, the term that multiplies delta H 2 will be F A 0 X 2, the term that multiplies delta H 3 will be FA 0 X 3. So, this is how it is formulated. And, therefore what happens is that this whole term a delta H k r k V; now, can be written as minus of delta H 1, F A 0 X 1, minus of delta H 2, F A 0 X 2, minus of delta H 3 F A 0 X 3. So, the whole idea of using this approach of multiple reactions is that you can conveniently replace r k V as F A 0 X

1 is that is the advantage. And, that is what makes much simpler to manage multiple reactions.

Now, our problem is very simple our energy balance; we have to calculate we started if you recall our idea was find out what is basically when we started we said the following that we want to calculate what is Q? And, to calculate Q you want to get read of this term r k V then only we can calculate Q that is what we have done. What we have done is that we have found out what is sigma of r k V and all that. And, we found out that this whole term is delta H 1, F A 0 X 1, delta H 2 minus delta H 2, F A 0 X 2, minus H 3, F A 0 X 3 which we can substitute in our energy balance that is what we have done here.

We said Q plus minus of delta H 1, F A 0 X 1, plus minus of delta H 2, F A 0 X 2 plus minus of delta H 3, F A 0 X 3. Now, we have already done a little earlier that X 1 is 0.9, X 2 is 0.8 and X 3 is 0.6 we have already calculated that based on our understanding equilibrium constant and so on. Now, all you have to do is that you substitute for delta H 1, substitute for delta H 2 substitute for delta H 3. What is delta H 1? What is given? It is given as10; so it is minus 10, this is given as 20 therefore, is minus 20, this is given as 30 so it is minus 30. So, you can simplify this and find that the heat that we must supply or remove is 43 kilo calories per minute. It is plus here; which implies when it is plus means that you must supply heat if it is negative it means you must remove heat.

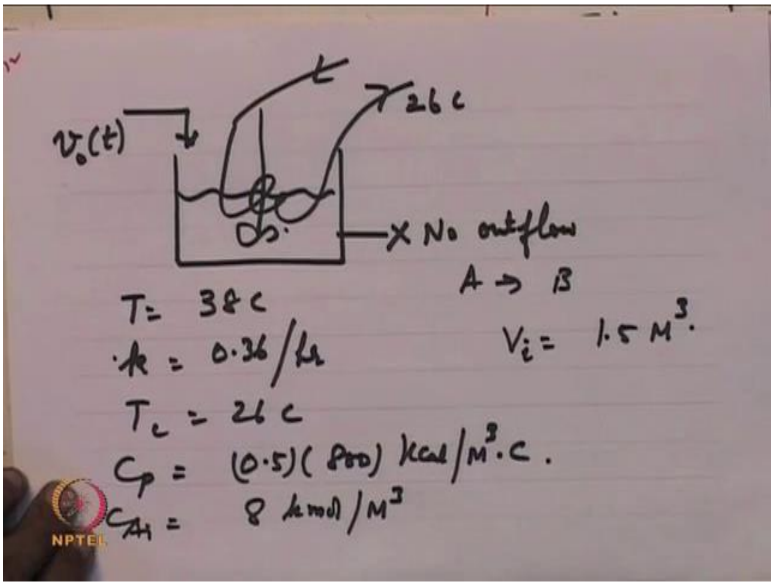
(Refer Slide Time: 27:12)



On other words what we have done? What we have done is the following. Let me just explain this once again; because this is something that we may have to do again and again what we started with? We started with a stirred tank and then in this stirred tank we have this reaction A going to B, B going to C, C going to D, D going to A. So, we call this 1, this is 2, this is 3, this is 4, this is 5, this is 6, this is 7, this is 8. So, because all these reactions this instantaneous; we said that the amount of and there all endothermic and so on.

Therefore, we have a cooling coil sorry; heating coil in this case heating coil which supplies the heat that is required to run the process at the temperature at which we want to run the process ok or in other words what we trying to say is that when you have instantaneous reaction. Then, the temperature at which you run the process it will determine what is the extent to which would be able to drive the reaction; whether it is endothermic or exothermic it is depending upon the situation that you will handle. But either case essentially the heat transfer will determine the extent to which you can push the reaction. And, this is the point that I trying to get across to you that. If you have instantaneous reaction then you only have to manage the heat load; so that you are able to push the reaction in the direction of your interest.

(Refer Slide Time: 28:54)



$T = 38\ C$

$k = 0.36/hr$

$T_c = 26\ C$

$C_p = (0.5)(800)\ kcal/M^3 \cdot C$.

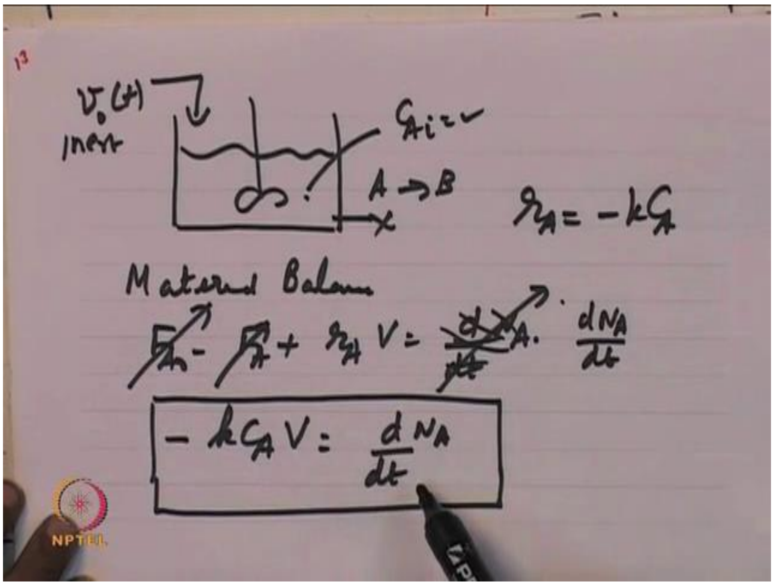
$C_{A1} = 8\ kmol/M^3$

$V_i = 1.5\ M^3$.

So let us go to another exercise; in this exercise also analyze illustration of energy balance. This energy balance this is what we have here you have a fluid entering there is very very exothermic reaction is taking place; there is no outflow, no outflow. So, the data is a following reactor temperature is 38 C, rate constant k is 0.36 per hour, coolant temperature; that means that is a coolant, that is 30, coolant temperature is 26 C, is 26 C, C p volumetric is 0.5 multiplied by density is 800. So, many kilo calories per cubic meter per C, C p is given.

C A i, A goes to B is the reaction C A i is given as 8 kilo mole per cubic meter and initial volume in the reactor given as 1.5 cubic meters. So, this is an instance where we are trying to control a reaction simply by adding a inert coolant; it is very exothermic reaction therefore we need to control the temperature. And, one way to control the temperature is to add your coolant. I mean add your inert medium to keep the concentrations low; so, the does not heat up ok all right. So, we want solve this problem and find out how we must vary the flow at to care of constancy of reaction temperature; that means we must fairy the flow in such a way. So, the reaction temperature does not change; so that is the exercise in front of us.

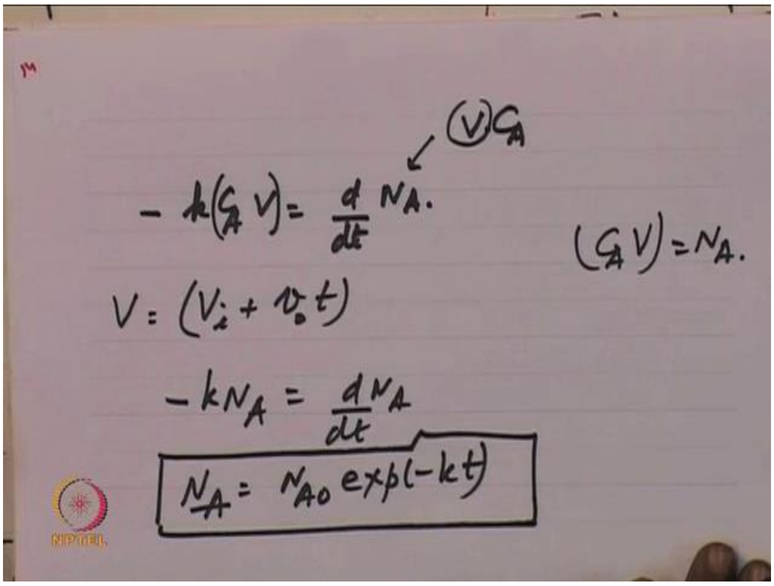
(Refer Slide Time: 30:57)



Let us recognize once more that we have we are adding and this temperature must be kept constant. So, let us write material A goes to products B reaction. So, material balance our material balance what does it give us input of material, output of material plus reaction equal to d by d t of material A. So, problem statement says there is no accumulation of A in the equipment number 1 there is no outflow. Therefore, whatever is coming in is can getting consumed is it right.

Now, is there anything coming in, this is the inert. So, this also goes, so you have r A equal to, so r A is what? By definition r A is given as minus of k times C A. So, it is minus of k C A times V equal to d by d t of N A. I am sorry is it clear, what is I am saying, I am sorry I delete to this term this not case that is d N A by d t; that means initially you are putting same. So, much of C A i here that is getting A reacted; I deleted this term by mistake ok. Now, what we have is that by virtue of the fact that there is no outflow, there is no component A in the inlet.

(Refer Slide Time: 32:30)



$$(V)C_A$$

$$-k(C_A V) = \frac{d}{dt} N_A.$$

$$(C_A V) = N_A.$$

$$V : (V_i + v_0 t)$$

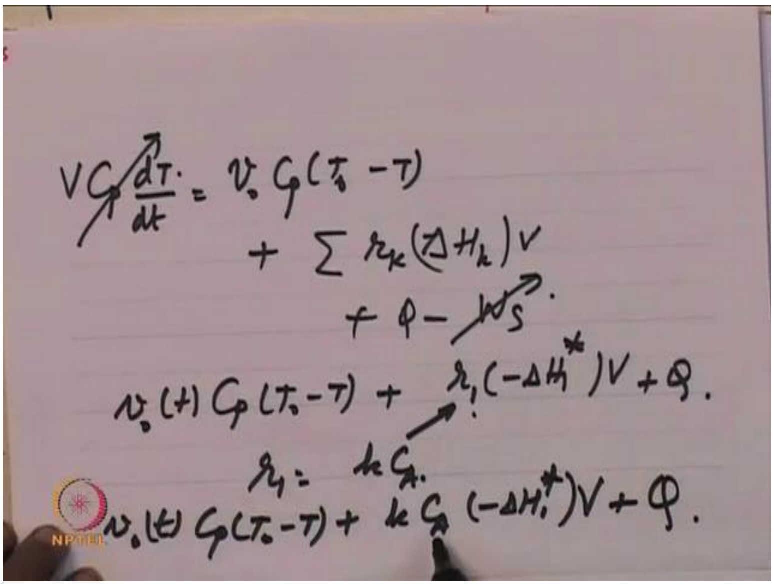
$$-kN_A = \frac{dN_A}{dt}$$

$$\boxed{N_A = N_{A0}\exp(-kt)}$$

Therefore, the rated which chemical reaction occurs must account for the variation of component A in the equipment minus k of C A times V equal to d by d t of N A. Now, we are V changes we know that V initial plus some V naught times t; V actually changes this is well known. But the point that is important to recognize here is that C A times V by definition is N A. Therefore, the left hand side is actually N A times k, k N A is d by d t of N A. So that N A equal to N A 0 or N A i into e rays power of minus of k t. The important point to recognize here is that here is an equipment where component A is all in the equipment initially.

And, when you add some inert coolant component total component A does not change. So, that is an important feature that you must recognize when you solve this problem. It is frequently what is observed is that you know we people write this N A as V times C A and then they substitute for this V. And, someone get lost in the algebra and loose the content of the problem is this that N A equal to N A 0 this is the content we should realize that; because A does not go out anywhere. So, A will d k as per a first order law that is what this means.

(Refer Slide Time: 34:09)



$$V C_p \cancel{\frac{dT}{dt}} = v_0 C_p (T_0 - T) + \sum r_k (\Delta H_k) V + Q - \cancel{W_s}$$

$$v_0(t) C_p (T_0 - T) + r_1 (-\Delta H_1^*) V + Q.$$

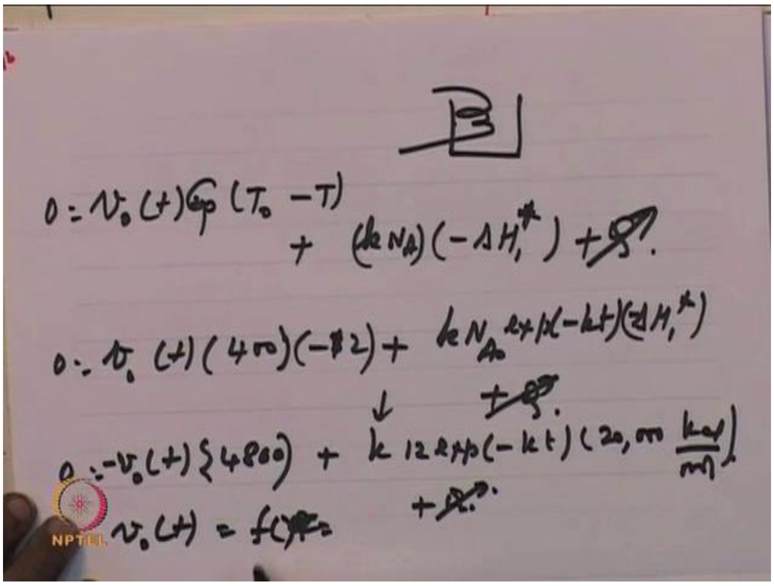
$$r_1 = k C_A.$$

$$v_0(t) C_p (T_0 - T) + k C_A (-\Delta H_1^*) V + Q.$$

Once, you recognize that A will d k as per a first order law; then, the question of you know ensuring that the temperature of the reactor does not change is one of trying to understand what happens in the energy balance. So, let me write the energy balance this is the energy balance which says plus reaction. And, then some heat added and removed; and then you have this work and all that. Now, we want to maintain this constant temperature.

So, this is left hand side is 0; should expect the rate at which we add a will be able to take care of the reaction. So, V naught is function of time C p t naught minus of t. So, this term there is only one reaction; therefore, I will write r 1 and minus of delta H 1 star times V there is no other plus Q ok. What is r 1 by definition k times C A. So, if we substitute this here we get V naught which is function of time C p times t naught minus of t that the first term. And, this term is k times, C A times minus of delta H 1 star multiplied by V plus Q. So, C A times V is N A correct.

(Refer Slide Time: 35:28)



$$0 = v_0(t)\, C_p\, (T_0 - T) + (k N_A)(-\Delta H_1^*) + \cancel{Q}.$$

$$0 = v_0(t)(400)(-12) + k N_{A0} \exp(-kt)(-\Delta H_1^*) + \cancel{Q}.$$

$$\downarrow$$

$$0 = -v_0(t)(4800) + k\, 12 \exp(-kt)\left(20{,}000 \frac{\text{kcal}}{\text{mol}}\right) + \cancel{Q}.$$

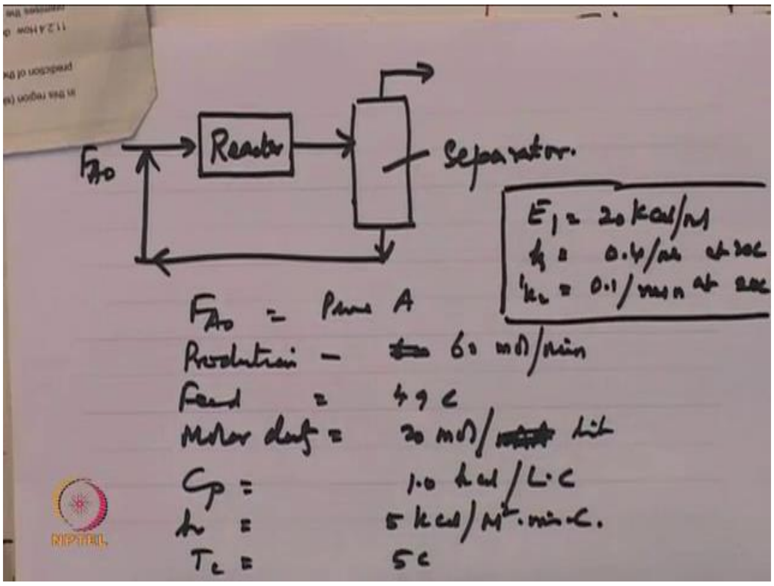
$$v_0(t) = f(\,)$$

We can simplify this further and write this as so our equation, energy balance equation 0 equal to V naught which is function of time C p, T naught minus of T that is the heat transfer term plus k times N A, k N A. Which is what we are saying is that C A times V is N A that is what we are saying times minus of delta H 1 star plus Q. So, we do not know V naught is what we want to find out C p is given as 400. And, T naught minus of T, T naught is 26, T is 30. So, it is minus 30, so minus 26, 38; so, it is minus 12 ok.

And, then what is k N A? N A is 0 times exponential of minus of k t times delta H 1 star with a minus sign plus Q. So, 0 equal to V naught t it is about 4800 with a negative sign. The next term is k N A is what is N A? Is 0.28 miles per liter it is 12 N A is 12 exponential of minus of k t; delta H 1 star what is that delta given as 20,000 kilo calories per mole. Essentially, what we have done we know k is known everything is known here. So, we have to find out Q; so, when you do all that Q terms out to be we do this calculations Q is plus Q.

Now, we notice here that in this problem we that is know there is no external transfer of heat; therefore, this Q is 0. So, all the heat is taken up by the fluid that we are added here itself. So, this is you know; so, you can calculate and find out V naught as a function of time. So, it is source that how V naught as a function of time can be handled in a situation like this. So, what we have try to do here in this exercise is that how do you control temperature by adding inert fluid that is the exercise.

(Refer Slide Time: 37:53)



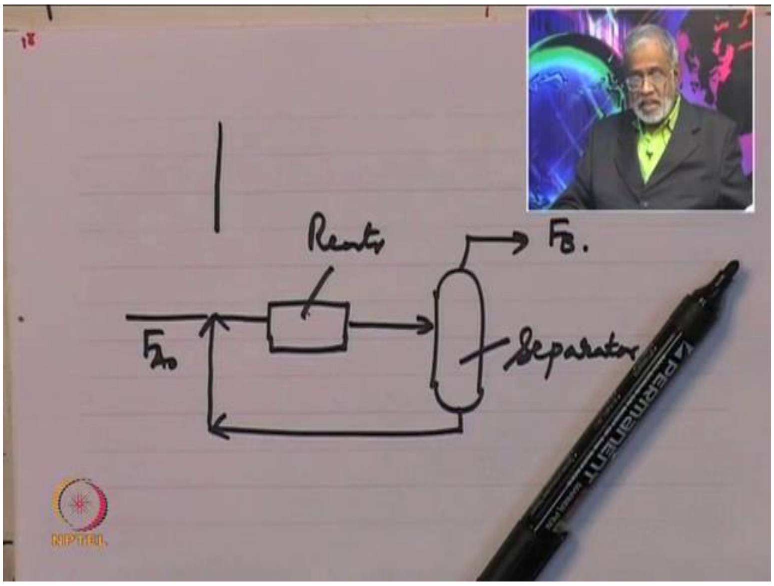
E_1 = 20 kcal/mol
k_1 = 0.4/min at 20C
k_2 = 0.1/min at 20C

F_{A0} = Pure A
Production – 60 mol/min
Feed = 49 C
Molar dens = 20 mol/ lit
C_p = 1.0 kcal/L·C
h = 5 kcal/M²·min·C.
T_c = 5C

Third exercise I would like to look at; so, here you have a reactor then it goes to separator. And, you have pure product here and then whatever is not reacted is returned. This is reactor separator and data is given just put down the data for the sake of all of you data is F A 0, F A 0 pure A desired production 60 mole per minute, feed temperature 49 C, feed temperature molar density 20 mole per mole, 20 moles molar density is given as 20 mole per liter; sorry, specific heat is given as 1 kilo cal per liter C, heat transfer coefficient is given as 5 kilo cal per square meter, per degree centigrade ok.

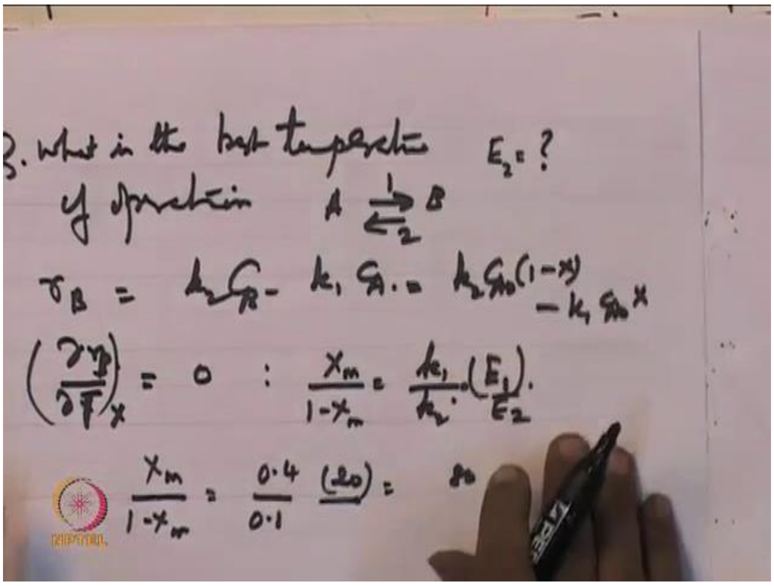
Coolant temperature T c is given as 5 c; large quantities available. So, reaction E 1 is given as 20 kilo call per mole, rate constant is given as 0.4 per minute at 20c, k 2 rate constant is given as 0.1 per minute at 20 c gas constant also given. So, we have this data in front of us, few data in front of us. And, then we have to see how best we can come up with a design which sort of is appropriate for our application. So, we have looked at similar problem at an earlier stage; if you recall.

(Refer Slide Time: 40:33)



So, this we do not have to do the whole thing again. So, you have reactor you have a separator; so it goes to the separator we can recycled. This is separator, this is reactor; so, we the number of questions, the questions here are that you know what is the best choice of conditions for running this process. Now, we have looked at problems similar to this where we have taken some objective function and try to optimize; this is something that we should do anyway. But when you look at exothermic is reversible reactions so on. Then, we will have look at the fact that you know there are more constraints that we can place on the system and get some more optimum numbers for our design.

(Refer Slide Time: 41:50)



3. What is the best temperature of operation $E_2 = ?$

$A \underset{2}{\overset{1}{\rightleftharpoons}} B$

$r_B = k_2 C_B - k_1 C_A = k_2 C_{A0}(1-x) - k_1 C_{A0} x$

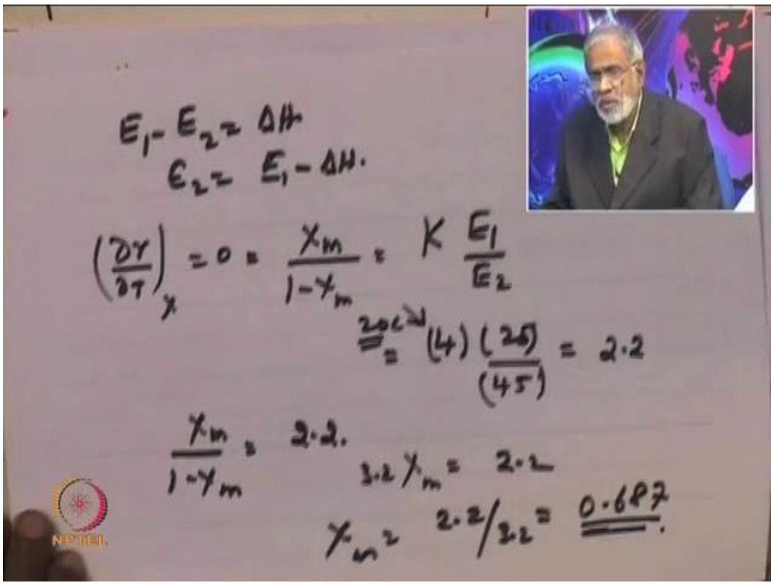
$\left(\frac{\partial r_B}{\partial T}\right)_x = 0 \quad : \quad \frac{x_m}{1-x_m} = \frac{k_1}{k_2} \cdot \left(\frac{E_1}{E_2}\right).$

$\frac{x_m}{1-x_m} = \frac{0.4}{0.1} \underline{(20)} = 80$

So, a question that is frequently asked is that what is the best temperature of operation? So, this is something that people will ask us. Now, for exothermic this instants of exothermic reversible reactions we have done all these things, we know that if r B, if our reaction is A goes to B and B goes to A 1 and 2. Then, r B is equal to A 2 c B minus of k 1 C A; we can maximize r B with respect to conversion. So, this is same as k 2 times C A 0 times 1 minus of X minus of k 1 C A 0 X.

So, what is this with respect to sorry temperature at constant X. So, when we do that we can differentiate the constant X put it equal to 0; you will find that X m by 1 minus of X m; while is equal to k 1 divided by k 2 in multiplied by E 1.This is what we have shown at an earlier stage that if you have an exothermic reversible reaction; the best choice of temperature for your reactor is this, is the best choice we can put all the numbers here. For example, X m divided by 1 minus of X m equal to k 1 by if k 1 is 0.4, k 2 is 0.1 and what is activation energy, which is 20,000. So, this comes to 80, X m by 1 minus of X m comes out to 80, X m k 1 by k 2, E 1 by E 2 7; we have shown this what is E 1? E 1 is 20 and what is E 2? I mean, I am sorry this is do properly. Now, I just E 2 equal to how do you find out?

(Refer Slide Time: 44:11)



$E_1 - E_2 = \Delta H$

$E_2 = E_1 - \Delta H.$

$\left(\frac{\partial r}{\partial T}\right)_X = 0 = \frac{X_m}{1-X_m} = K\frac{E_1}{E_2}$

$[illegible] = (4)\frac{(25)}{(45)} = 2.2$

$\frac{X_m}{1-X_m} = 2.2.$

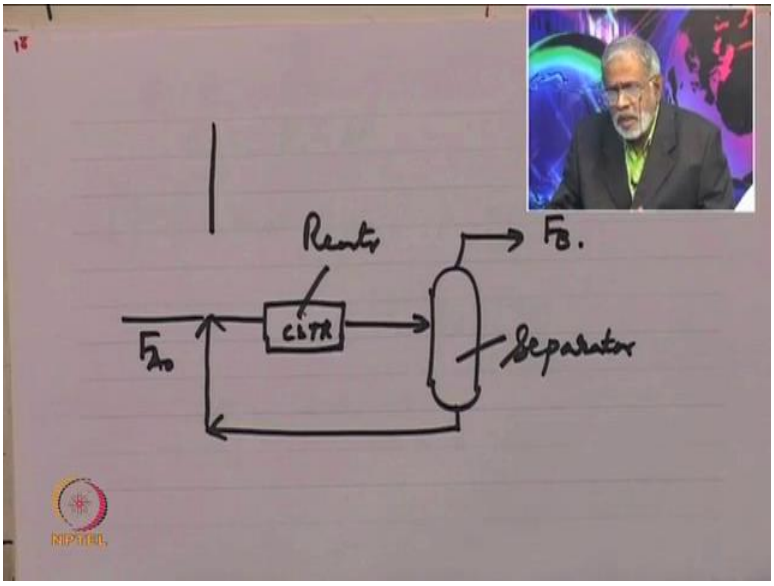
$3.2 X_m = 2.2$

$X_m = 2.2/3.2 = \underline{\underline{0.687}}.$

Let us find out something you have done when we many have forgotten we can do it again ok. So, what we have shown already this doing it once again del r by del T at constant X equal to 0; gives us X m divided by1 minus of X m equal to k equilibrium constant E 1 by E 2 is it clear. So, in this particular case equilibrium constant is 4, E 1 is 20 and E 1 minus of E 2 equal to delta H. Therefore, E 2 equal to E 1 minus of delta H in this case delta H is what is the delta H here? Delta H here is given as heat of reactions 20000 exothermic.

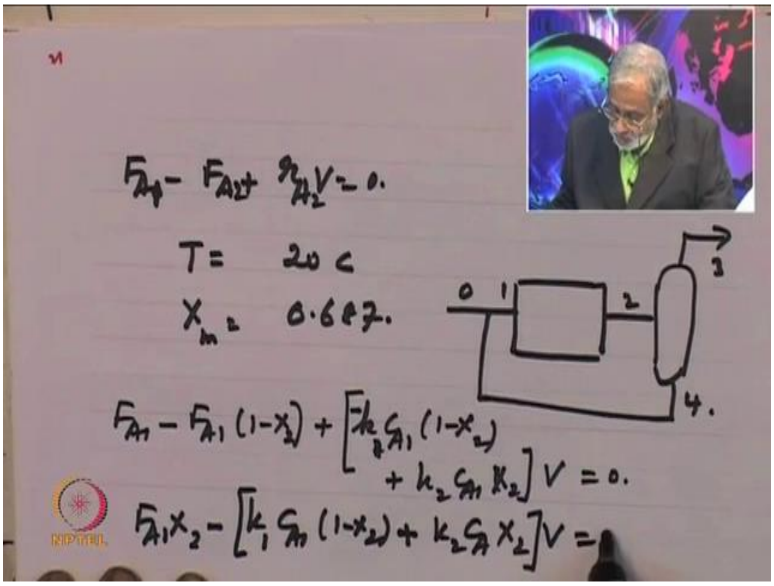
So, delta H is 20. Therefore, 25 plus 20 is 45, this is 25, this is 45. So, it comes out to be so it is 100 by 4500 divide by 45 equal to 2.2. So, X m divided by 1 minus of X m equal to 2.2. Now, this k is at 20 degrees c. So, in other words what we are trying to say is that if you have a stirred tank. And, if you have choice at of temperature of which we want to operate then immediately this fixes the value of X m at which you must operate. So, X m equal to take it here as 3.2 X m equal to 2.2. So, X m equal to 2.2 divided by 3.2 that is equal to 2.2 divided by 3.2 equal to 0.67, 0.687. So, what we are trying to say here is that in an exothermic reaction you can choose the temperature which will give you the highest reaction rate in that environment.

(Refer Slide Time: 46:16)



In this particular case our environment is this is the c s t r this is the c s t r. And, what is the best temperature, what is the best way to operate this? The best way to operate this choose it is temperature it will tell you what is the conversion that you should run at mound you know the conversion you can specify the residence time. Basically, you specify temperature you would that way you would term in conversion. And, once you know conversion from you material balance you can determine what is the residence time. Let us do that.

(Refer Slide Time: 46:46)



$F_{A1} - F_{A2} + r_{A2} V = 0.$

T = 20 c

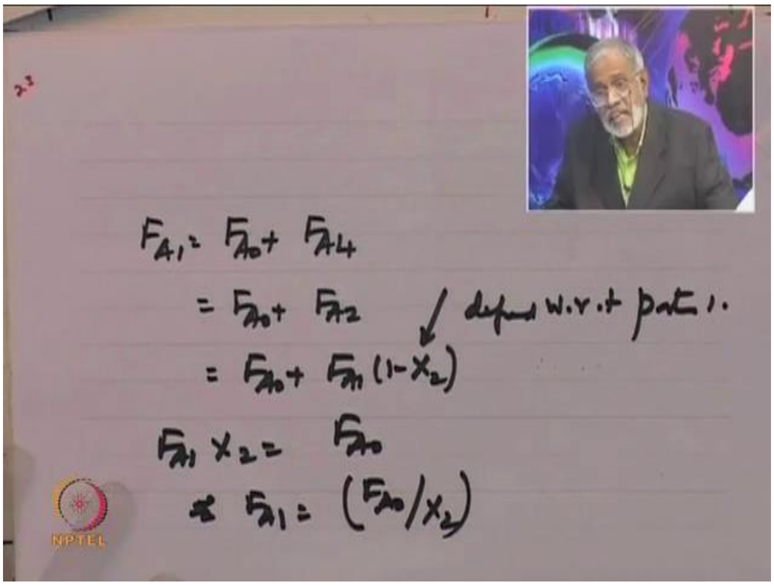
$X_m = 0.687.$

$F_{A1} - F_{A1}(1-X_2) + [-k_1 C_{A1}(1-X_2) + k_2 C_{A1} X_2] V = 0.$

$F_{A1} X_2 - [k_1 C_{A1}(1-X_2) + k_2 C_{A1} X_2] V =$

So, we have here our material balance which is F A 0 minus of F A plus r A B equal to 0. So, you know that best temperature operation is 20 c you have taken and corresponding to that X m should be 0.687 ok. What is this X m? This X m is with respect to inlet flow this X m. Let me just draw your attention here if you call this 0, 1, 2, 3 and 4. So, what you have done is that the way we have find X m is that X m is define with respect to this point position 1. So, F A 1 minus of F A 2 times r A 2 must be equal to 0 s. F A 1 minus of F A 2 by definition is F A times 1 minus of X plus. What is r A 2 by definition it is k times CA 1 times 1 minus of X at position 2, this is at position 2. This is within brackets r A is minus sign here plus k 2 sorry, this is k 1, this is k 2 times CA 1 times X 2 times V equal to 0 ok or on other words F A 1 times X 2 then we have minus of k 1 c A 1 times 1 minus of X 2, minus, plus k 2 c A 1 X 2 the whole thing multiplied by V equal to 0.

(Refer Slide Time: 48:46)



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

$= F_{A0} + F_{A2}$ ↙ defined w.r.t posit 1.

$= F_{A0} + F_{A1}(1 - X_2)$

$F_{A1} X_2 = F_{A0}$

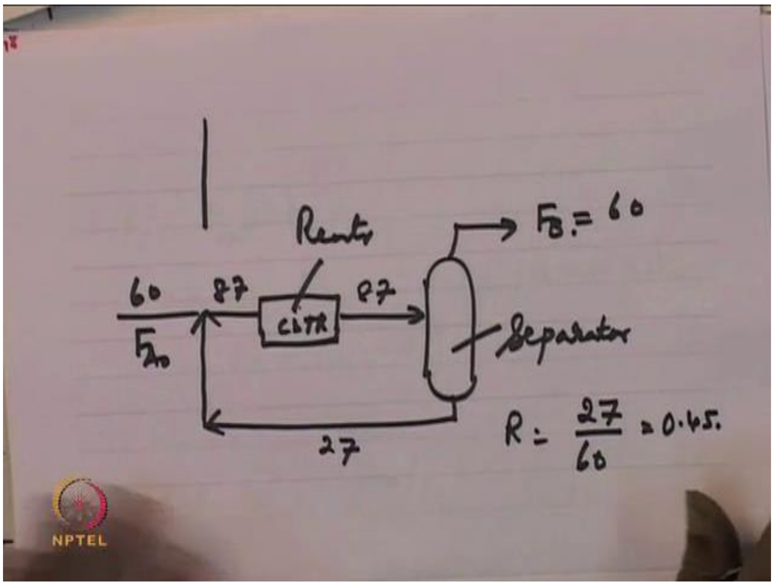
$\therefore F_{A1} = (F_{A0}/X_2)$

Let me go throw this properly now; so, what we F A 1, X 2 minus of k 1 C 1 minus of X 2 plus k 2 C 1, X 2; the whole thing I put V we have V equal to 0. So, we have able to find out the value of X 2 from here; because we know k 1 and k 2. Because temperature is fixed at 20; the best temperature you just taken the temperature as to 20 we can choose any other temperature, having chosen the temperature it tells what is the value of X 2 with respect to X F A 1.

Now, we also said at an earlier stage if you recall how F A 1 and F A 0 are related we have done all that. Let me do it once again we have F A 1 equal to F A 0 times F A 4 we have said that before. Because B is fully recover; therefore, this is pure A is that clear. Because of pure A, this C A 4 equal to CA 0 something that we have said. So, F A now that is F A naught plus F A 2 notice here that F A 4 is F A 2 only. Because B is fully recovered; so, that is equal to F A naught times F A 1 into 1 minus of X 2 where X is defined with respect to position 1. So, we have F A 1 times X 2 equal to F A 0, F A 1 equal to F A 0 divided by X 2 is that clear.

Now, please just look back for a minute and realize, recognize this X m is defined; this is defined with respect to position 1 we already said that. On other words this is the value of X 2 is 0.687 defined with respect to position 1. So, this is known as .687 is it clear. So, if you substitute value of X 2 as 0.687, F A 0 is given in our data F A 0 is already specified production is 60 mole per minute that is given. So, this is 60 mole per minute and X 2 0.687. So, let me 1 is so 60 divided by 0.687 that comes out to be 87 mole per minute is that clear?

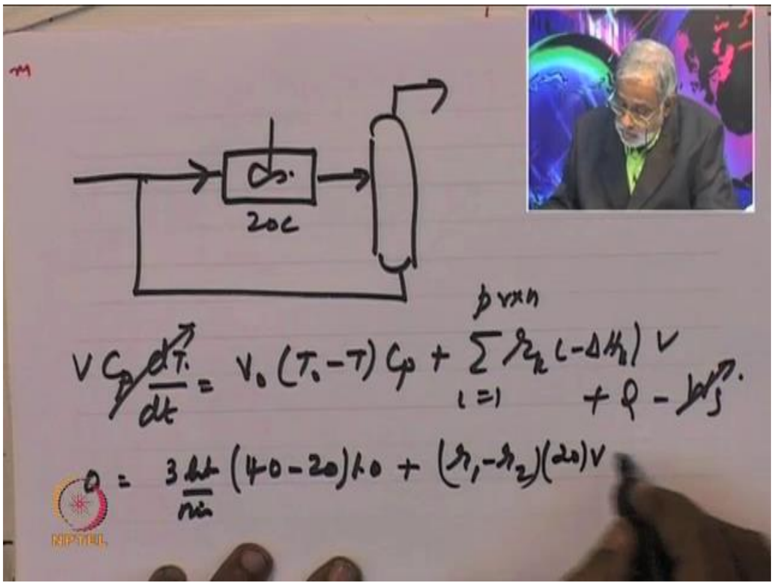
(Refer Slide Time: 51:46)



Now, with this we can put all our numbers here. Now, we can put this is 60, this is 87 and then and 0.687 multiplied by 0.687 that is equal to 59. So, this must be equal to 60; because what over is coming must go out correct. So, what is returning here? It is 27 is that right. So, this is 87, 60 goes out; therefore, 27 will come back here. So, if you are ask you what is recycle ration? What will tell us; recycle ratio is defined as what is going out divided by what is coming in correct. So, recycle ration is 27 divided by 60 it comes to 0.45 is it all right what we are saying.

So, what is it that we have done? What we have done is component A coming in and since it continuously getting reacted, un reacted with recycle; so, whatever comes in must go out. And, therefore what is recycle is un reacted alone is recycled and therefore, this becomes 87. Now, the question that we have to now ask is we have chosen this reacted temperature T as 20 c. Now, what is the best choice that we can wake this is question that we can ask. And, then of course, this is many of this decisions are dependent on you know cost factors and so on.

(Refer Slide Time: 53:40)



$$\cancel{V C_p \frac{dT}{dt}} = v_0 (T_0 - T) C_p + \sum_{i=1}^{p\,rxn} r_k (-\Delta H_k) V + Q - \cancel{W_s}$$

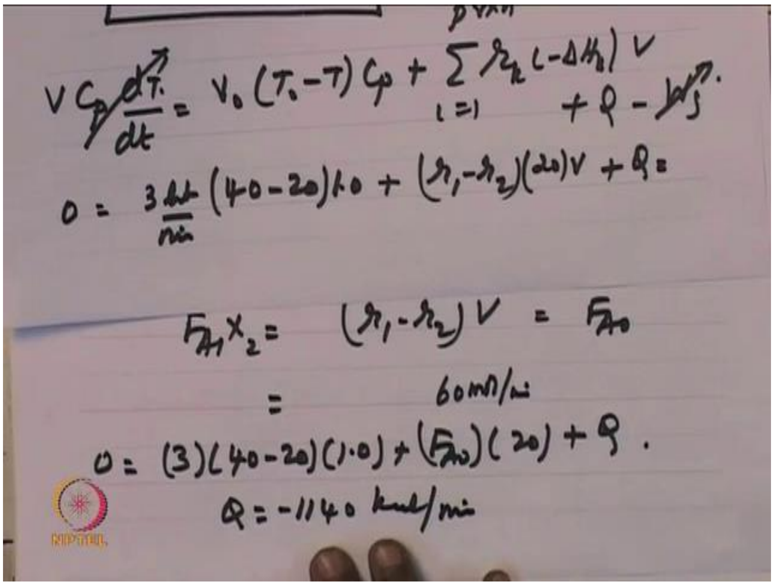
$$0 = 3 \frac{lit}{min} (40 - 20) 1.0 + (r_1 - r_2)(20) V$$

Therefore, we will have to look at different temperatures of operations; and see what is the cost of doing this at different conditions? But before we do that we have to recognize that we also have to ensure that the temperature of our choice is the temperature and which you want to work. So, we want to make sure that the heat transfer that is needed is available. On other words we have this reactor, we have this separator this is going out, this is coming back like this.

And, this is the c s t r; so, we want to operate this at this conversion the everything is given to us. So, what is the amount of heat to be added or removed this question we need to answer ok. Plus sigma all the reactions r k times minus of delta H k times V, i equal to 1 to p reactions we have done all these things plus Q minus of WS. Now, this is steady state; therefore, the amount of the heat generation this you have to balance by this T naught is given, T is given everything is given. So, which be able to calculate what the heat to be added or removed.

Let us do that now ok. So, how do we ensure that the temperature that we have chosen this 20 that it operates at the temperature we ensure this by an appropriate choice of the heating or cooling mechanism? So, we will have to substitute for all the numbers so that we can get. So, what is let us just quickly do all the numbers; So, let me 0 equal to molar density is 20. So, 60 divided by so it is flow is 3 liters per minute T naught feed temperature is 40, reactor temperature is 20 C p what is the C p? Specific heat of reaction mixture is 1. So, 1 kilo calories per this 1 plus there are reactions r 1 minus of r 2 c r 1. So, I will write here r 1minus of r 2; and what is minus delta H is 20 into V plus Q all right.

(Refer Slide Time 55:44)



$$V \cancel{C_p} \frac{dT}{dt} = v_0 (T_0 - T) C_p + \sum_{i=1} r_i (-\Delta H_i) V + Q - \cancel{W_s}$$

$$0 = 3 \frac{lt}{min} (40-20) 1.0 + (r_1 - r_2)(20) V + Q$$

$$F_{A1} X_2 = (r_1 - r_2) V = F_{A0} = 60 \text{ mol/min}$$

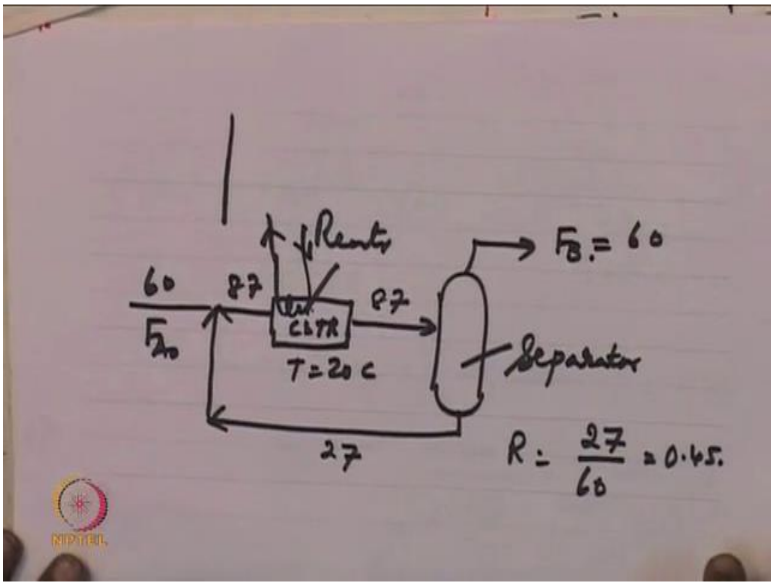
$$0 = (3)(40-20)(1.0) + (F_{A0})(20) + Q.$$

$$Q = -1140 \text{ kcal/min}$$

Now, what is r 1 minus of r 2? If you write our material balance; what is our material balance? F A 1 coming in minus of F A 1 times 1 minus of X 2 is going out. And, then the reaction which is forward reaction is r A goes to B; therefore, r 2 minus of r 1 multiplied by V equal to 0 is this clear. So, this is becomes minus of F A 1 times X 2 plus X plus r 2 minus of r 1 is it correct. Input minus of output F A 1, FA equal to 0; therefore, F A 1 times X 2 equal to r 1 minus of r 2 times V. And, therefore now they agree know r 1 means what is what we trying is say here is that. Please understand that r 1 minus of r 2 times V is F A 1 X 2 and what is the F A 1 X 2 equal to F A 0 that we have already said in this particular case; because of this recycle and so on.

Therefore, we get 0 equal to 3 multiplied by 40 minus of 20 times specific heat plus F A 1 this is basically it is F A 0 multiplied by 20 plus Q. Therefore, we calculate Q equal to 26 and then F A is 60 mole per, this is 60 mole per minute ok. So, it is 1200 it is roughly the answer about 1140 with a minus sign, kilo cal per minute is that minus sign means is what? Minus sign means you have to remove heat is this clear?

(Refer Slide Time: 57:43)



Now, there are some more free issues to be handled here with says that what is the heat transfer area? That is required for carrying out this reaction; that means Q is given as minus of 1140 kilo cal per minute. What is the heat transfer? You know the Q is equal to U times A by delta T. Therefore, Q is given as what is the heat transfer coefficient it is given as 5 kilo cal per square meter per minute; it is degree C this is given A is not known. And, what is the delta T reactor temperature? Delta T is 20 C and coolant temperature is 5, T C is given as 5 C. So, you delta T is 20 minus of 5 equal to heat this is heat to be removed. Therefore, it is 1140 we have put here; therefore, A equal to 1140 divided by 5 into 15. So, if you divided by 5 into 15; so, let comes out to be 1140 divided by 75 it is about 15.2 square meters ok.

So, in a sense what that we trying to put across to you is that I mean this is something that we all will encounter process that we have feeding the material it is under goes reaction not does not get converted fully; we will have to separate the desired product. And, then and converted must go back; because it is an expensive material. So, in a situation like this you need to see that this particular heat; that is needed must be taken out. So, you will have to put a heat heating coil and take over the heat. And, that particular case it turns out to be 15 square meters it is to be putted.

Now, the point is that is important is that to be able to put in 15 square meters of heat transfer area; you can do it by putting a coil or you can also do it by jacket. So, this choice is yours. And, then you might find in many cases the jacket may be better; if the heat transfer area is not very large. If the heat transfer area requirements becomes very large you cannot do it by jacket, you cannot do it by cooling coil; inside it has to be separate external heat exchange equipment. So, this is matter of design that you will have to be look at it could be external, it could be internal or it could be jacket. And, these are issues that you take for a design; I will stop there.

Thank you very much.