Advanced Chemical Reaction Engineering

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Lecture - 23

Illustrative Example: 1) Plug Flow with Heat Effects
2) Multiple Reactions

So, we continue with advanced reaction engineering.

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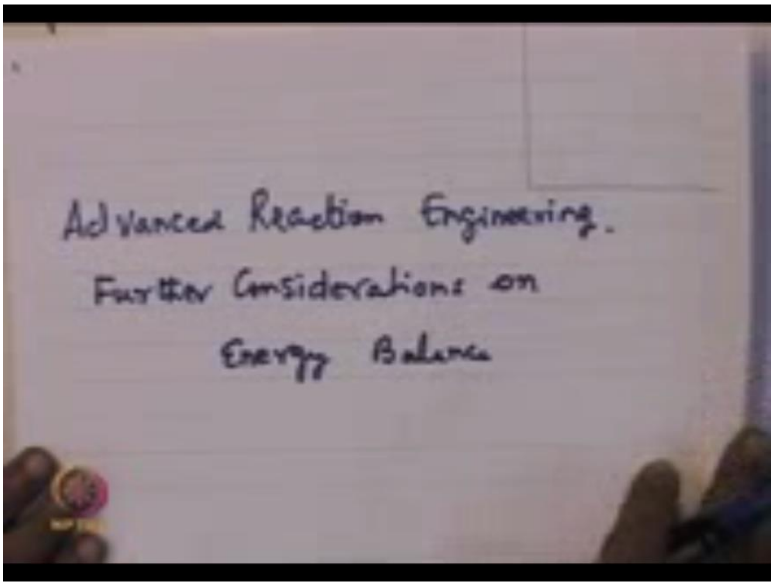

Advanced Reaction Engineering.
Further Considerations on
Energy Balance

Now, we look at further considerations on energy balance now, the point of looking at this is the following.

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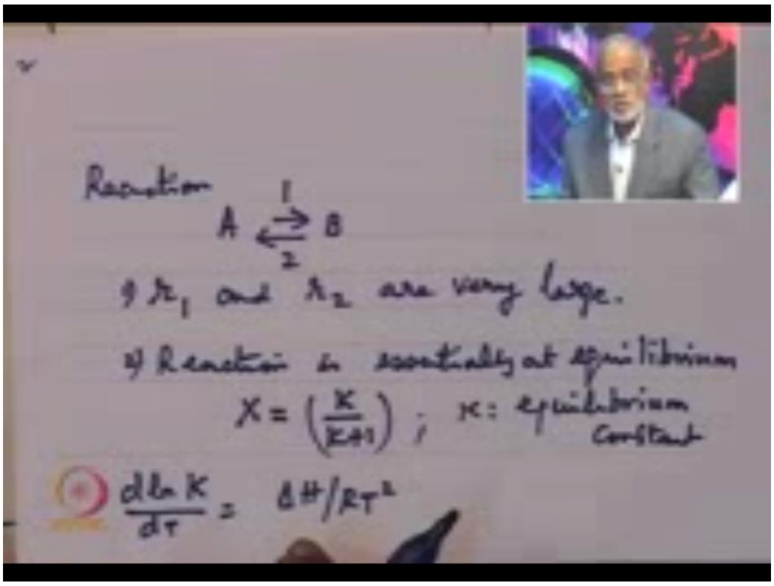

Reaction

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

1) r_1 and r_2 are very large.

2) Reaction is essentially at equilibrium

$X = \left(\frac{K}{K+1}\right)$; K: equilibrium constant

$$\frac{d \ln K}{dT} = \Delta H / RT^2$$

For example, let us say we have a reaction which is instantaneous, what is mean by instantaneous? That reactions r r 1 and r 2 are very large; we can also say that r 1 and r 2 are such that it is in equilibrium. In other words the reaction this is 1, one we have looking at other way we looking at is reaction is essentially at equilibrium. Which means, what? Which means that the conversion at any is given by K by K plus 1 where K is given by is vectors equation which is d l n K by d T equal to delta H by R T square. This is one way by which we can understand that the reaction is instantaneous means that conversion is K by K plus 1 where K is equilibrium constant. And equilibrium constant is given by the vector’s equation d l n K by d T d is delta H by R T square. Now, what are the situations where you are likely to encounter such fast reactions? There could be many situations in which we can be looking at.

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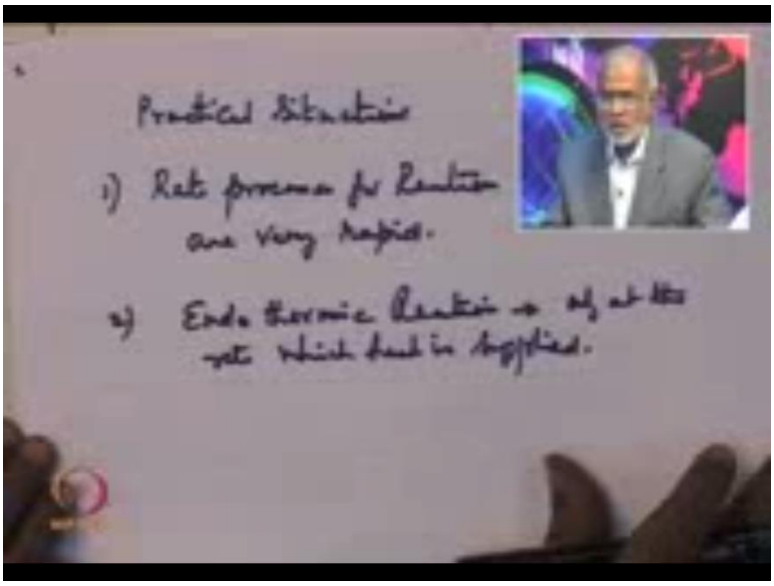

Practical Situations

1) Rate processes for Reaction are very rapid.

2) Endo thermic Reaction → only at the rate which heat is supplied.

First situation, of course, the rate processes are very fast I mean practical situations. Let us say practical situations so, rate processes for reaction rate processes are very rapid. This is 1; the second instance which would be of relevance to us is for example, when for example, let say an endothermic reaction. It proceeds only at the rate at which heat is supplied. So, heat is an instance of a reaction which simply moves depending upon the rate of heat supply. So, these are all situations in which you know we need to able to use our basic equations with some care. So, let us look back at our basic equations the energy balance and the material balance.

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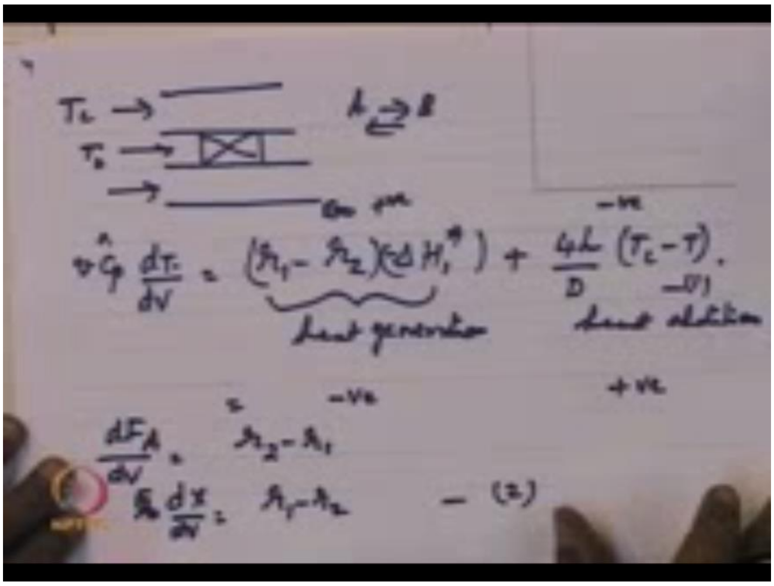

$$v\hat{C}_p \frac{dT}{dV} = \underbrace{(r_1 - r_2)(-\Delta H_1^0)}_{\text{heat generation}} + \underbrace{\frac{4h}{D}(T_c - T)}_{\text{heat addition}}$$

−ve

+ve

$$\frac{dF_A}{dV} = r_2 - r_1$$

$$F_0 \frac{dx}{dV} = r_1 - r_2 \quad — (2)$$

So, let me write that means we have a situation like this we have a reactor may be is a catalytic reactor. And it is cooled or heated by a fluid this is coolant this is the reagents coming in T naught all right. Now our energy balance, we have done written the energy balance v 4 which looks like this if there is a going to b this is the reaction. So, I am this is writing it an r 1 minus of r 2 times minus of delta H 1 star this is the. Then this is 4 h by D multiplied by T c minus of T. So, this is heat generation shall we say heat generation and this is heat addition.

Now, if it is a exothermic reaction of course, this is positive therefore, this must be a negative if it is a exothermic reaction if it is an endothermic this exo, exo means this is positive this is negative. Therefore, then if it is endothermic this is negative and then this must be positive. This something that we all know endothermic means heat is to be supplied and it is supplied by this term. And this difference is what you see on the left hand side all right. Now, keeping this in mind let us look at this is look at the material balance which says d f. Let us say d f a d V equal to r 2 minus of r 1 or F A 0 times d x d V equal to with a equal to r 1 minus of r 2. So, you notice here if I call this is reactor equation 1 call the equation 2.

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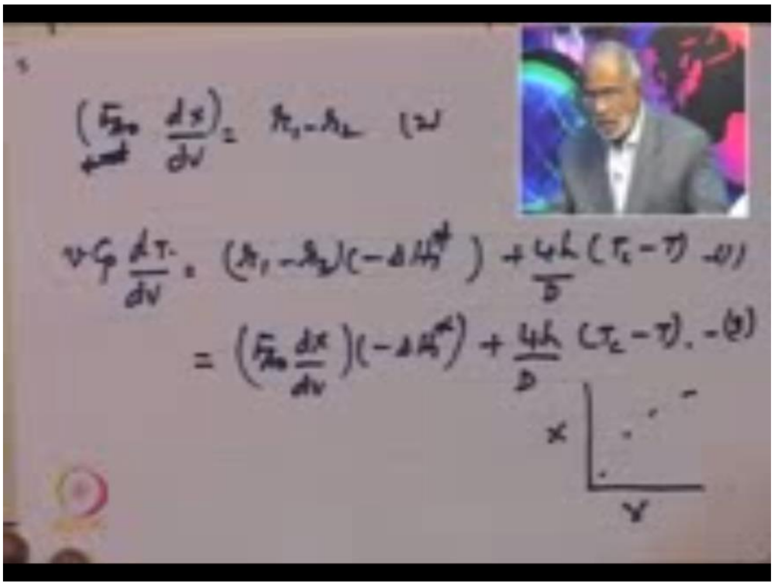

$$\left(F_{A0}\frac{dx}{dV}\right) = r_1 - r_2 \quad (2)$$

$$v c_p \frac{dT}{dV} = (r_1 - r_2)(-\Delta H_1^*) + \frac{4h}{D}(T_c - T) \quad -(1)$$

$$= \left(F_{A0}\frac{dx}{dV}\right)(-\Delta H_1^*) + \frac{4h}{D}(T_c - T). \quad -(3)$$

Then we have v c P d T d V equal to which is r 1 minus of r 2 I will write here minus of sorry plus F A 0 times d x d V equal to r 1 minus of r 2. This is minus of delta H 1 star Plus 4 h by D into T c minus of T and then you have a this is this is equation 1 and this is equation 2. Now, what we are trying to point out here is that r 1 minus of r 2 if r 1 and r 2 are very large. For example, so that r 1 minus of r 2 we do not know how whether it is large small no idea. So, in cases where r 1 and r 2 so large then we are not able to measure them clearly you know this is not going to be easy to handle this equation. So, in such cases we can replace this first term by this d x d V multiplied by minus of delta H 1 star plus 4 h by D T c minus of T.

Now, the important thing here is that now it may be possible for you to measure this term left hand side d x. This term may be possible to measure which cause we can take samples of the components. Therefore , we can measure the left hand side we can even plot even you may even plot this x versus v showing that some data may be available. Therefore, this term is something that you can experimentally determine. So, that it is more convenient to replace this r 1 minus of r 2 in terms of what you can measure. And therefore, if you look at this equation I will call this is equation 3. Number of things we can do with this equation now if and just thought of look at this in some detail there be just write this once again.

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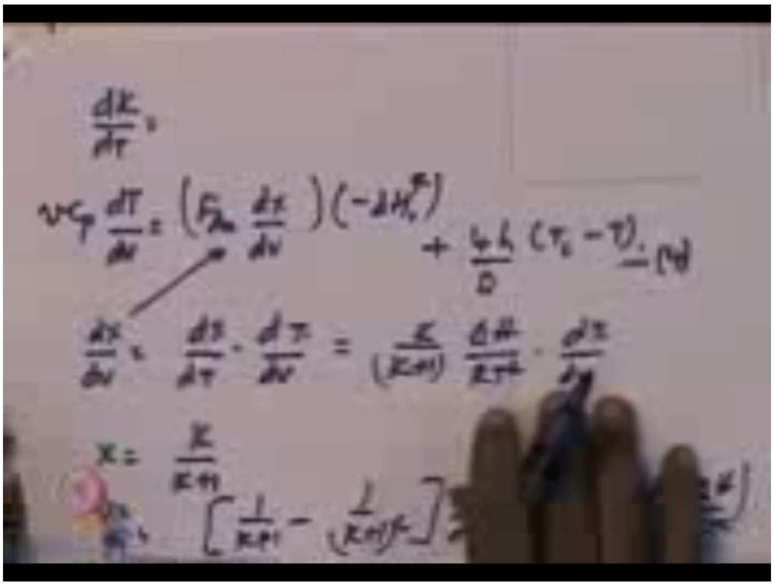

Just for the sake of explaining equal to F A 0 d x d V multiplied by minus of delta H 1 star plus 4 h by D T c minus of T. Now, this term d x this term we are able to measure experimentally. For example, if it so happens the, this reaction this reaction r 1 minus of r 2 is so rapid hat reaction is at equilibrium all the time inside the equipment that. Then you can recognize that d x d V which can be written as d x d T and d T d x d T d T d V. What is d x d T? If it if our reaction x is given by K by K plus 1 then what is d x d T d x d T is derivative of this which is what 1 by K plus 1 minus of 1 by K plus 1 whole square d K d T. And what is d K d T? I will write here d K d T d K d T is simply where are, we go where is grant of equation this is go back to vectors equation.

And then ask this question what is d d T d k I will just write here d K this is implies d K d T is what is 1 by K d K d T is delta H by R T square. There is d K d T, because K times delta H by R T square all. So, what it mean is that this simplifies as this is equal to 1 by K plus 1 whole square d K d T is K times delta H by R T square. Therefore, you can see here d x d V is simply this whole term 1 by K plus 1 times K delta H by R T square all right. So, you can substitute for d x d x d T this is whole thing d x d V you can replace this in this way. And then you can replace as d T d V therefore, our equation I will call this is equation 4. So, I can replace equation 4 in this form Let me just do this I will not take too long.

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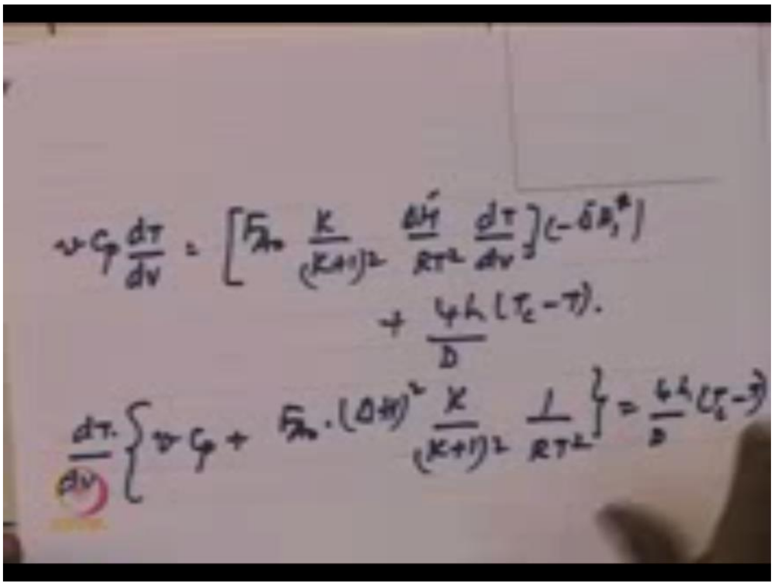

$$\nu C_p \frac{dT}{dV} = \left[F_{A0} \frac{K}{(K+1)^2} \frac{\Delta H}{RT^2} \frac{dT}{dV}\right](-\Delta H_1^*) + \frac{4h}{D}(T_c - T).$$

$$\frac{dT}{dV}\left\{\nu C_p + F_{A0} \cdot (\Delta H)^2 \frac{K}{(K+1)^2} \frac{1}{RT^2}\right\} = \frac{4h}{D}(T_c - T)$$

So, I will have this energy balance equation d T d V equal to F A 0 you have d x d V this d x d V term. I am writing from here which is K which is K divided by K plus 1 whole square delta H by R T square d T d V. That is the first term that is this I have to written this term I would multiplied by delta h. So, I will multiplied by minus of delta H 1 star then plus 4 h by D T c minus of T. Notice here that this is d T d V this also d T d V.

Therefore , we can take d T d V common you get v c P I will put a plus sign, because this is a plus sign goes a, this side F A 0 delta H square I have taken these 2 terms.

Then you have K by K plus 1 whole square I have taken this by 1 by r T squared this is the term here equal to 4 h by D T c minus of T. So, what is that we have done, what we have done is that for us for this case where the reactions are very fast. And therefore, the whole thing is equilibrium at the every position in the equipment this equation represents what happen to the reaction. So, let us understand what this equation means.

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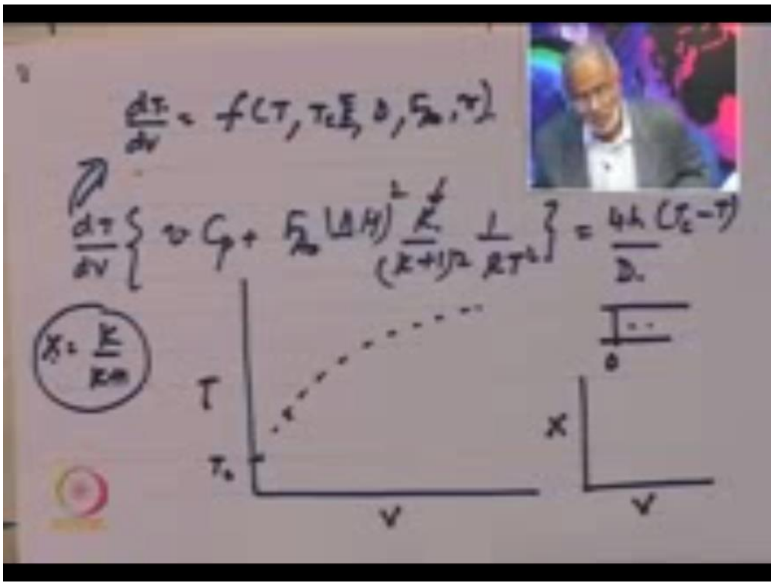

So, if you make a plot actually I should have this equation in front of us I will write it here for our sake d T d V within bracket. So, v c P plus f a 0 delta H squared K by K plus 1 whole squared 1 by r T squared equal to 4 h T c minus of T divided by d. Suppose I want to make a plot make a plot of let us say versus v, how do a find out? Now, this differential equation I have to solve notice here that I can this I can write this I am putting it here. So, d T d V d T d V equal to what it is I can take it to the other side so that essentially d T d V is a function of K is a function of temperature. So, it is essentially a function of temperature, the right hand side everything is a function of temperature and T c. And of course, it is also depends upon the tube size I will put deep tube size anything then F A 0 and then volumetric flow.

So, what are we saying, what we are saying is that the temperature variation at different positions of the equipment depends upon temperature, coolant temperature, reactor diameter, inlet flow rate and volumetric flow rate. So, basically if you can once temperature is known in there all the rest follows. So in other words if you want to find out how what is how T is varies with position what you have to do? You start with T 0. So, you start somewhere it T 0 and therefore, you can forward march, because everything is known from the initial state that means from position here 0 position everything is known.

Therefore, you can do a forward march and then calculate what is the temperature as a function of volume? And once you know temperature similarly, once you can plot x as a faster volume, because once you know temperature you know vectors you know this K K by K plus 1 all ready you know this. Therefore, movement you know temperature you know x therefore, you can plot x versus volume. So, what we are trying to put across T u is that if you have a reaction where in the reaction rates are such that is very large reaction rates are very large. And therefore, it conforms to equilibrium at every position in the equipment.

Then you are able to tell how T changes with volume and the equation that describes this variation. This is what we have derive; this is what we have done so far; this is the equation describes the variation of temperature with volume. And then once you know the, it is variation of temperature with volume we said we can plot T versus v. And therefore, you can plot x verses v therefore, the complete the whole system is fully specified. So, for the case of a instantaneous reaction we find that from the energy balance, we are able to tell what happens. Now, second related situation which is interest to us is suppose for example, let us look at let me write once again just for the sake of explaining to you.

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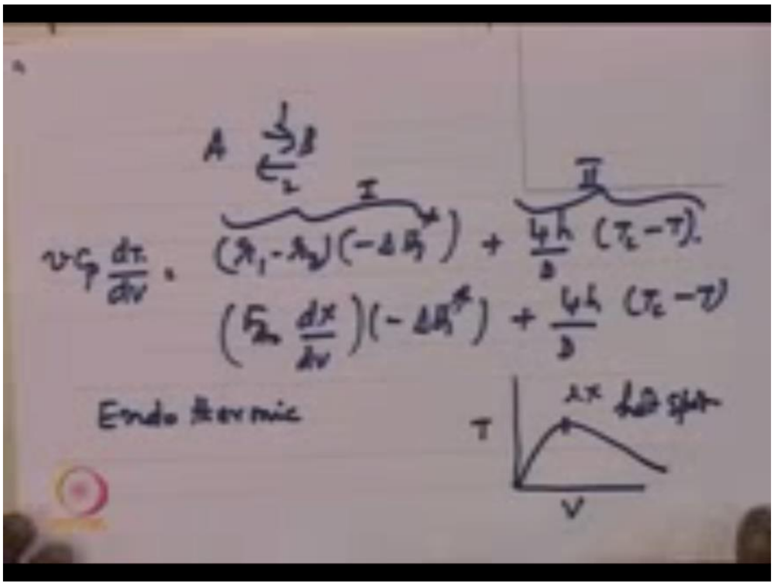

$A \underset{2}{\overset{1}{\rightleftarrows}} B$

$$v c_p \frac{dT}{dV} = \overbrace{(r_1 - r_2)(-\Delta H_1^*)}^{I} + \overbrace{\frac{4h}{D}(T_c - T)}^{II}$$

$$\left(F_{A0} \frac{dx}{dV}\right)(-\Delta H_1^*) + \frac{4h}{D}(T_c - T)$$

Endothermic

V c P d T d V equal to r 1 minus of r 2 minus of delta H 1 star plus 4 h by D T c minus of T. This is one form; the other form is F A 0 d x d V times minus delta H 1 star plus 4 h by D T c minus of T. The reaction is A goes to B and B goes to A 1 and 2 this is the reaction. Now, there could be a second situation the situation there is the, this term which this is I will call this term 1 and I will call this term 2. Now, there are situations where term 2 is quite small, the sense that you are not able to supply enough heat. Therefore, essentially they rate at which let us consider as an example that this is an endothermic reaction.

What is an endothermic reaction? You have to supply heat then only this reaction will move otherwise heat will not move. So, this is an instance is an instance in which this essentially the reaction moves forward as you supply heat. And if this reaction is reversible may not be instantaneous it is a reversible therefore, to the extensive supply heat it will move forward. Therefore, even in such cases you are able to conveniently use this form. If you find that this is not convenient to use you can use this form and take necessary action on the questions of our interests.

So, in all these cases if it is if it is exothermic if it is exothermic then you will see it will be thing like this. So, if this is the process industry there was so many instances are exothermic reversible reactions. Therefore, this is what is called is the hotspot it is of much interest to the designer. Because hot spot temperature of the catalyst is a specification on the catalyst you should not exceeded preferably. And therefore, lot of design has to take into account on that we design. So, that the hot spot temperatures are not reached. So, this is something that I want to do reemphasize, what was said in the last lecture just to bring to you attention, that this formulation is very useful from the point of view of dealing with very fast reaction where r 1 and r 2 may not be known T u. So let us take one more example, illustrate how we can manage what is called as a the energy balance.

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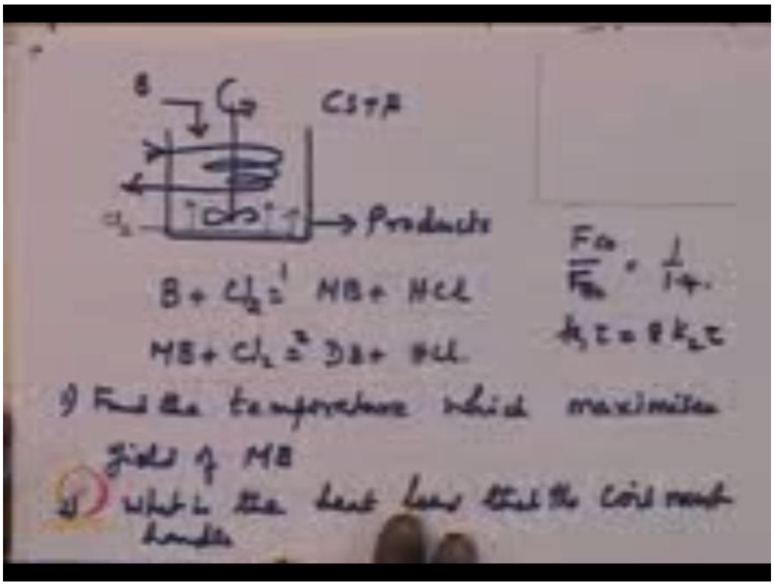

$B + Cl_2 \overset{1}{=} MB + HCl$

$MB + Cl_2 \overset{2}{=} DB + HCl$

$\frac{F_{C0}}{F_{B0}} = \frac{1}{1.4}$

$k_1\tau = 8 k_2\tau$

i) Find the temperature which maximizes yield of MB

ii) What is the heat load that the coil must handle

Second exercise in which we want to look at once again it is a it is a reaction where lot of heat is involved in a lot let me just describe the process. And then we can look at the details, what do we have? We have a, we have chlorine coming in chlorines; coming in this is chlorine and then products. We have benzene plus chlorine equal to monochlorobenzene plus H c l and then monochlorobenzene plus chlorine equal to dichlorobenzene plus H c l. So, some data is given what is the data given the data given is that chlorine is it correct F C 0 by F B 0 So, F C 0 divided by F B 0 that is given as 1 by 1.4 this data is given.

See if we look at problem like this, how is energy balance important here is that you have a chlorination reaction. Now, you know this benzene these are all compounds which get chlorine lot of heat is released. And generally it is not very easy to handle such reactions in A, because it is not enough mixing. And therefore, heat release such that is a very difficult to manage a reaction in a stirred tank such as here this is the stirred tank. We can comfortably in a appropriate design put a cooler cooling coil and then remove the heater. In other words it is possible to manage highly exothermic. Very rapid reactions in a stirred tank by appropriate choice of the feed this is the benzene feed here.

So, we can adjust the feed and the chlorine feed such that heat releases within manageable limits. So, the first part of the question is what is first part of the question is what is the, find the temperature which maximizes yield of monochlorobenzene. This is the first part of the question. And of course, once you have done that, what is the, what is the heat load? Heat load that the coil must handle is that clear? So, there are 2 part to this I mean gets chlorinated lot of heat is released. And what is the temperature which maximize the yield of after all many cases you are intermediate you are interested in the intermediate you what is maximize the yield of monochlorobenzene having done that.

So, what is the amount of heat that this coil must handle? So, this is the 2 questions that we must address some data is given which says some more data is given which says this is reaction 1; this is reaction 2 which says that K 1 tau equal to K 2 tau or K 1 by K 2 is 8 this data is given. Now, chlorination's are very very common in the process industry and many of the refrigerants that we use have some chlorine and fluorine in a fluorocarbons. So, these are all reactions involving in halogenations and this is very important halogenations. And then benzene in chlorination is of course, very important, because traditionally benzene chlorobenzenes are involved as insecticides in several applications.

Of course, lot of issues coming up these days. But that a side that it has several long purpose of insecticides for a very long time it will continue to be. So, it will be find out later so, we need to handle chlorination. Now, benzene is one of them, methyl chlorination is another. You know very important products that we use in our, what is called as the refrigeration industry and so on. Now, that we have this question in front of us our question is what is the temperature which will maximize monochlorobenzene? This is the question that we want to answer and of course, once you do that you will do there as. So, let us do the material balance as usual our job is to rise the material balance.

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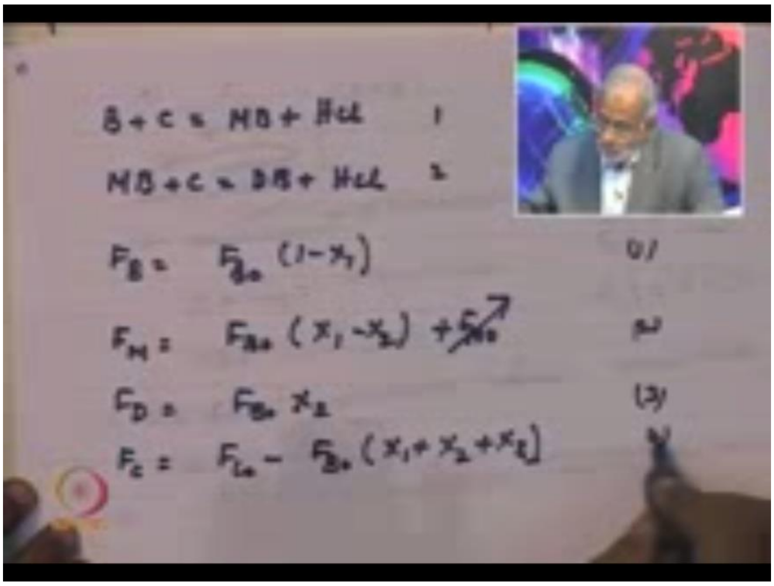

$B + C = MB + HCl$ 1

$MB + C = DB + HCl$ 2

$F_B = F_{B0}(1 - X_1)$ (1)

$F_M = F_{B0}(X_1 - X_2) + \cancel{F_{M0}}$ (2)

$F_D = F_{B0} X_2$ (3)

$F_C = F_{C0} - F_{B0}(X_1 + X_2 + X_3)$ (4)

Let us write the material balance benzene plus chlorine gives you monochlorobenzene plus H c l then monochlorobenzene plus chlorine gives you dichlorobenzene plus H c l. So, our our stoichiometry is says F B equal to F B 0 F B 0 times 1 minus of X 1 this is reaction 1 reaction 2. Then comes f monochlorobenzene equal to F B 0 X 1 minus of X 2 plus F M 0 which we taken A 0. Then we have dichlorobenzene which is F B 0 times X 2 then of course, you want to find out amount of fluorine consumed F C equal to F C 0 minus F B 0 into X 1 plus X 2 plus X 3.

Shall we say, is this clear what we are said? So, the amount of chlorine that is consumed is whatever is the chlorine that, you put in minus whatever is consumed. So, I will call this 1 2 3 and 4 in this exercise, what is said this that the chlorine is added at a rate. So, that chlorine is completely consumed chlorine is completely consume and the fluid here is saturated in chlorine you understand if you here is saturated in chlorine. So, what is it mean? It means a following it means the, if you look at let us say look at reaction 1 if you look at reaction 1 this is reaction 1. So, what is the rate constants says reaction therefore.

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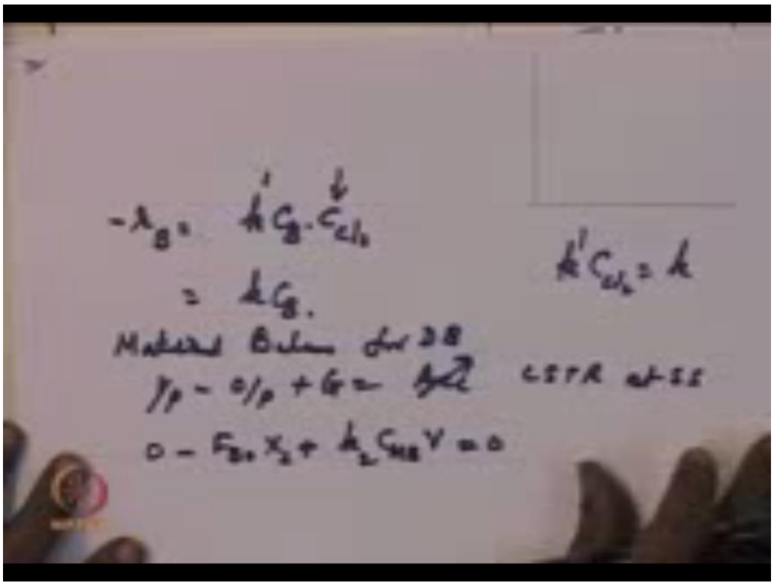

If I say r say r benzene rate of formation rate of is I will put a minus sign here K times C B times C C l what are we saying. And now since this C C l to this c l to concentration in the liquid does not change. We can I will call this K dash K dash times C I will say that K dash times C C l 2 equal to K therefore , it becomes K C B. So, what is being said is the following that the chlorination reactions that are taking place in the liquid phase. The, it second order reactions, but in view the fact that chlorine concentration in the liquid does not change. We can assume it; we are pseudo first order reaction that is what is being said.

With this we can write the material balance for so, let us say life for dichlorobenzene so material balance for D B. So, what is a input? What is output? What is generation equal to accumulation? And we are talking about C S T R at steady state at steady state. So, what is a input 0? What is a output? F B 0 times X 2, what is a generation dichlorobenzene is generate in reaction 2? It must be equal to K 2 times M B times C l 2 concentration C l 2 concentrations is constant. Therefore, it becomes a pseudo first order in M B. So, it becomes K 2 C M B times v equal to 0 so we got equation for dichlorobenzene. Let us do for one more so that we can finish it off. So, if suppose write the balance for benzene.

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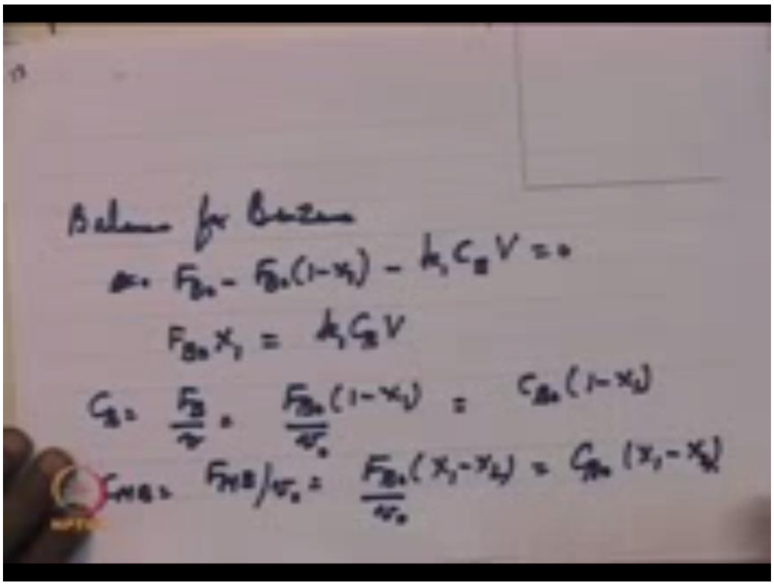

Balance for Benzene

$$0 = F_{B0} - F_{B0}(1-x_1) - k_1 C_B V = 0$$

$$F_{B0} x_1 = k_1 C_B V$$

$$C_B = \frac{F_B}{v} = \frac{F_{B0}(1-x_1)}{v_0} = C_{B0}(1-x_1)$$

$$C_{MB} = F_{MB}/v_0 = \frac{F_{B0}(x_1-x_2)}{v_0} = C_{B0}(x_1-x_2)$$

Balance for benzene what is a balance for benzene F B 0 minus of F B 0 into 1 minus of X 1 minus of K 1 c benzene times v equal to 0. So, this becomes F B 0 X 1 equal to K 1 C B v is it all right. Now, what is C B is F B by small v volumetric flow which is F B 0 times 1 minus of X 1 divided by. Let us say it V 0 V equal to v 0 volume changes are small is equal to C B 0 times 1 minus of X 1. So, similarly, C M B equal to F M B by v 0 what F M B equal to F B 0 times X 1 minus of X 2 divided by v 0 is equal to C B 0 times X 1 minus of x 2. So, why have we done this? We have done this, because we want C M B and also we want C B in terms of X 1 X 2 that what we have got. So, we have got everything in the form in which we required therefore, we can now use it to go forward. So, we can substitute appropriately.

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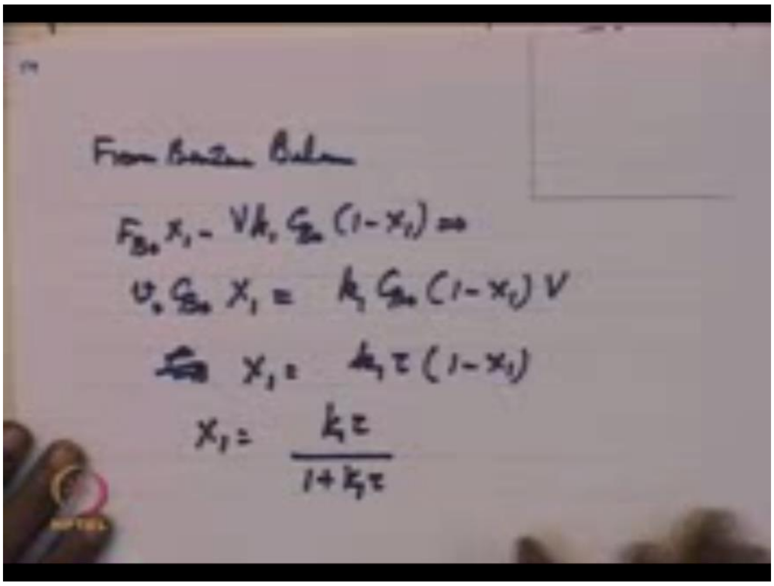

From Benzene Balance

$$F_{B0} X_1 - V k_1 C_{B0} (1 - X_1) = 0$$

$$v_0 C_{B0} X_1 = k_1 C_{B0} (1 - X_1) V$$

$$X_1 = k_1 \tau (1 - X_1)$$

$$X_1 = \frac{k_1 \tau}{1 + k_1 \tau}$$

Therefore we have benzene balance that is do from benzene balance, what do we get from benzene balance? We get F B 0 X 1 minus of K 1 C B 0 times 1 minus of X 1 equal to 0 please I am not seeing anything new something that benzene balance. So, this is what I have written C B I have written C B 0 times 1 minus of x 1. So, this we can write this as v naught C B naught X 1 equal to K 1 C B naught 1 minus of X 1. Now, you can collect coefficients and 1 v is missing v is missing. So, with this we can be written as X 1 equal to K 1 tau 1 minus of X 1. Therefore, X 1 equal to K 1 tau divided by 1 pus K 1 tau. This is one relationship that we have got notice K 1 is given K 1 by K 2 is given all right once we do that similarly, for dichlorobenzene. So, what is dichlorobenzene we got?

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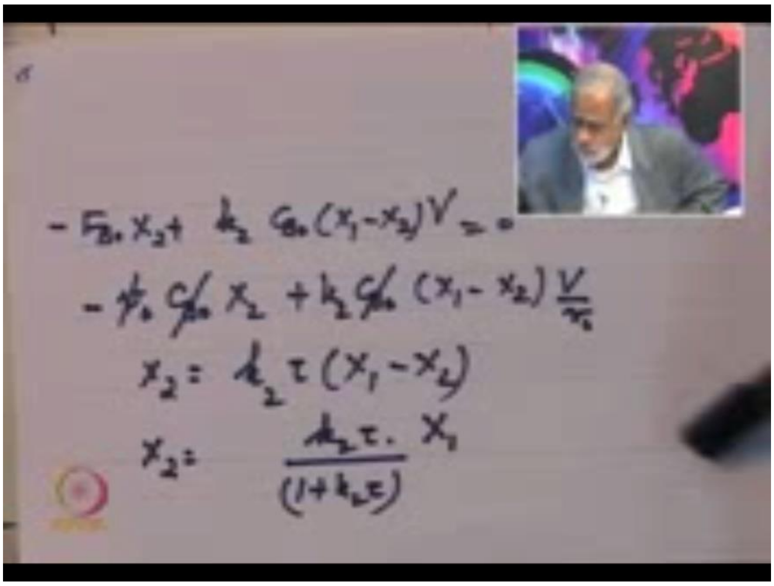

$$-F_{B0} X_2 + k_2 C_{B0}(X_1 - X_2) V = 0$$

$$-\cancel{v_0} \cancel{C_{B0}} X_2 + k_2 \cancel{C_{B0}} (X_1 - X_2) \frac{V}{v_0}$$

$$X_2 = k_2 \tau (X_1 - X_2)$$

$$X_2 = \frac{k_2 \tau .\ X_1}{(1 + k_2 \tau)}$$

For dichlorobenzene F B 0 X 2 minus of this is minus; this plus K 2 times C M B is what C B 0 times X 1 minus of X 2 times v equal to 0 so we can collect coefficients and so on. And therefore, we get v naught C B naught X 2 plus K 2 C B naught X 1 minus of X 2 times v divide throughout by v naught becomes tau. So, this becomes tau so this is because C B naught can be cancel of. So, we get X 2 equal to K 2 this is K 2 time's tau X 1 minus of X 2. Therefore, X 2 equal to K 2 tau divided by 1 plus K 2 tau multiplied by X 1. So, what are we got we got our relationship both X 1 and X 2, we now know in terms of K 1 tau and K 2 tau now if I ask.

Now, the problem says the problem statement let us understand the problem statement once again. Problem statement is what is being said is the following what is being said is that in this chlorination reaction chlorine which is admitted in to the C S T R which is maintain at an appropriate temperature. All the chlorine gets consumed on other words if chlorine input is a F C 0 all the chlorine get consumed. Therefore, if you look at if you look at the chlorine balance what are we saying? We saying in chlorine balance all the chlorine get consumed that means this is 0 which means what which means F C 0 divided by F B 0.

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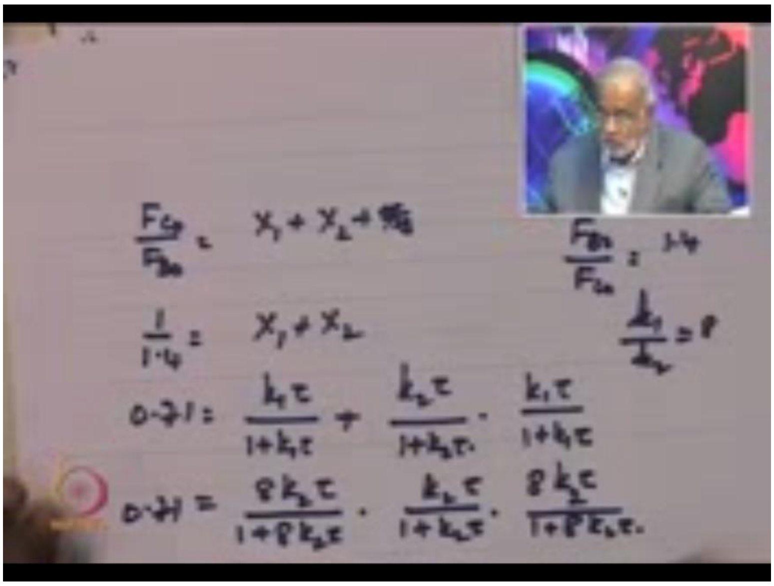

$$\frac{F_{C0}}{F_{B0}} = X_1 + X_2 + \cancel{X_3}$$

$$\frac{F_{B0}}{F_{C0}} = 1.4$$

$$\frac{k_1}{k_2} = 8$$

$$\frac{1}{1.4} = X_1 + X_2$$

$$0.71 = \frac{k_1\tau}{1+k_1\tau} + \frac{k_2\tau}{1+k_2\tau} \cdot \frac{k_1\tau}{1+k_1\tau}$$

$$0.71 = \frac{8k_2\tau}{1+8k_2\tau} \cdot \frac{k_2\tau}{1+k_2\tau} \cdot \frac{8k_2\tau}{1+8k_2\tau}.$$

Let us write it here F C 0 divided by F B 0 equal to X 1 plus X 2 plus X 3 and if the data says F B 0 by F C 0 equal to 1.4. Therefore, this is this is 0.1 by 1.4 equal to X 1 plus X 2 X 3 is not this 1 plus X 2 so this is 0.71 equal to X 1 what is the X 1 K 1 tau 1 plus K 1 tau. What is X 2? K 2 tau divided by 1 plus K 2 tau multiplied by X 1 which is K 1 tau 1 plus K 1 tau now K 1 divided by K 2 is given as 8. Therefore , here this can be written as what K 1 by K 2 is therefore, K 1 equal to 8 K 2 So, I can put K 1 is late here I will get 8 K 2 tau divided by 1 plus 8 K 2 tau first term.

Then K 2 tau divided by 1 plus K 2 tau multiplied by 8 K 2 tau divided by 1 plus 8 K 2 tau equal to 0.71. What I have done now? Now, we can solve this to find out what is K 2 tau? Correct. Now, let us not get the context the context is this generally it is possible to find out these ratios more easily. Then the absolute values, that is the point so here what we have done these ratios have come out from the experiment. Therefore, you can find out by solving this, what is the value of K 1 tau? Correct. What is the value of K 1 tau by solving?

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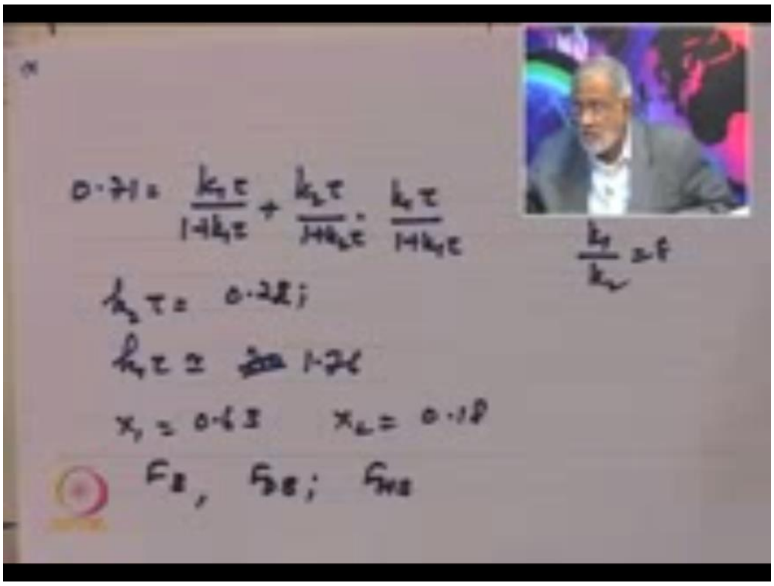

$$0.71 = \frac{k_1\tau}{1+k_1\tau} + \frac{k_2\tau}{1+k_2\tau}\cdot\frac{k_1\tau}{1+k_1\tau}$$

$$\frac{k_1}{k_2} = 8$$

$k_2\tau = 0.22;$

$k_1\tau = 1.76$

$x_1 = 0.63$ $x_2 = 0.18$

F_B, F_{DB}; F_{MB}

When you solve this you get 7 1 equal to K 1 tau by 1 plus K 1 tau plus K 2 tau K 2 tau by 1 plus K 2 tau multiplied by K 1 tau divided by 1 plus K 1 tau where K 1 by K 2 equal to 8. We can solve this it find out that K 2 tau terms out be about 0.25. And therefore, K 1 tau terms out to be 2.0 sorry 0.22 is this 0.22 and 1.76. So, with this we can find X 1 equal to point six 3 and X 2 equal to 0.18. Once you know X 1 X 2 we can find out F M B F benzene F dichlorobenzene, F monochloro, F monochlorobenzene and so on. All these can be found out, because so why have we done this problem? What is the moral of whole story? So, moral of the story is that if you have a series reaction like this you can find out the compositions. If we know the rate constants that is what is being said, but we want to go a little bit further. And find out what is the best temperature which optimizes the production of this what is it called as monochlorobenzene.

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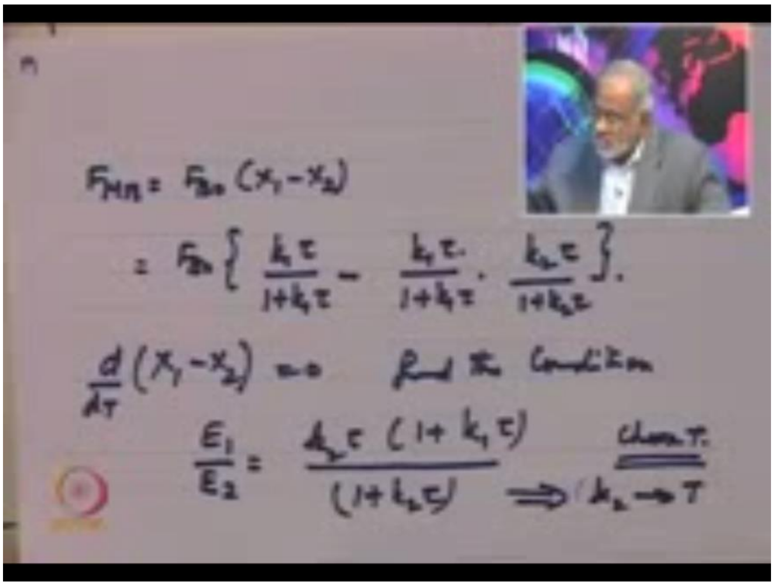

$$F_{MB} = F_{B0}(X_1 - X_2)$$

$$= F_{B0}\left\{ \frac{k_1\tau}{1+k_1\tau} - \frac{k_1\tau}{1+k_1\tau} \cdot \frac{k_2\tau}{1+k_2\tau} \right\}.$$

$$\frac{d}{dT}(X_1 - X_2) = 0 \quad \text{find the condition}$$

$$\frac{E_1}{E_2} = \frac{k_2\tau\,(1+k_1\tau)}{(1+k_2\tau)} \Rightarrow \underline{\underline{\text{choose } T.}} \quad k_2 \to T$$

So, monochlorobenzene F M B equal to F B 0 times X 1 minus of X 2 or that is equal to F B 0 multiplied by K 1 tau divided by 1 plus K 1 tau minus K 1 tau divided by 1 plus K 1 tau K 2 tau divided by 1 plus K 2 tau. Now, we have to differentiate this that means this we want maximize this means we need d by d T of X 1 minus of X 2. And we have to said this equal to 0 and find the condition under which under which this difference goes to a maximum from very fundamental as well. We should recognize that as benzene goes to monochlorobenzene monochloro goes to dichlorobenzene.

So, therefore, this intermediate there would be conditions under which this intermediate would be maximized. And our interest is always to find conditions so that our product of our interest is as high as possible that is our interests. Therefore, we like to see what is the temperature at which this X 1 minus of X 2 goes throw a maximum? Now, it is not very difficult to do this differentiation. You know it is not messy, but there is some algebra involved etcetera. Therefore, I prefer this condition it is not difficult show this that this condition becomes that this is the condition under which you will find that this is goes to maximum.

What are we saying? That the maximum value of X 1 minus of X 2 are monochlorobenzene attained when you choose your temperature of operation you have to choose T temperature operation. So, that E 1 see E 1 and E 2 are the activation energy of the reactions 1 and 2 or well documentary. What is not clear from here is the, what is the temperature which sort of when these equality becomes applicable. So, that we have to put the numbers or K 1 K 2 this is everything and then that will give a value of K 2 and once value of K 2 is known suppose this particular equation uses K 2.

And then from that you can find the temperature once you know K 2 then you can find temperature corresponding to that K 2, because E 1 and E 2 are the activation energies are no. So, what are we saying? What we are saying is that if you have a reaction taking place in a stirred tank If it is a series reaction there is a choice of temperature at which this the desired product goes to the has a maximum it takes highest value. So, this temperature T tells you the conditions under which the intermediate which is monochlorobenzene goes to a maxima. The next question of course, is that how do you achieve this which means.

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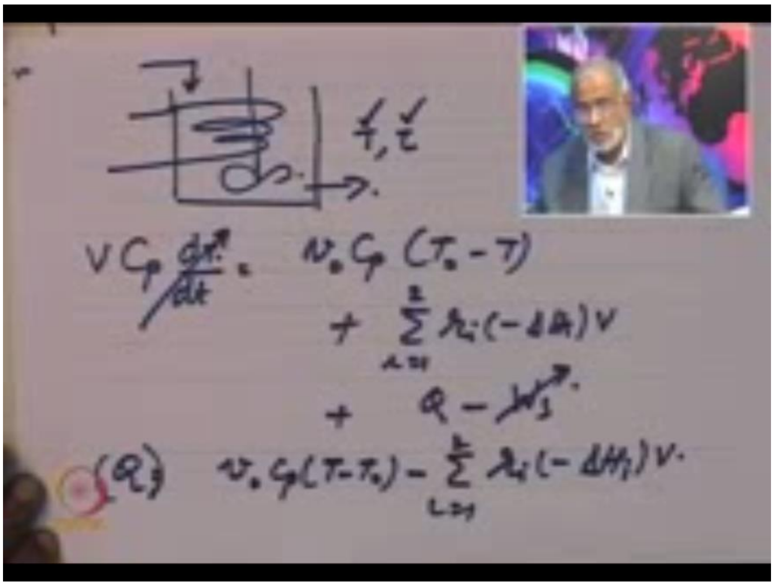

$$V C_p \cancel{\frac{dT}{dt}} = v_0 C_p (T_0 - T) + \sum_{i=1}^{2} r_i (-\Delta H_i) V + Q - \cancel{W_s}$$

$$(Q) \quad v_0 C_p (T - T_0) - \sum_{i=1}^{2} r_i (-\Delta H_i) V$$

What is the question is that you have found from this from our calculations and so on. And that that you know you have to operate this at some temperature T at some residence time tau. Now, given this temperature T and residence time tau, how do you ensure that you know all these are possible that we come by looking at the energy balance. So, this is the heat generation plus q minus of w of course, there is no work done. So, what we are saying is that if it is at steady state. Then the heat taken up by the fluids this coming in and going out.

So, this is the heat generation so you must supply so much of heat so heats heat to be supplied simply what v naught C P T minus T naught minus sigma I equal to 1 to 2 r I times minus of delta H i star V. So, what we are saying then is that for a for a series reaction like ours once you if you want to choose a temperature choose a residence time. Then you will have to adjust you will have to ensure the, this amount of heat can be added or removed so, that you can get the conditions of your choice. So, this is what is been said keeping in mind they require means of the process.

So, just to sort of summarize what you are trying to say here is that there are several new considerations of energy balance that we must barren mind. So, what we are try to do is that we have try to write the energy balance and then try to see carefully the right hand side of the energy balance to see how we can make better use of of the available facilities to reach our requirements. So, we considered case 1 in which reaction was instantaneous we said if it is an instantaneous reaction then the, compose the extent of reaction is govern by equilibrium. And therefore, you can use that condition to eliminate the reaction rate functions from the equation.

And therefore, we get answers which we can handle and quite comfortably. The second case you considered was that case in which the reactions are reversible, but they are not instantaneous in such situations. What we said is that it could so happen that the heat additions is at a rate or heat removal as at a rate which is so small compare to the reaction rates. Therefore, the reaction just does not move it only moves to the extent that you are able to supply or remove heat this is the second case at we considered.

The third case we considered here is that the stirred tank in which you have a very very rapid reaction occurring where K 1 and K 2 are very large, but these are irreversible reactions and the case you have considered. So, how did we handle? That we handle that by recognizing that our material balance equation, we can eliminate one of the rate functions rate constants. So, that we can solve that the find out the values of residence time multiplied by rate constant K 1 tau or K 2 tau which is able to give us the final result of our interest. So, these are the three cases we considered by which we are able to better in get better sides in to the energy balance. So we will consider one more exercise.

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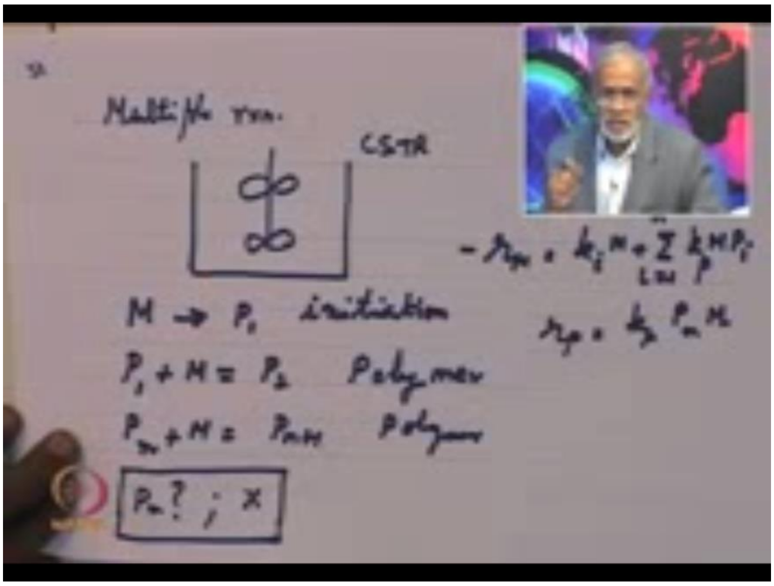

Multiple rxn.

CSTR

$M \rightarrow P_1$ initiation

$P_1 + M = P_2$ Polymer

$P_n + M = P_{n+1}$ Polymer

$\boxed{P_n ? ; x}$

$-r_m = k_i M + \sum_{i=1}^{n} k_p M P_i$

$r_p = k_p P_n M$

This is a multiple reaction what is this reaction? Let me just explain you have a stirred tank. You have a stirred tank that is this reaction M going to P 1 this is called initiates the formulation initiation. Now, P P 1 reacts with M give you P 2 this is a polymer P n reacts with M. It will give you P n plus 1 this is also polymer r m which is the rate of formation of this is k i m plus sigma I equal to 1 to n k p M P I. This is the rate at which monomer is consumed and then the rate of production of polymer r P is given as k p P N M rate of production.

So, we are our job here is to set up equations that will tell us how the reaction will move forward. That means basically it has set of equations that will tell us what is P n and then what is x and so on. So, we want to find out based on our material balances what will be the amount of polymer that is formed at any instants of time and so on. So, let us write all the equations so that you know we can answer many questions not just. Now, the context once again that is not forget the context the context is that when you look at polymerization. Because polymers are very long molecules they have petty viscous.

And of course, we can handle viscous in fluke flow devices through appropriate mechanism, but it is easier to handle very viscous fluids when you have as starrer. If you have stirrer you can this stirring itself takes care of you know many of these are shear thinning in the sense. When you start sharing it that is call steel comes down much easier to conduct the reaction when it is under stirring so a stirred tank or C S T R for a polymerization reaction it is a convenient. And plus we can set up equations for P n and find out conditions under which P n goes to the highest value. So, when we do get the highest value for P n also we can find out through our equations. So, let us try to do one by one.

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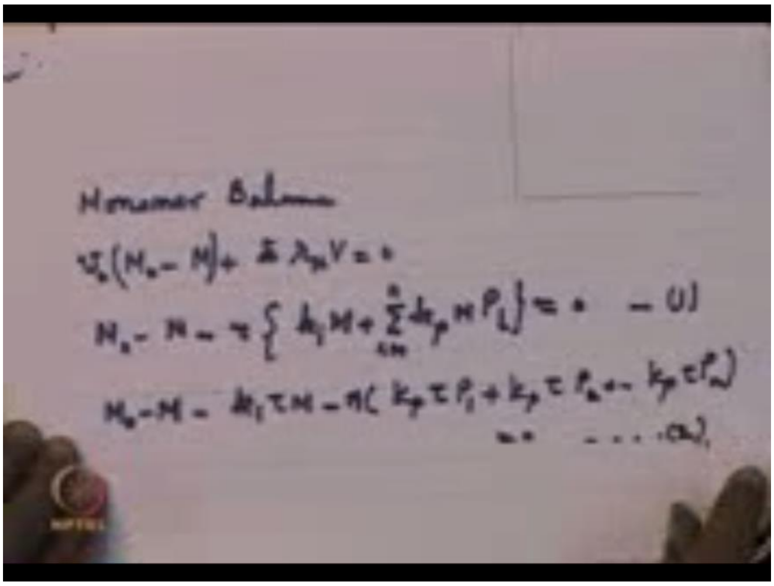

Monomer Balance

$v_0(M_0 - M) + \Sigma R_M V = 0$

$M_0 - M - \tau\{k_i M + \sum_{i=1}^{n} k_p M P_i\} = 0 \quad -(1)$

$M_0 - M - k_i \tau M - M(k_p \tau P_1 + k_p \tau P_2 + \ldots k_p \tau P_n) = 0 \quad \ldots(2)$

Let me write a monomer balance, what is a monomer balance? You have input; you have output plus you have monomer. Now which can also be written as in this form that is minus tau k i m plus sigma k p M P I equal to 0. Now, is this clear? I divided throughout by volume. Therefore, it becomes solids it should be so v naught only when we divide throughout by volume it becomes tau. So, I will call this is equation 1 what is it saying that monomer input monomer output residence tank k i is the initiation rate constant multiplied monomer concentration.

And these are the all the polymerization reactions k p multiplied by M it is takes care of the i-th monomer multiplied by M and so on. So, let me simplify this where it becomes m naught just help me M minus k i tau M. First term is taken minus within bracket k p tau P 1 plus k p tau P 2 k p tau P n multiplied by M equal to 0. So, this is this some equation 1 or 2 or whatever so we have write the monomer balance we write one of the polymer balance so, that we can do all these simplifications. So let us write balance for P 1.

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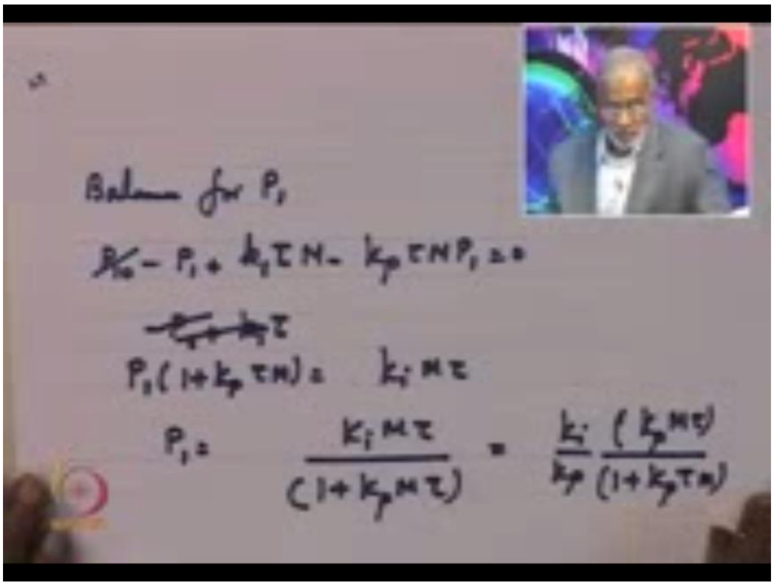

Balance for P_1

$\cancel{P_{10}} - P_1 + k_i \tau M - k_p \tau M P_1 = 0$

$\cancel{P_1 + k_i \tau}$

$P_1 (1 + k_p \tau M) = k_i M \tau$

$$P_1 = \frac{k_i M \tau}{(1 + k_p M \tau)} = \frac{k_i}{k_p} \frac{(k_p M \tau)}{(1 + k_p \tau M)}$$

So, you have P 1 P 1 0 is not there P 1 plus k i tau m minus of k p tau n P 1 equal to 0 I hope this is clear. So, this takes care of P 1 plus k i tau minus of so we just what a simplify and write. So, P 1 multiplied by 1 plus k p tau m equal to k i M tau this is correct P 1 multiplied by 1 plus k p tau m into P 1. So, you have taken to the other side fine very good or P 1 is simply k i M tau divided by 1 plus k p M tau. This is also can written as k i by k p within brackets of k p M tau divided by 1 plus k p tau m. They have done nothing very new here please this is very elementary material balance only clubbed terms containing P 1 together. And then k i then adjust divider and multiplied by k p nothing very fancy has been done. So this is P 1 now the idea of putting in this form we will soon see why it is useful let me write for a polymer P 2.

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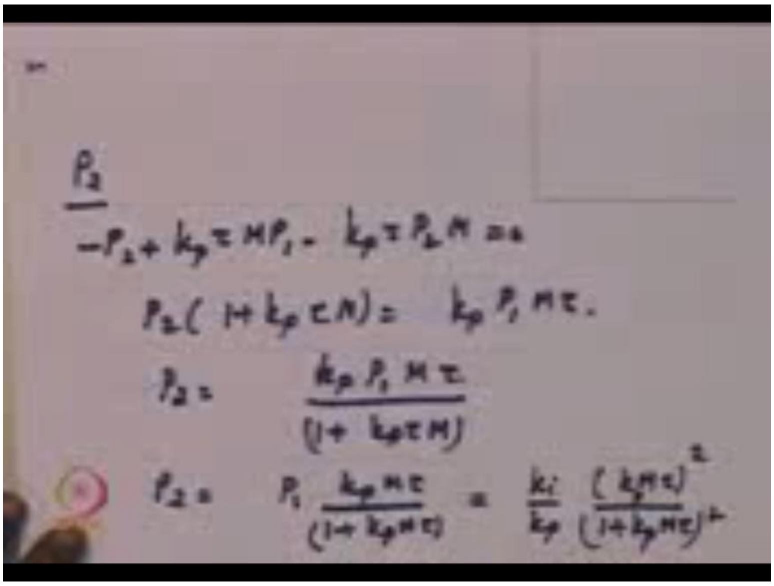

$\underline{P_2}$

$$-P_2 + k_p \tau M P_1 - k_p \tau P_2 M = 0$$

$$P_2(1 + k_p \tau M) = k_p P_1 M \tau.$$

$$P_2 = \frac{k_p P_1 M \tau}{(1 + k_p \tau M)}$$

$$P_2 = P_1 \frac{k_p M \tau}{(1 + k_p M \tau)} = \frac{k_i}{k_p} \frac{(k_p M \tau)^2}{(1 + k_p M \tau)^2}$$

So, we have want to P 2 so what is P 2 plus k p tau m P 1 minus k p tau P 2 m equal to 0 therefore, M P 2 multiplied by 1 plus k p tau m equal to k p P 1 M tau. Therefore, P 2 equal to k p P 1 M tau divided by 1 plus k p tau M. I am not doing anything new here pleas just elementary material balances for a stirred tank. So, that P 2 becomes P 1 k p M tau divided by 1 plus k p M tau this is all right. This notice here P 1 and P 2 are related by similarly, we can write in our, for others. So, we write this, this is also we can substitute for P 1 from here. So, we can write this as k i by k p you can see here. So, this is becomes k i by k p within brackets of k p M tau whole square divided by 1 plus k p M tau whole square. So k i by k p k p M tau 1 plus k p M tau P 1 for P 2 it is squared. Therefore, we can write for P n the object of sort of doing in this form is only show that is. So, you want to look at P n.

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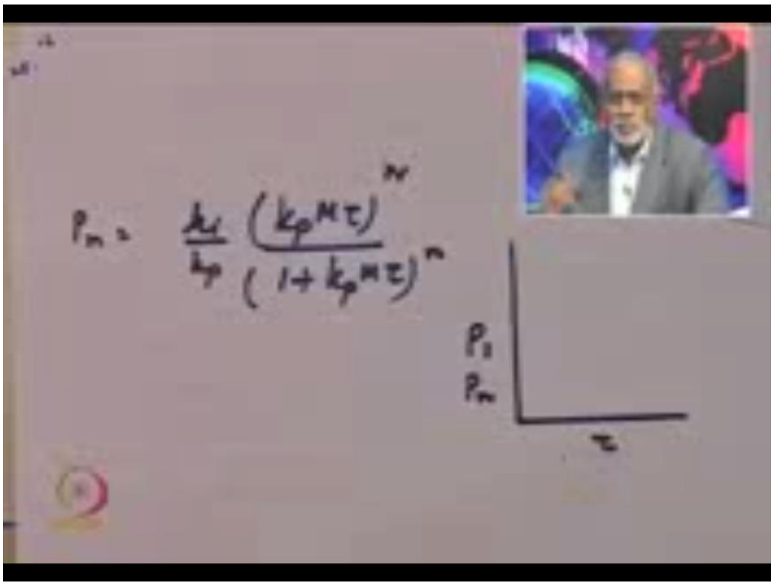

$$P_n = \frac{k_i}{k_p}\frac{(k_p M \tau)^n}{(1+k_p M \tau)^n}$$

P n becomes k i by k p k p M tau to the power of n do the 1 plus k p M tau to the power of n. So, this is the idea of showing it in this form therefore, the n-th polymer which is given by this equation. Now, let us just we just try to understand what I am saying are try to understand this. What we are trying to say here is that in a stirred tank polymer 1, polymer 2, polymer 3 polymer n. All of them depend on k i by k p multiplied by this term k p M tau divided by 1 plus k p M tau k p is formulation reaction rate constant, M is the concentration of monomer and tau is the residence time. So, in a sense that we can plot these functions we can plot these functions so P 1 versus tau P 1 similarly, we can plot for P 2 P n and so on. And we can actually choose the residence time so which is appropriate to our interest.

So, essentially what we are trying to say is that we are able to know adjust the conditions of the stirred tank. So, that our product of interest is maximized I think this is the point that is and stirred tank gives you an advantage that you can stir and maintain at good level of shear. So, that the processing can be continued number 1 2 it also ensures the good heat transfer so that whatever heat is to be added or removed becomes facilitated. So, two important features that are so crucial to success of a process stirred tank is able to achieve for you that is where our big interest comes. Now, the illustrates if all is straight forward, but just to for the sake of completeness I will just write the final form it is very easily shown that.

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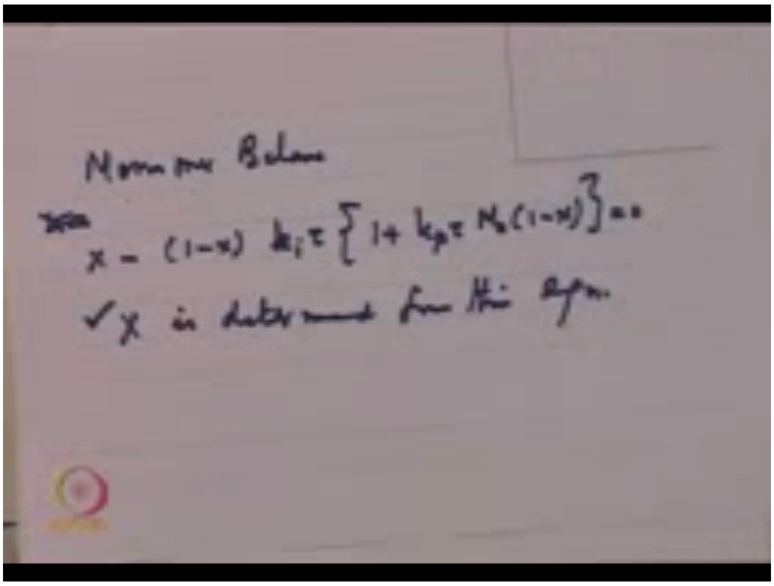

Monomer Balance

$$x - (1-x)\, k_i \tau \left\{ 1 + k_p \tau M_0 (1-x) \right\} = 0$$

✓ x is determined from this eqn.

The extent of reaction x is we can show this I will not show this minus of 1 minus of x times k i tau within brackets 1 plus k p tau M naught into 1 minus of x equal to 0. Or in other words you can determine x that means x is determined from this equation. So, this is the monomer balance so, what we are saying is that we are able to determine. What is the, what is over all conversion we are able to determine what is the amount of different products which are found? And therefore, you can now decide how best to make good use of your monomer in relation to the polymer that you are forming. So, just look at this long stories short what we are said is that this is whole idea, the whole idea of looking at energy balance from the point of view of trying. I have seeds new features we have looked at 3 or 4 new features all of it tells you how the energy balance equations able to appropriately take care of the processes that we are interested in carrying not.

Thank you.