Lecture - 19
Energy Balance 4: Temperature Effects on Rate and Equilibria

We get started today. We are looking at temperature effects on rate and equilibria in this lecture.

(Refer Slide Time: 00:30)

Now, temperature effects; we try to put together by looking at the Vant Hoff's equation, a celebrated equation d l n K by d T is delta H by r T square. Now, K is the equilibrium constant; T is temperature in Kelvin; delta H is heat of reaction and r is the gas constant. Now, if delta H is not a strong function of temperature, in which case, we can integrate equation 1, and then get this relationship; l n k by K 2 98 is given by minus of delta H by r, multiplied by this term.

Now, how good is the assumption, the delta H is not a strong function of temperature. In many cases, this is not such a bad assumption. The change is in delta H due to temperatures are not very serious. So, it is not such a bad assumption. So, we can use this relationship to find out if you know K at a given temperature. You can find out K at any other temperature using this relationship. Delta H is heat of reaction. Now, we also know from our basic thermodynamics, that r t l n K is minus of delta G, which is this standard

heat of free energy of formation. So, these also another relationship we might use, if you are know the standard heat of free energy of formation; you can find K at accurate temperature. So, that is how K 298 comes, and you can get the value of K at any other temperature using this relationship.

Now, let us see what it means from the point of view of our application to various situations. If delta h is positive, which means what? It is an endothermic reaction; therefore, what do we expect as temperature rises; suppose, our temperature is more than 298, what happens to this term? This term is negative and term outside, is also negative. So, what it means? The whole term is positive, implying that l n K by l n 298 is positive. So, K at any other temperature, greater than 298 is much greater than K 298, showing that equilibrium constant for an endothermic reaction keeps on increasing with temperature; a relationship that we all know from our basic understanding of thermodynamics.

Now, if delta H is negative, which is an exothermic reaction. The opposite is the kind of relationship, you will get; l n K by l n 298. Now, this becomes negative, correct. So, for an exothermic reaction, you will find that the right hand side term is negative, and therefore, value of K at temperature greater than 298 is less than value of K at 298, showing that equilibrium constant for an exothermic reaction keeps decreasing with temperature, as with increased temperature; once again, something that we all know from our basic thermodynamics. With this, let us just look at one example to understand what we are trying to say.
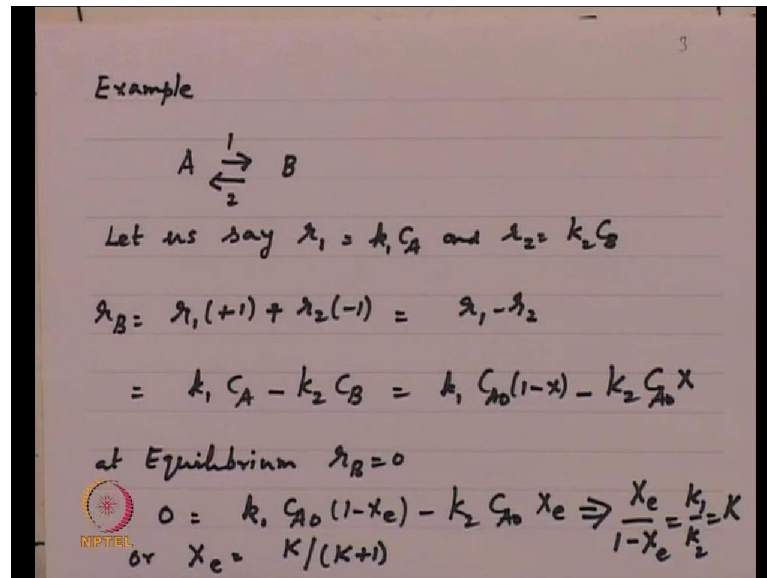
Let us take an example, simple case of A going to B where, we say that it is a first order representation for r 1 and r 2. There too, are forward and backward reactions; therefore, the rate of formation of B; we write it as k 1 C a minus of k 2 C b and in terms of conversion, it is written as k 1 times a 0, 1 minus of x and minus of k 2 c 0 x, and at equilibrium, of course, the r b is 0. Therefore, the equilibrium conversion is simply k by k plus 1; something that we also know from our basics.
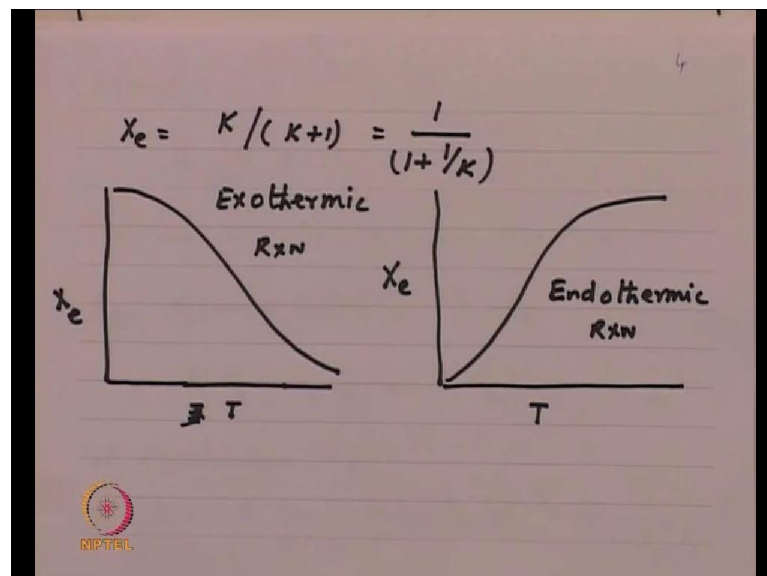
Now, if you make a plot of the equilibrium conversion versus, temperature; it look something like this. Why it looks; for the case, this is the exothermic; this is endothermic. So, we can easily understand here, as k increases, if it is an endothermic reaction, k keeps on increasing; therefore, the denominator, what happens is the denominator x e; what happens? Denominator x e keeps on decreasing; therefore, x keeps on increasing. So, you will expect that x keeps on increasing with temperature for an endothermic reaction; x keeps on decreasing with temperature for an exothermic reaction. So, the equilibrium conversion keeps deceasing; for endothermic, keeps increasing. Let us go forward.

(Refer Slide Time: 04:42)
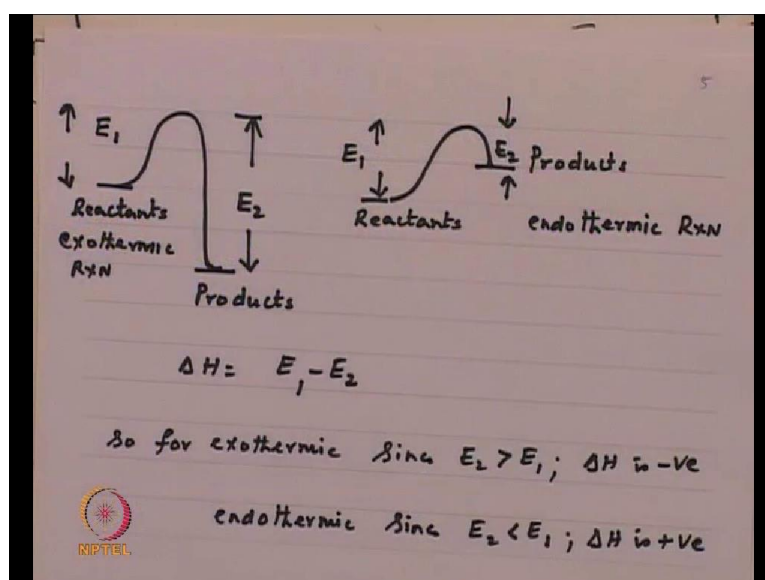
Let us look at how, see for an exothermic reaction as you can see here, that the reactants and products; products are at the lower energy than reactants; therefore, E 1 minus E 2, which is delta H; since, E 2 is greater than E 1, delta H is negative, which is what we know. Exothermic reactions; delta H is negative. For endothermic reaction, the products are at higher energy than reactants; therefore, E 1 minus E 2 is positive, because delta H is positive. So, we can use all these relationships to understand our rate function r b; what happens in the case of an exothermic reaction and an endothermic reaction. Let us look at that now.
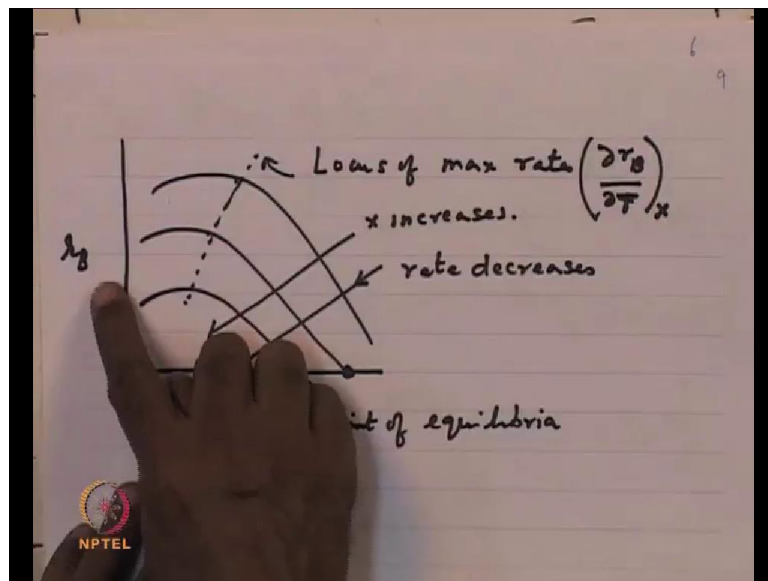
(Refer Slide Time: 05:16)

So, if a rate function r b is k 1 C a minus of k 2 C b, then we represent them in terms of the <mark>(( ))</mark> dependence k 1 0 E. So, power of minus E 1 by r t and so on. So, this function, which can be we put in this form; I have just taken k 2 0 outside; it can be put in this form where, the left hand side, outside the bracket is essentially, rate constant k 2 and inside, is the effects of conversion and so on. If you look at this term for the case of an endothermic reaction, what happens to an endothermic reaction in this case? For an endothermic reaction, this r b is equal to; for an endothermic reaction, delta H is positive; therefore, this term inside as temperature rises, what do we see, the term inside?

For an endothermic reaction, delta H is positive. As temperature increases, what happens to the term inside? It increases the temperature, and this is the rate constant. As temperature rises, rate constant increases the temperature. Therefore, you have for the case of an endothermic reaction, the term outside the bracket increases the temperature. Term inside the bracket also, increases the temperature, showing that the rate of chemical reaction keeps on increasing, as you increase temperature. This is for an endothermic reaction. Also stands to reason; we should expect that. It is endothermic; the higher the temperature, better it is. So, that is what we see for the case of an endothermic reaction.

Suppose we look at the case of an exothermic reaction. The term outside bracket, as you increase temperature, you find that the rate constant keeps on increasing, but the term inside the bracket, what we find is that as delta H, as temperature increases; delta H is

negative; therefore, this whole thing is positive. Therefore, as temperature rises, this whole term decreases. So, for an exothermic reaction, we find the term inside bracket decreases; term outside bracket increases, showing that there is a maxima. In other words, what we trying to say is that exothermic reversible reactions; you see a maxima in reaction rate. You do not see any maxima in reaction theory, if it is in endothermic reaction. So, this is what we are trying to say by looking at this rate function.

(Refer Slide Time: 07:35)

Suppose you make a plot of rate of chemical reaction.

(Refer Slide Time: 07:37)
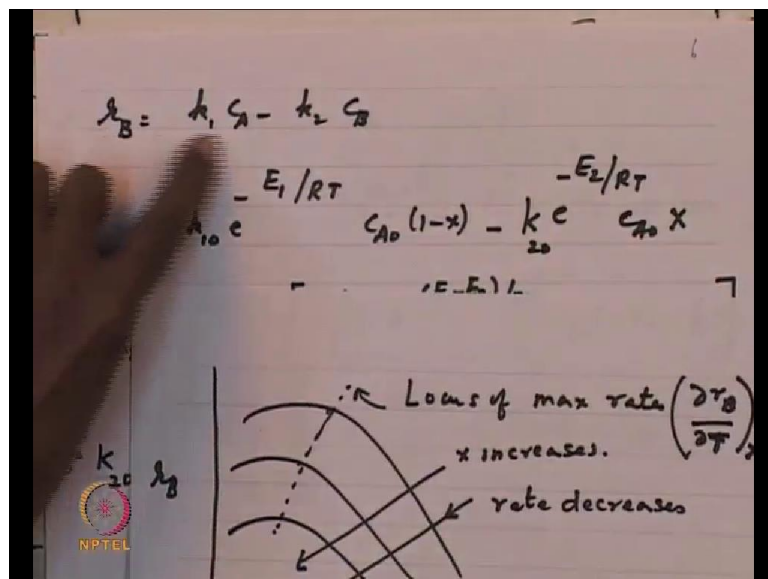
This is the rate function; r b is this. Suppose you make a plot of rate of chemical reaction versus, temperature, what we would expect to see for an exothermic reaction is that it keeps on going up, and then comes down going up and comes. So, you will see there is a point at which, the reaction rate becomes maximum. When you plot this, you will see functions like this.

(Refer Slide Time: 08:00)
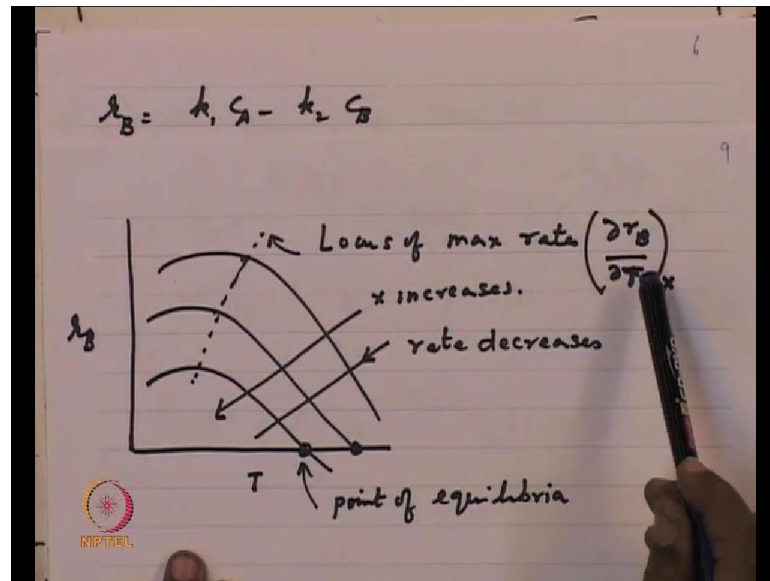
On other words, this dotted line is the locus of maxima in reaction rate. Our interest is to find out what is the equation to this locus, if we can find out, if the rate expressions are very nice, we can find the equation to the locus. In some cases, you may not be able to find an expression for the equation to the locus, in which case, we will do it graphically. In other words, this curve can be determined either, graphically or mathematically, in both cases. So, our interest in understanding this function is that we would like to have our designs, running around this locus of maximum reaction rate, because that is when, the reaction rates are the highest. So, you would like to see there, our systems operate as close to the maxima in reaction rates as possible. Also, you notice here, this I have shown here; graphs of r b versus, T and as you can see here, as x increases; if you look at this function, this is the rate function here.
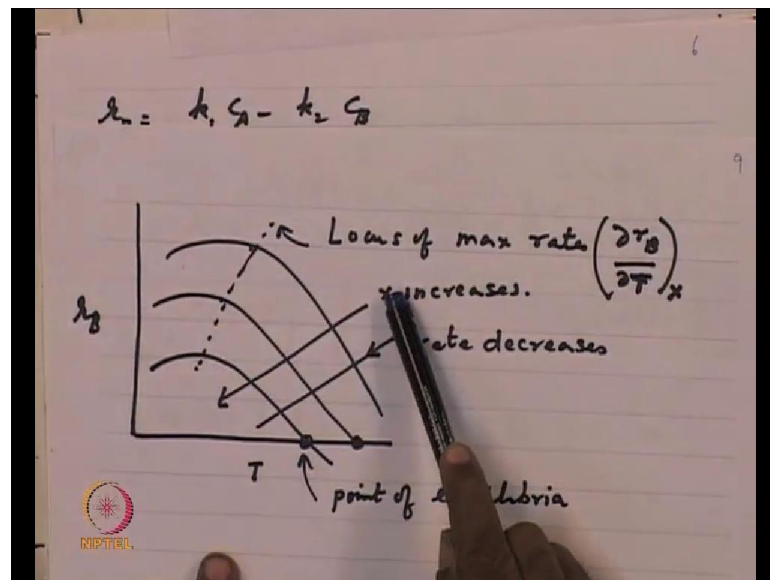
(Refer Slide Time: 08:54)

So, what happens; as x increases, this term decreases, correct. So, what do you except to see; why I have shown here?

(Refer Slide Time: 09:05)

I have shown here, as x increases, we are moving in this direction. What it means? As x increases, the magnitude of the reaction rate keeps on decreasing, which is also understandable, because you are approaching equilibrium. So, as x increases, these lines go inwards; you understand what I am saying. As x increases, this term, what I am saying is that as x increases, these two terms have the effect of these terms that you move

inwards, because you are moving towards the equilibria. Therefore, the net reaction rates are smaller and smaller. Therefore, rate is decreasing in this direction, as x; that is what we are saying.

(Refer Slide Time: 09:58)

So, our interest is to find out what is the equation to this locus? How do you determine the equation to the locus? As for something, that we have done before is that you simply, look at that function, and see where the maxima lies. So, we take the first derivative of this del r b by del T is constant x; that means, you are looking at what happens to r b at constant x. So, we can differentiate this, and then said it equal to 0; I term this x is x m; that means, the equation to locus of x versus T is given by this equation, 1 minus x m by x m is k by k E 1 by E 2. This is for the case of a first order reaction, which is reversible. So, if these rate functions are more complicated, it will not be such nice functions, but whatever, that may be; you will able to determine that function and plot that function.
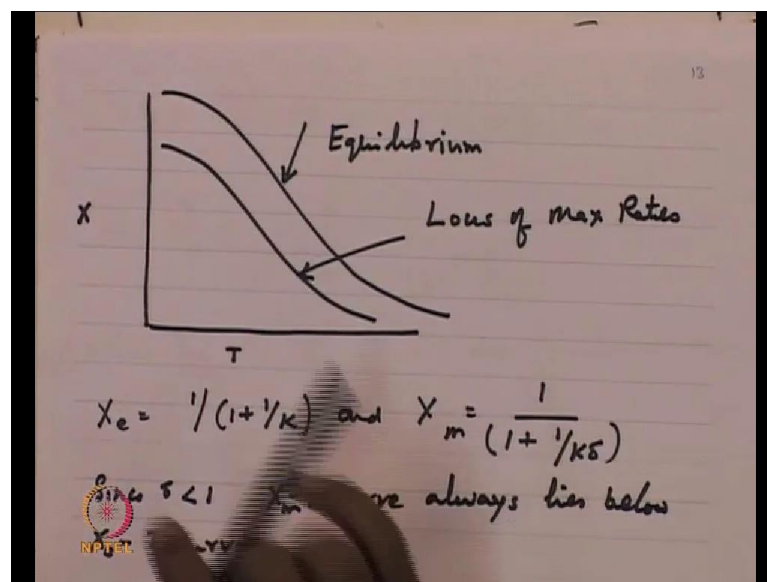
(Refer Slide Time: 10:42)

So, we can put it in this form that x m is given by k delta; I have got delta is E 1 by E 2. Notice here, E 1 by E 2 is less than 1; therefore, x m equal to k delta by 1 plus k delta or x m equal to 1 by 1 plus 1 by k delta; this whole term is what x m is all about.

(Refer Slide Time: 11:00)

So, when we make a plot of x e versus T, and then x m versus T, you notice here, that x m always, lies below the equilibrium curve. Why is it? You can look at this function here. You can say that since, delta is less than 1, x m we will have to lie below the x e curve. So, you have an equilibrium curve; you have the locus of maximum reaction rate

curve and therefore, you have all the information that is required for you to look at various design alternatives, that might be available to you. What is that we have done? If you have an exothermic reversible reaction, there is something called a maxima in reaction rate curve; there is something called the equilibrium curve, and we have to operate around these regions, and therefore, we look for strategies that will give us an appropriately, good design.

(Refer Slide Time: 12:00)

Let us say we are looking at a CSTR as a possible strategy for our operation. Let us look at one example, operating on the locus of maximum reaction rates; CSTR is in our mind. What is a CSTR? CSTR operates at a given temperature or in other words, the advantage is that you can operate at whatever, temperature you want.
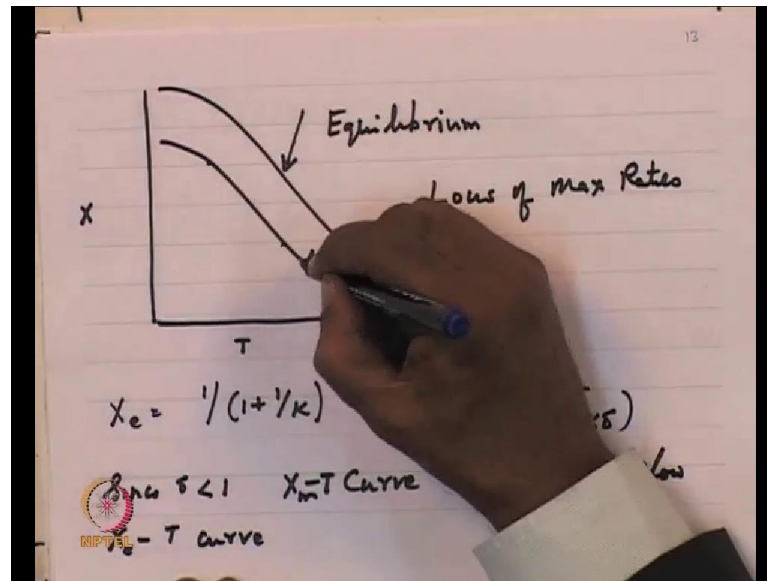
It can be here; it can be here; it can be here; whichever temperature at which, you want, you can operate. Let us say you want to operate at the highest, I mean, highest conversion. Let us say you want this; I call this as 0.8. Suppose you want to get 0.8 conversion in one go, or in other words, you want to get 0.8 in one go; therefore, you will choose this temperature of operation. Suppose you want a conversion of 0.2 at the maximum reaction rate, you will use this temperature of operation. On other words, CSTR is a device, which permits you to operate at the maxima in reaction rate curve. You can choose that point and run your process at that point. Then, question is how do you make it happen.

(Refer Slide Time: 13:02)

Operating on the Locus of Max Rates (CSTR)
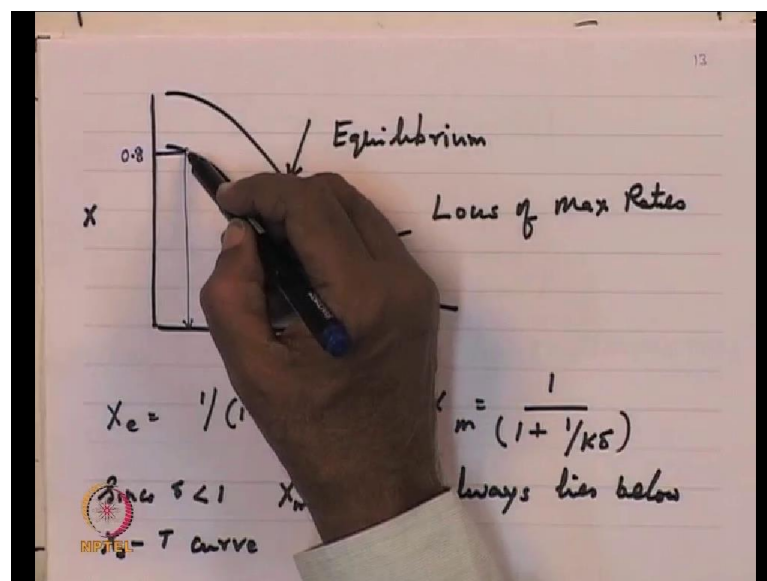single independent Rxn + at steady state
Design Eqn:

$$\frac{F_{A_0} X}{-r_A} = V \qquad -(1)$$

$$V C_p \frac{dT}{dt} = v_0 C_p (T_0 - T) + \sum_{i=1}^{p=1} (r_i \cdot \overset{?}{V})(-\Delta H_i^*)$$

$$+ Q - W_s \qquad -(2)$$

$$\frac{X_m}{1-X_m} = \frac{K \delta}{1 + K \delta} \qquad \left(\text{where } \delta = \frac{E_1}{E_2}\right) \quad ..(3)$$

You make it happen by recognizing that you have a material balance equation; you have an energy balance equation; you have a constraint, which is defined by the maxima in reaction rate curve. We have three equations and depending upon the number of variables, which is specified, you have to choose the variable, which is not specified, which is consistent with these three equations. Then, you will be able to operate on the maxima in reaction rate curve. So, most important point; we must recognize is that CSTR is the device, which permits you to operate on the maxima in reaction rate curve.

(Refer Slide Time: 13:41)

Equilibrium

Locus of Max Rates

$$X_e = 1/(1$$

$$_m = \frac{1}{(1 + 1/K\delta)}$$

always lies below

Since $\delta < 1$ X_m

— T curve

The second point, which is also important is that suppose, you want a very high conversion; 0.8, 0.8, whatever, 0.95 of the equilibria. So, you will be operating at somewhere here, which means, you will choose this temperature. This temperature can be very low. The reason is exothermic reversible reactions; if you want to get higher and higher conversions, your equilibrium constant will tell you the ratio to go to very low temperatures, and therefore, that reactor operates at a very low temperature. Therefore, your reaction rates are very low. So, you are looking at a huge device; a device, which is very large in size. Even though, you can do it in one stage, but you might find an equipment, which is so large; it is not satisfactory from an economic point of view. Therefore, you will often have to go through what is called as an optimization to get a proper size for which, you will choose stage 1 here; stage 2 here; stage 3 here; stage 4 here.

(Refer Slide Time: 14:38)
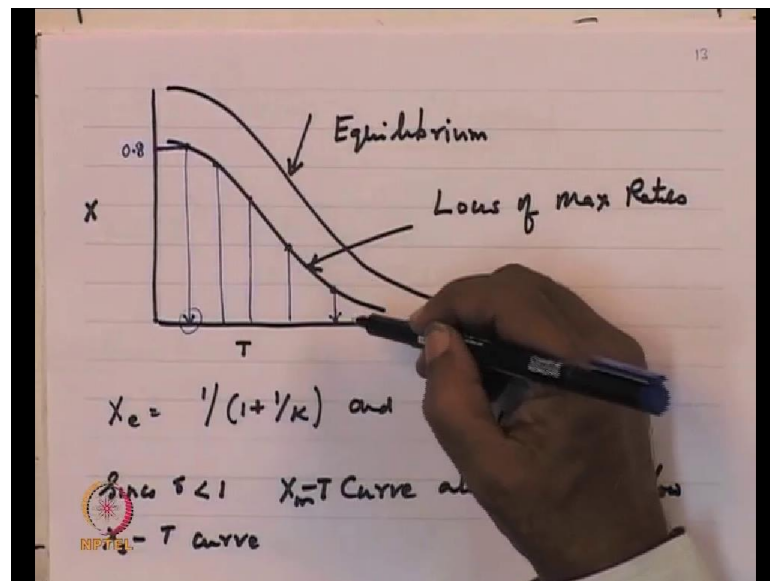
In other words, you will operate 1, 2, 3, 4, 5, 6 number of stages. At each stage, the temperature of operation is as per the maxima in reaction rate curve.

For each of these stages, the heat load that you must add or remove will be specified by these three equations; 1, 2, 3. So, having chosen the temperature from here, this defines x m; this defines conversion, sorry, resistance time and this will define the heat load. You can see here. If I specify temperature, it will tell you what is the conversion at which, you should operate. The moment you know conversion, I can determine the resistance time from here. The moment you know resistance time, I can determine from here, the heat load to be added or removed. In other words, for every choice of temperature, the equations 1, 2 and 3 will specify the conditions under which, you should operate your process. So, 1, 2 and 3 tells you how to make sure that you get what you want. We also recognize that an optimal choice is a choice of decreasing temperature.

(Refer Slide Time: 15:57)
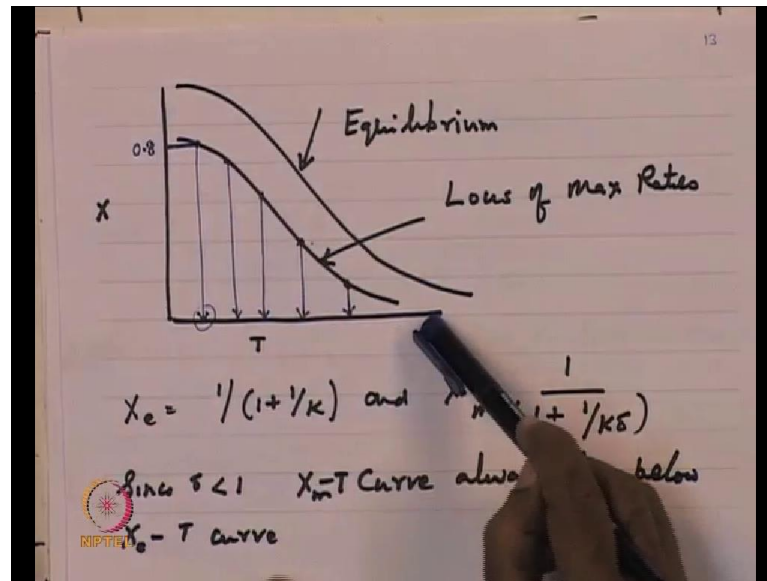
Exothermic reversible reaction; the optimal choice is a choice of decreasing temperatures, and therefore, a choice of decreasing reaction rates. Therefore, larger and larger equipment; this is what this curve tells you. Yes, number of CSTRs; stage 1, stage 2, stage 3, stage 4, stage 5. Instead, you can do this; go up to 0.8 or 0.9 of the equilibria in one stage, but the reaction rates are very low, because of the fact that you are operating at such a low temperature. Yes, size; see, if you are going to operate with conversion at 0.8, what it means is that the actual concentrations are very low, and to get along this maxima in reaction rate curve, you will choose a temperature as per this curve, and that will turn out to be a very low temperature, compared to higher conversions. So, this temperature being very low; reaction rates are very low; low temperature; low reaction rates and therefore, the equipment sizes are very large. Instead, if you operate a multistage; stage 1 at this temperature; stage 2 at this temperature; stage 3 say, you will find that the net size of that equipment will be much in superior, compared to a single stage operating at 0.8.

So, what we are trying to say is that a multistage CSTR design; the optimal design will be a design of decreasing temperatures, chosen along the maxima in reaction rate curve. The fact that the temperatures are decreasing, the reaction rates are decreasing; therefore, the sizes are necessarily large. Suppose, instead, we have a multistage PFR.

A question is often asked; why a multistage PFR when you can as well, operate a multistage CSTR along the locus of maximum reaction rates? We will try to address this question as we go along. Once again, we have our reaction, A goes to B. You have a design equation; this is for the design equation of a PFR which, we have p c p d t d v r 1 minus of r 2, times delta H 1 star q. Let us, for the moment, think that it is an adiabatic, so that, we remove this term and these two terms. So, that we have only an adiabatic process. This is the material balance, F a 0 d x d v, r 1 minus of r 2. There are two equations, dividing one by the other.

You get a relationship, which tells us that the temperature variation; this is the temperature variation in our process v c p F a 0 divided d t d x minus of delta H. Now, if in this particular case, for example, A goes to B; the volume change due to reaction is not there, but there could be change in temperature. As a result of which, volumes may change. Suppose for example, we assume that volume does not change, as an example. Then, v becomes v naught; therefore, this term becomes v naught by F a 0 is C a 0. Therefore, you will find C a 0, multiplied by delta H. This is how I have written it in the next page.

(Refer Slide Time: 18:36)


See therefore, d t d x becomes C a 0 times j, which is a constant. Therefore, d t d x becomes a constant, times C a 0. What we are saying is that if you have a reaction, A goes to B; you conduct this reaction adiabatically, in a PFR; if v equal to v naught is a satisfactory assumption, then d t d x becomes a constant, which is C a 0 times j. What is j; j is heat of reaction, divided by volumetric specific heat; it is a known quantity. A constant d t d x means what? If you make a plot of T versus x, it will be a straight line. So, when you make a plot, let us just do that.

(Refer Slide Time: 19:23)
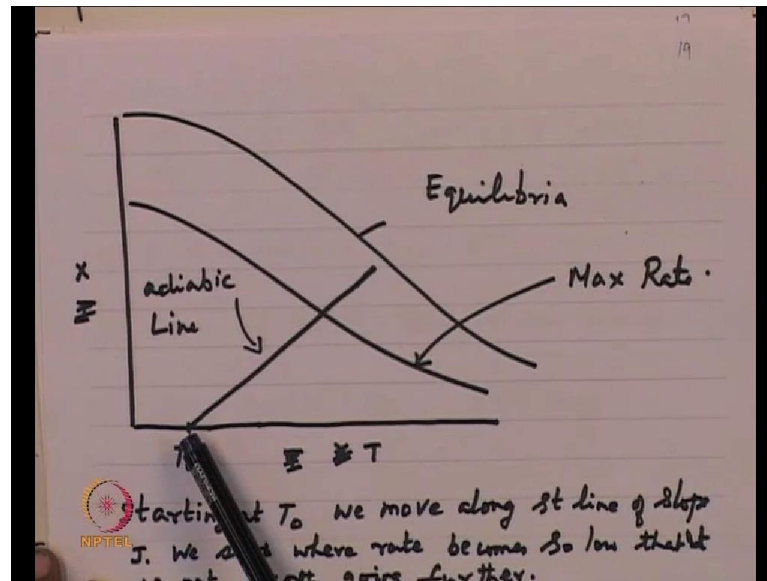
When you make a plot of x versus T, if you are starting at T 0, then this is a straight line. It can go up to the equilibrium curve. We go, you can go up to equilibrium curve. As you are moving along this curve, what do you expect? The temperature is increasing; conversion is increasing. At this point, the reaction rate has reached a maxima, and as you move from this point towards the equilibrium curve, the reaction rates are decreasing. On other words, from point T 0 as move towards, reaction rates are increasing up to this point and it is decreasing. Now, if you are doing a design of a single stage, of course, you will find, because of the fact that it is a reversible reaction; you are able to reach only up to this point. Say sulfur dioxide for example or ammonia for example, or instances where, the reactions are reversible; therefore, in one stage, you are not able to push the reaction to its completion. So, the question is what is it that you do? So, what people do is that they cool this, and run another stage. They will cool this.

(Refer Slide Time: 20:26)
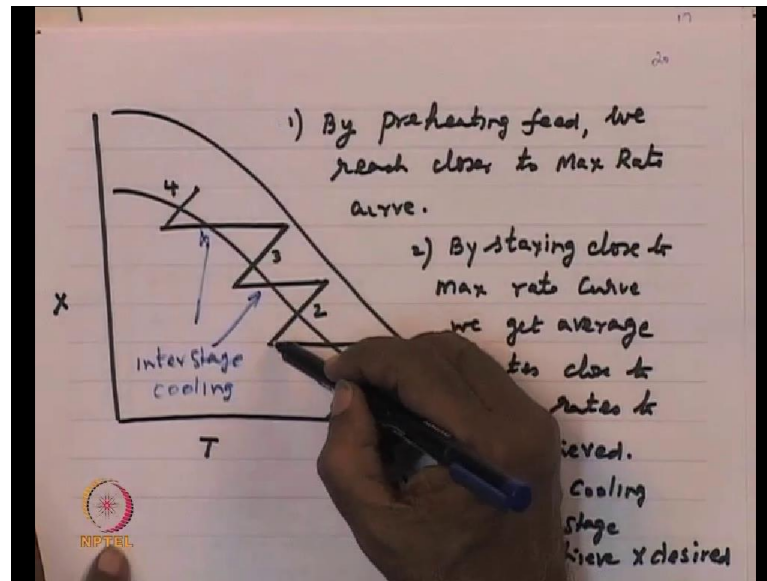
So, if you are starting from here, they will cool, run another stage, run another still, you are able to get the extent of reaction that you expect. Why multistage?
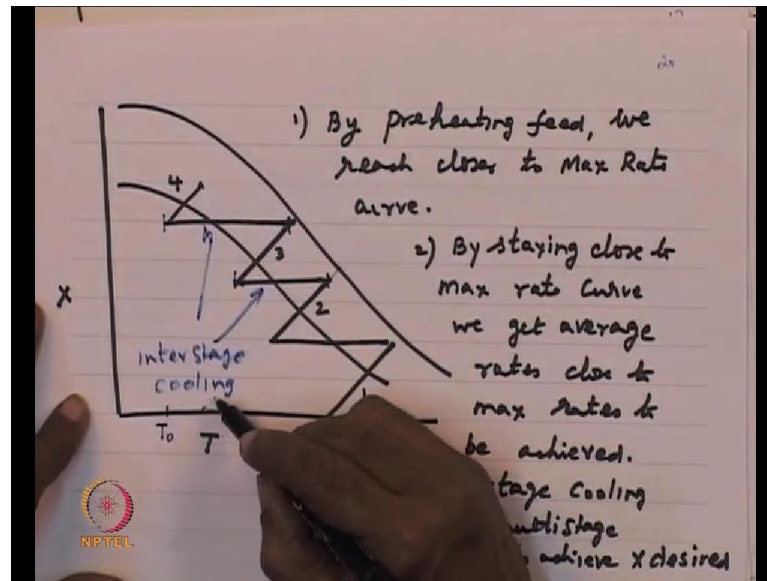
(Refer Slide Time: 20:42)
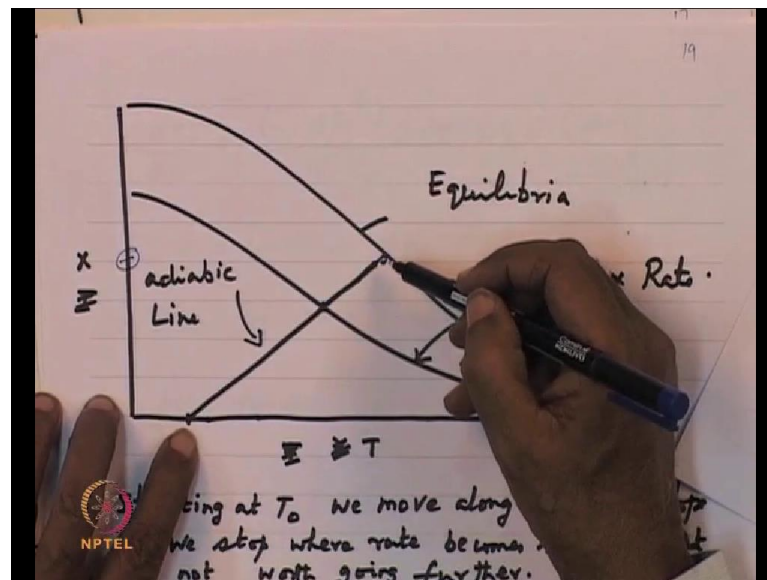
The answer to why multistage is that in one stage, we are not able to push the reaction to the end point that you desire. Why you are not able to push it to the end point of your desire, because your reaction is reversible and therefore, as you move along the reactor, you will at least, you will end up in the end point at the equilibrium point. Therefore, you cannot go forward and since, the reaction rate becomes very small, you will stop

somewhere, in little earlier than that; otherwise, it will become unwilling to operate. So, you will stop the process slightly, before it reaches equilibrium, and then you will run the next stage after cooling it.

(Refer Slide Time: 21:14)

So, the idea of this cooling from one point to another is to give you the ability to go to higher level of conversion. So, this point, this point; all these points are points of design decisions; decisions that will determine the economics of your process. So, how far you go in one stage; how far you cool during the interstage cooling, and all these are decisions, coming from economics only. So, you will have to do a number of iterations, before you get the design that satisfies your economic criteria; is that clear? Of course, criteria is not just economic; there are safety criteria; there are various other issues that goes into your objective function, but once the objective function is defined, you can definitely, take care of all those calculations and come up with the best kind of design.

There is another issue that frequently, we encounter is that if our initial temperature is T 0; therefore, let us say this is our T 0; I will just draw here; this is T 0. Now, you notice here, that if your T 0 becomes much higher; that means, if you are able to preheat your feed to a higher temperature, then you are able to, I mean, achieve a far better extent of reaction, because you are able to go forward to the end point. On other words, if you can heat the feed to as high as temperature as possible, you are able to approach as close; let us say you are able to heat it up to this point; you are much closer to the maxima in reaction rate curve. On other words, preheating the feed, facilitates you to reach as close to the maxima in reaction curve as possible, and to that extent, you are able to save on this size of your equipment.
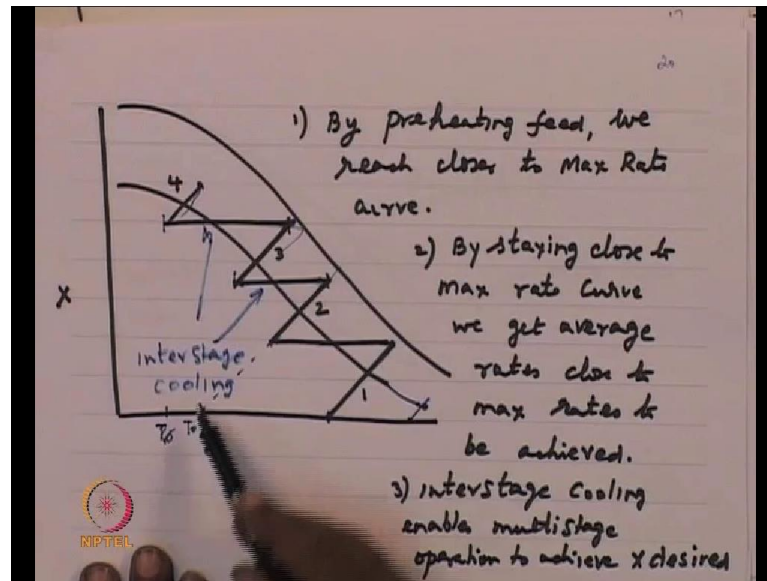
So, the idea of preheating is this; if you start here you will get a much bigger reaction equipment, but if you start here, it is a much smaller reaction equipment, because you are much closer to the maxima in reaction rate curve. This is something, you will see if you go to ammonia or if you go to the sulfur dioxide reactor, these are things that is done routinely, to provide the appropriate optimization. Now, this interstage cooling, as you can see; these are all interstage cooling; which actually, permits you to go to higher and higher conversions. For a gas phase reaction, this interstage cooling is a huge investment. Why is it, because gas phase heat transfer coefficients are small, and therefore, and if the reaction is at high pressure for example, you are talking about high pressure equipment, at the same time, very small heat transfer coefficient. Ammonia is such an example.

What? Yes, number of stages might increase, but the overall size of the equipment will come down. Yes, this is the optimization you will do. See, you have to do this optimization to find out what is the best. I mean, too many stages; there are problems; all those issue are part of your objective function that you will have to set for yourself, but even more important is that, this interstage cooling where, if it is a gas phase reaction; it is a huge investment, because its heat transfer coefficients are very low, and therefore, the size of this, size of the reaction equipment and size of the cooling equipment; we have to take both into account, so that, your cost optimization is taken care. Ammonia and sulfur dioxide; these are all instances; these are all gas phase reactions; (( )) and all those issues associated with problems that you will encounter.

So, you have to do both the cooling equipment design, as well as the reaction equipment design, so that, you are able to get the overall objective as per you are objective setup. Now, if you if you go to sulfur dioxide, they say what is called as DCDA, the process that operates around the world, is called double contact double absorption. What is meant by double contact?

(Refer Slide Time: 25:13)
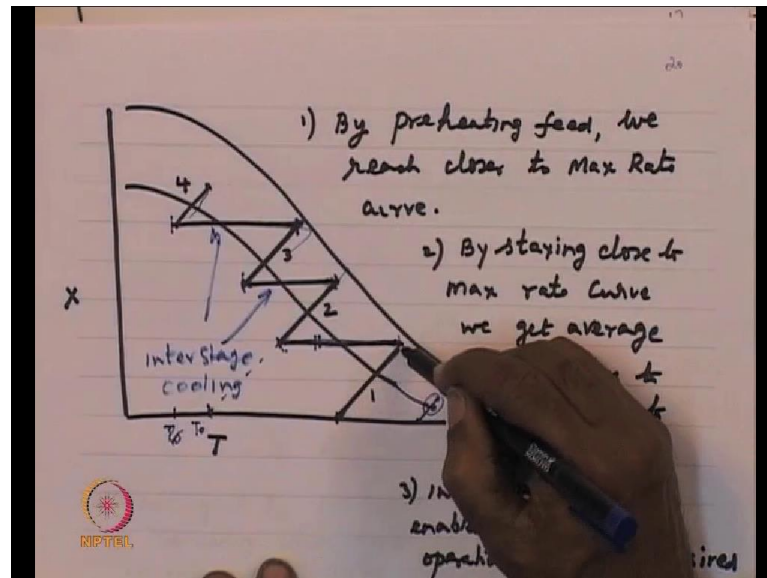
See, you have this contact; this is contact; that means, you have pushed the reaction to a certain extent. Then, you take this gas for absorption; that means, you observe this O 3, and then you bring them back into the process. Absorb means automatically, it cools. So, this cooling and absorption go together, and then you do another stage. So, this is contact. Then, this is absorption; contact absorption. So, they have double contact, double absorption; this is what is in the sulfur dioxide process. It is only two stage process where, you take it to the end point. This is something that you will see. With ammonia, I mean, ammonia; nowadays, people do what they call as radial flow. You may have come across this radial flow. The advantages of radial flow; let me just do a small calculation for you.

(Refer Slide Time: 26:15)
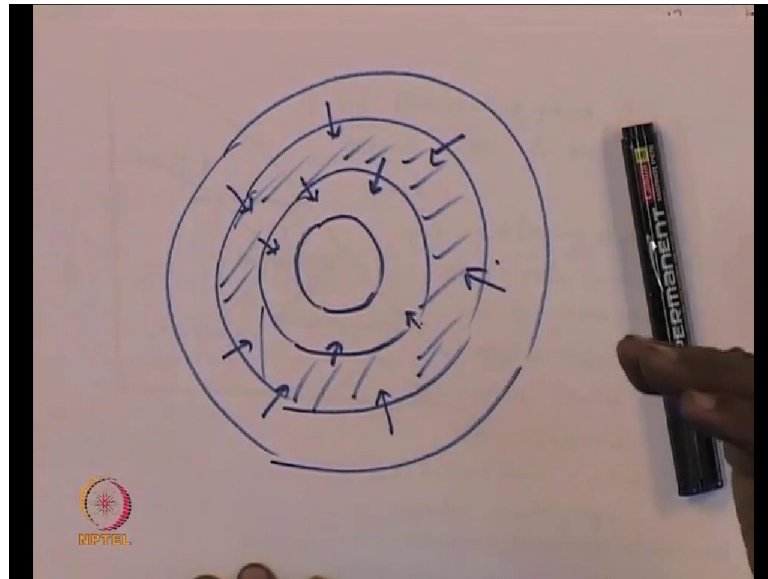
These are concelentric cylinders; your catalyst is here. You have fed; the gases are moving in like this. This is perforated, and then it goes out through this. This is also perforated. So, gases are moving inwards. Now, if it is a reaction, in which, there is a decrease in volume; s o 2 plus half 4 2 is the s o 3. There is a decrease in volume. You can see the facilitation. So, the volume decreases; the volume of flow volume also decreases. So, radial flow has certain advantages, and by keeping this thickness very small. So, you can keep this thickness very small by choosing the size of the cylinders and therefore, the amount of reaction, the extent of reaction is controlled; number 1. The extent of heat, I mean, heat release or what is called as temperature rise, is also within the limits that you would have specified.

So, the important thing about this radial flow is that you are able to regulate all that; ensure that the catalyst, I mean, does not deactivate, because of very high temperatures. So, ammonia and sulfur dioxide are good examples in which, this kind of issues become serious.

Now, there is another point we want to look at is we looked at del r b by del t at constant x, and we showed plots of r b versus x, and r b versus T, and then now, what we want to see is that what happens to this function, del x del t at constant r b; del x del t at constant r b or in other words, what we are saying that we will take this function r b as some constant value, some gamma, and see, how this function del x del t at constant r b looks like. Why we want to do this? We will see shortly. So, we want just like we have done del r b del t at constant x. Now, we are going to look at del x del t at constant r b.

To do that, what I have done is setup this function once again; that means, I have taken r b as constant, and then it is k 1 C a 0, 1 minus 0 x, k 2 C a 0 x. Just setup the rate function in the form that we all know, and then I divided throughout by k 1 C a 0, so that, the right hand side looks like this; 1 minus of x, x divided by k. Why is it divided by k? This k 2 divided by k 1 is k; is it all right? I have divided throughout by k and C a 0; is this all right, what I have done? When you do that, first term is 1 minus of x; the second term is C a 0 cancels off; k 2 by k 1 is written as capital K. Now, I have combined x together; it looks like this.

(Refer Slide Time: 29:09)

Therefore, the relationship between x and temperature looks like this where, the temperature dependence is involved in capital K and small k. So, x, for a given reaction rate, x is related to that by this equation 3; is it ok? Now, if you differentiate x with respect to t; del x del t at constant r b; constant r b means constant gamma; gamma does not change. So, we want to do del x del t at; why do you want to do this? What is the rationale for doing this? The rationale for doing this is the following; what is this term k by k plus 1? I put it in this form.

I have just this term, k by k plus 1 is 1 by 1 plus k. As temperature increases, if it is in exothermic reaction, what happens to k; it decreases. So, what happens to this whole term? So, k by k plus 1; what happens? Decreases, k by k plus 1 decreases as x increases. What happens to the first term, 1 minus gamma by k 1 C a 0? As you increase temperature, k increases and therefore, this whole thing decreases. Therefore, this whole thing increases. So, what we are saying is that for an exothermic reversible reaction, x equal to this term; the first term increases this temperature; the second term decreases temperature. Is this point clear to all of us? This function, what we have done? We have done; just run through this once again.

(Refer Slide Time: 30:42)
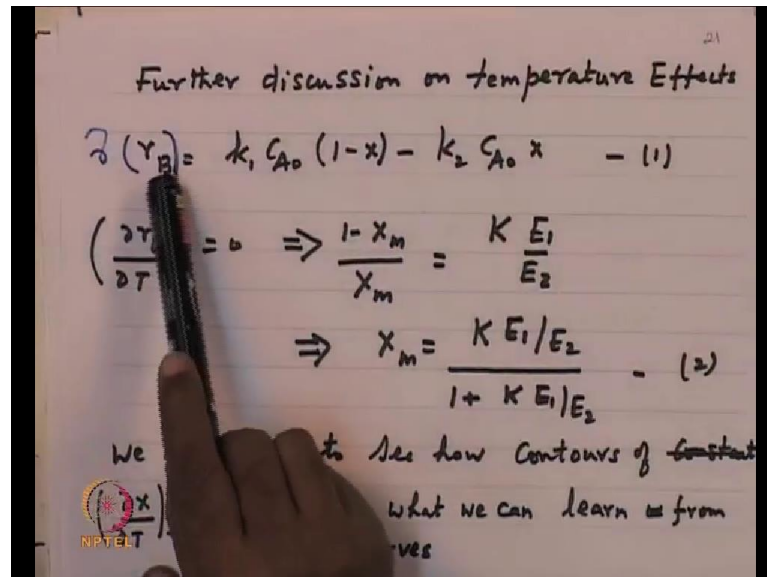
We want to look at this function r b for the case, when r is held constant, and we change temperature. This is what we are trying to do. So, we want to see what happens to that function, for which, we have said we have divided throughout by k 1 C a 0 and got this function and so on.

(Refer Slide Time: 31:00)
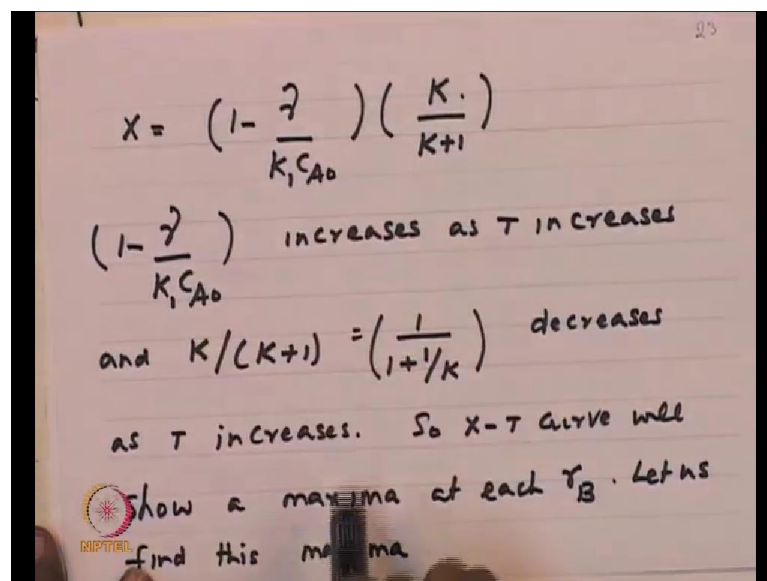
So, this increases; this decreases; and therefore, there is a maxima for the value of x. So, x versus T should show a maxima. To find out what that maxima is, what we have said is that we want to see how that function looks like. Let us do this once again.

(Refer Slide Time: 31:21)

What we have done previously? What we did was del r b del t at constant x; that means, rate of change of rate with respect to temperature, keeping x constant. What we are now doing is that rate of change of x with respect to T, keeping r constant. So, we are looking at the same function in two different ways. These contours need not be the same; it depends on the function and so on. So, we are looking at the same thing in a different way to see whether, there is something more to be learned at least, from the point of veiw of a design.

So, we are now doing, not del r b by del t; this we have done already. We want to see del r; we want to keep r b constant, and see what happens to this function as temperature changes. Now, we are doing del x del t at constant r b. To do that, what we have done is the following. We have said this is; I must have misplaced; I put it somewhere else; anyway, does not matter.

Anyway, this is our function, which is r b equal to gamma. This is the function we want to understand. To understand how x versus T changes when gamma is constant, I divided throughout by k 1 C a 0. Then, our x looks like this where, gamma is the constant. We want to now do del x del t at constant r b; del x del t, gamma is constant. When you do that, this function; this is the function we want to maximize. So, this is the function, x equal to 1 minus gamma k by k plus 1, del x del t at constant r b. So, this is what we want to do now. Here, this k 1 is the function of temperature, sorry, k 1 is the function of temperature. This k is also a function of temperature, correct. So, we want to differentiate this by parts. This is what was done. So, I am differentiating this by parts.

Let me write this here, so that, we remember; x equal to 1 minus gamma k 1 C a 0 into k by k plus 1. This is what we are differentiating. So, we are differentiating this. You can see here del x del T is 0. So, I have got minus k 1. Minus and minus cancels off; k 1 C a square; d k 1 by d t is k 1 E 1 by r t squared; it is there, k by k plus; this is the first term; is first term ok? Differentiate the first term. See, this minus term has disappeared, because k 1 squared with the minus n comes.

So, that is ok, and then d k 1 by d t is k 1 E 1 by r t square; that is fine. So, this term is all right. Second term; first this remains, and then multiplied by; you have to differentiate this. When I differentiate this, it will become 1 by k plus 1 d k d t, is fine. Then, differentiate the denominator, k plus 1 whole squared, correct, with the minus sign d k, fine; looks all right. So, equal to 0; this is how it looks. Now, I have to do some manipulation. What manipulations have I done; d k d t; what is d k d t? I have got here d k d t is; d l n k d t is delta H by r t squared. So, 1 by k d k d t is; I put d k d t is k delta H by r t square; is this ok? So, I have replaced this d k d t by k by r t square delta H, all right. So, this only, we have to simplify.

(Refer Slide Time: 34:42)

Now, let us see how we simplify. See, this is what we had, correct. This is what we had. This is gamma k 1 E 1 delta H. Now, I am writing it like this; 0 gamma k 1. What happened to k 1? k 1 got cancelled, correct, k 1 C a 0 squared k by k plus 1, 1 minus of k, k by k plus 1 whole squared; k plus 1 whole square is coming from where? Which one; this term.

Student: Yes sir.

Prof: What should it be? This one?

Student: Yes sir.

This would be C a naught; thank you. Now, it can be rearranged like this. I think I have missed it there, but I have got it right here, I think. So, what we are saying is that del x del t at constant r b; if you set it equal to 0, this relationship is what we get; that means, this relationship is what comes out of that differentiation, and I have done some more manipulations; some very elementary algebra is involved. What I have done is that I have replaced this delta H as E 1 minus o.

$$\frac{\gamma}{k_1 c_{A0}} = \frac{-(E_1 - E_2)}{E_1(K+1) - (E_1 - E_2)} \qquad \because \Delta H = E_1 - E_2$$

$$\frac{\gamma}{k_1 c_{A0}} = \frac{E_2 - E_1}{E_1 K + E_2} \qquad . \quad (5)$$

$$1 - \frac{\gamma}{k_1 c_{A0}} = \frac{E_1 K + E_2 - E_2 + E_1}{E_1 K + E_2} = \frac{E_1(K+1)}{K.E_1 + E_2} \quad - (6)$$

So, this delta H; I am putting it as E 1 minus of E 2. This delta H; where are we? This delta H; I have put E 1 minus of E 2; it simplifies like this, anyway. Basically, what we are saying is that gamma k 1 C a 0 actually, turns out something like this. This is the final form in which, we get 1 minus of gamma k 1 C a 0 comes out to be E 1 k 1 plus. So, a relationship which is involved some amount of algebra. Gamma is the reaction rate, which is held constant.

$$X = \left(1 - \frac{\gamma}{k_1 c_{A0}}\right)\left(\frac{K.}{K+1}\right)$$

$$\left(1 - \frac{\gamma}{k_1 c_{A0}}\right) \text{ increases as } T \text{ increases}$$

$$\text{and } K/(K+1) = \left(\frac{1}{1 + 1/K}\right) \text{ decreases}$$

as T increases. So X-T curve will now a maxima at each r_B. Let us find this maxima

We started with this equation, correct; x given by 1 minus of gamma k 1 C a 0; this is basically, this is the basic balance. So, what we are saying is that equation 1 holds, as well as if you want maxima, del x del t at constant r b; this also should hold; equation 6 and this is equation 1.

(Refer Slide Time: 36:53)

If we manipulate further, you get essentially, you end up with this relationship that for the case of del x del t at constant r b equal to 0, you get x equal to k delta by 1 plus k delta. After going through this algebra, what we have done?

(Refer Slide Time: 37:13)

We started with this rate function; r b equal to this.

(Refer Slide Time: 37:18)
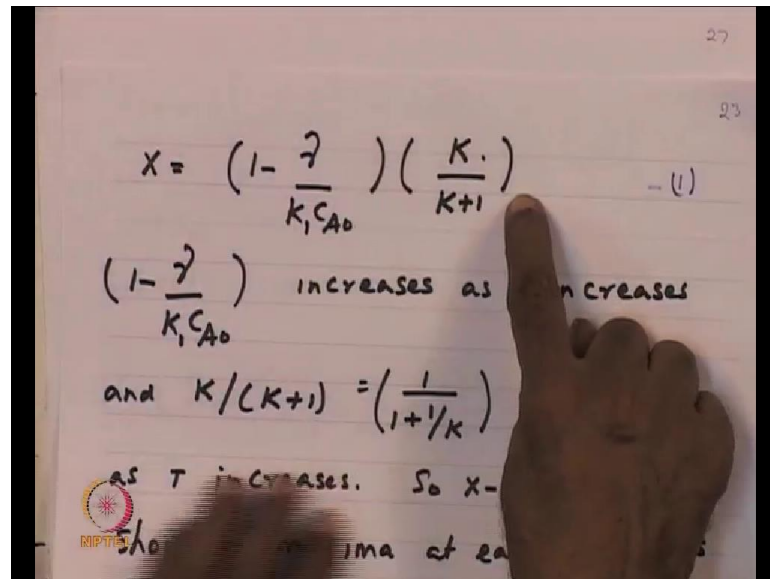
Then, we said that this can be simplified to x equal to this. Then we did del x del t at constant r b and found that the relationship that satisfies del x del t at constant r b is given by x equal to k delta by 1 plus k delta, and this is exactly, the same relationship we got for del r del t at constant x. So, what we are saying is del r del t at constant x, and then del x del t at constant r b; the locus is the same. What we are saying is the following.

(Refer Slide Time: 37:51)
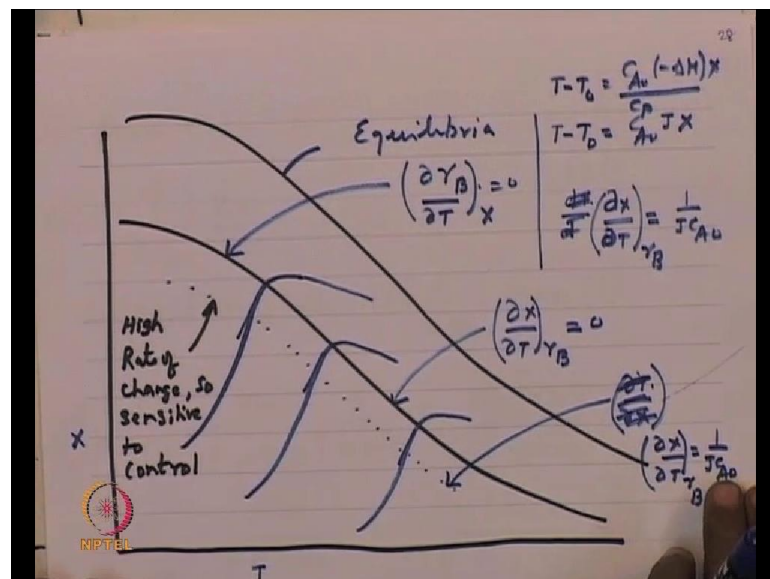
Let us just run through the whole thing. We started and said this is see, del r del t at constant x; it is this.

(Refer Slide Time: 38:08)

This, we have done earlier, and what is the equation; del r del t constant x or x m is given by k delta by; this is x m given k delta by 1 plus k delta. That is for the case of del r del t at constant x.

(Refer Slide Time: 38:19)

Now, what we are saying is that for the case of del x del t at constant r b also, gives you k delta by 1 plus k delta. In other words, we are saying that this locus also, applies for del x del t at constant r b.

(Refer Slide Time: 38:29)
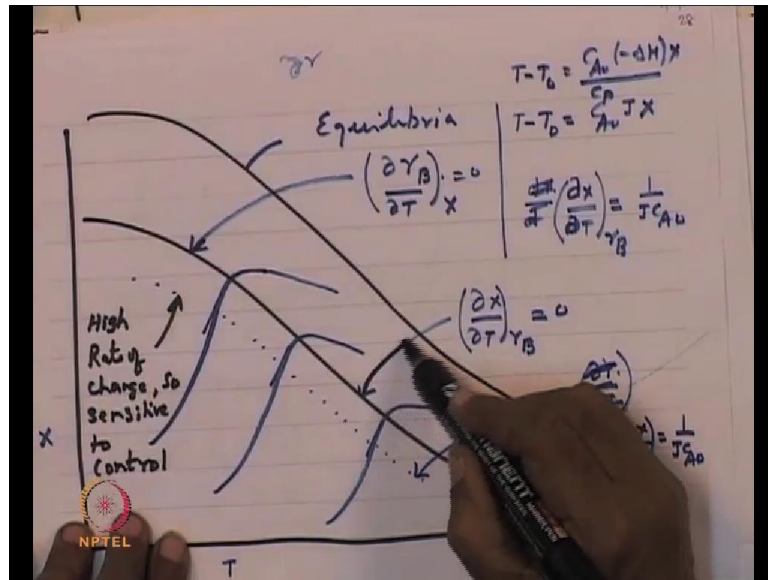
So, this also applies for del x del t at constant r b; the locus is the same. So, what we are trying to do is that to show that locus of del r del t at constant x and del x del t at constant r b; it is the same. Somehow, this is not clearly brought out in many text; that is what I find. There is a book written in 1965, in which, he says in passing that you see; it is the same, but somehow, it is not proved anywhere. So, I thought it is worth, sort of going through this effort and proving this. It comes nicely, actually.

(Refer Slide Time: 39:12)

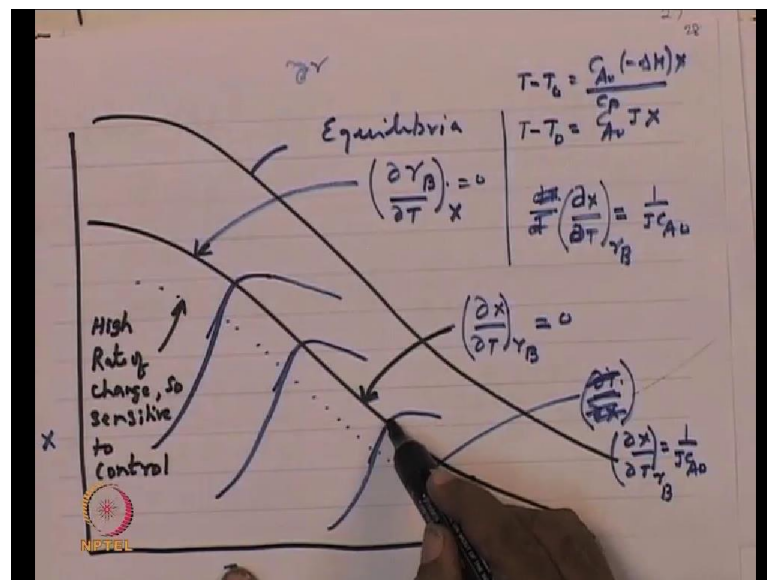So, let us look at where is our function r; this is our function r, correct; r equal to k 1 C a 0, 1 minus k 2 c. So, we can plot this function, correct. This function r can be plotted for different values of r. When you plot this, see, I have just plotted for different values of r.

(Refer Slide Time: 39:26)

So, what are we getting here? For different values of r, you are getting your maxima. The maxima is coming at that point only. The reaction rates for the assumed values of r where, the maxima appears and the other one; both are coming out on the same locus. So, the point that we trying to get across here is that if you look at a point somewhere

here, somewhere here, which is what; these are the points what is called as d x d t. This is our equation here; T minus T 0; we did this a little earlier; I would not be able to find it now, but let me write here; T minus of T 0; this is what adiabatic PFR, is given by C a 0 delta H, x divided by C p. We have done this a little earlier.

(Refer Slide Time: 41:09)
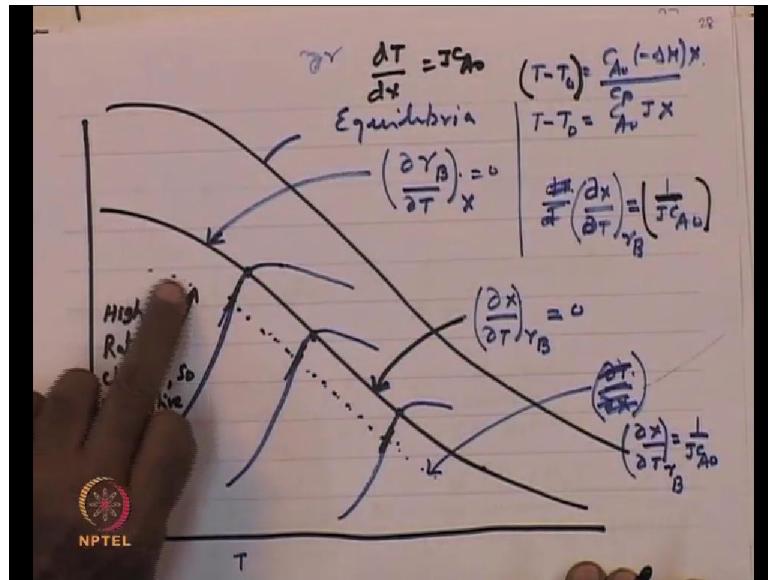
What is d t d x here; d t d x or d x d t is 1 by j C a 0; d t d x is j C a 0. Therefore, d x d t is. So, what is that? Suppose, I want to locate that point; I can locate that point here. You can see, locate this point. These are the points at which, d x d t is 1 by j C a 0 or d t d x is j C a 0. Is that clear? So, d t d x; actually, the highest value that d t d x will takes is j C a 0. In other words, plots of x wards, in the plots of x t curve, the point where, d t d x is the highest value; I have shown by dotted line here. You see this is the dotted line, showing locus of points on this x t curve where, the rate of change of t versus x is the highest value, which is j C a 0. This is shown as a dotted line.

So, we have three; one is the equilibrium curve; one is the maximum reaction rate curve, you call it del r b del t at constant x or del x del t at constant r b; both are the same. There is a third line, which is shown as a dotted line, which is corresponding to d t d x equal to j C a 0. Now, the interesting point about d t d x at j C a 0 is that d t d x means, the rate at which, temperature changes as conversion changes. This is the point where, the process is most sensitive to control, because here, the change is the highest. Whatever the process may be, you are seeing your change as the highest. So, d t d x has the highest value as j C
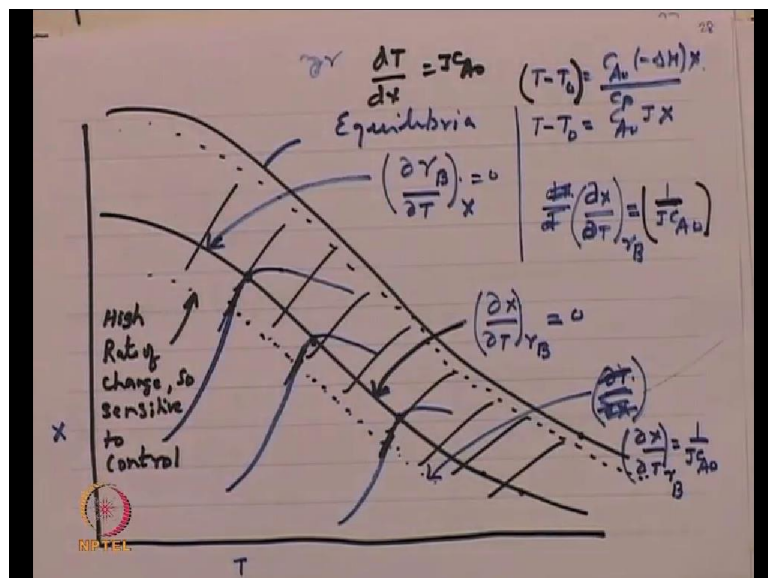
a 0. So, a process control around this point, would be most effective. At any other point, it may not be as effective.

(Refer Slide Time: 42:13)
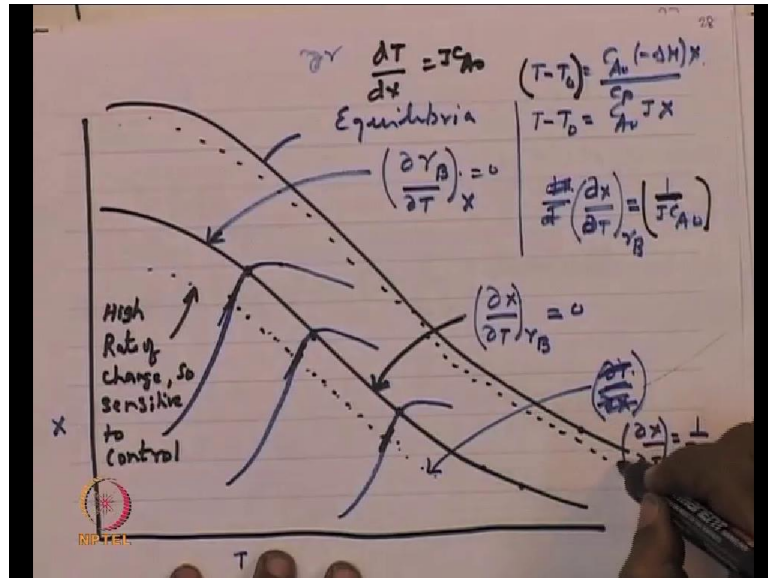
So, the region of design; often people draw a point there, point here, which is something like, some, let we say 98 percent of equilibrium conversion.

(Refer Slide Time: 42:21)

Say this is the region in which, your design must lie. Your region of design is between this dotted line, and a line, which is not at the equilibrium curve, but somewhere, close to

the equilibrium curve. Some people take it 98 percent equilibria; some people do less; depends upon the objective function that you set for yourself.

So, what we have tried to put across here is that looking at the temperature effects on chemical reaction; we have defined a region over which, you should look at your design, and with respect to the objective that you would set for yourself. This objective may involve cost; may involve safety; may involve consumption of water; consumption of utility; so many. See, some people look only at cost, but in many cases, cost alone, may not be criteria. In many designs today, the most important criteria is water. There is not enough water, I mean, water may not cost you so much; it may cost you some 50 rupees or 40 rupees. The fact is that it is not there. So, consumption of water is something that has to enter your objective function. There are various issues like this which, enters and as a result of which, the design that you will finely end up, will have all the compromises. That is required to make sure that the plant actually, runs satisfactorily.

I will stop there.