Advanced Chemical Reaction Engineering
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Lecture - 25
Illustrative Example:
1) Hot Spot as Design Basis
2) Design for Instantaneous Reaction

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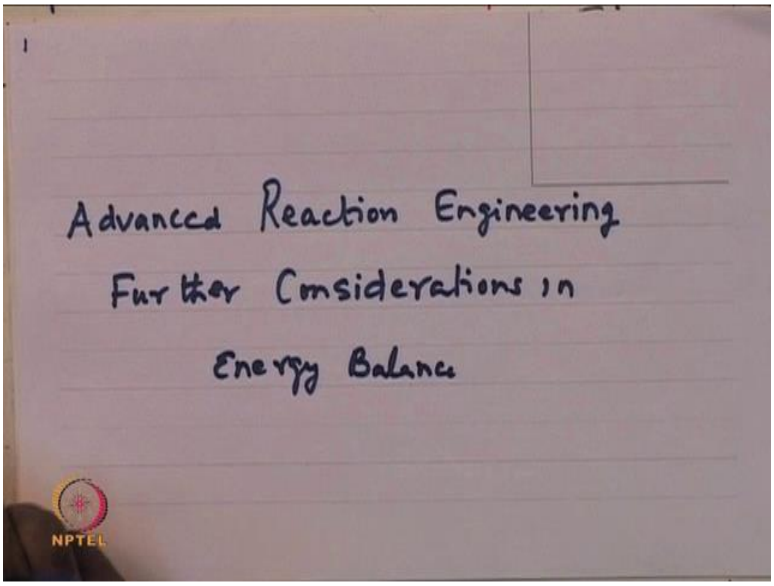

Advanced Reaction Engineering

Further Considerations in

Energy Balance

Today, we will look at some further considerations in energy balance. Now, the context to this is the following; when you are running a chemical reaction equipment we find that we need to control the process. And then, for controlling a process as you all recognize at we need good measurements and, not just good measurements that will help us to regulate the process the way we are looking at. On other words; we really must be able to make such measurements, on such variables which actually provide a good control over the process. So, in order to illustrate, what we want to do now is to look at this problem we will some context, and understand how this chemical be done.

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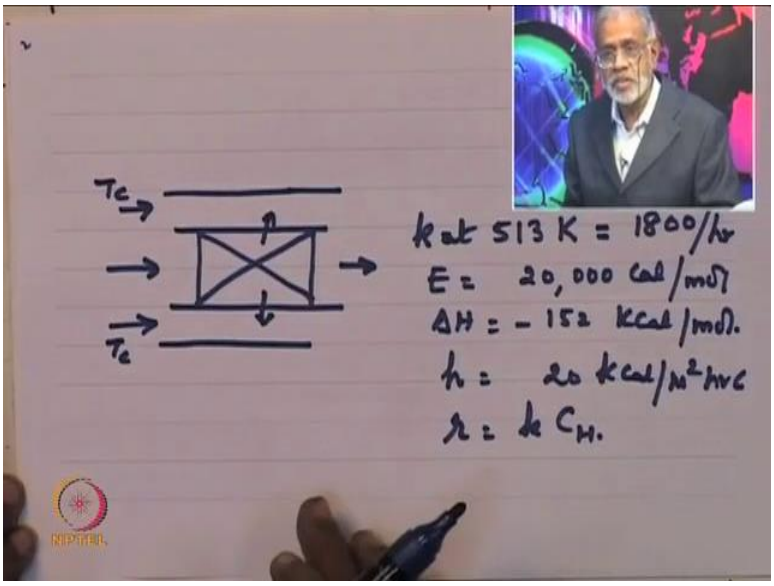

k at 513 K = 1800/hr

E = 20,000 Cal/mol

ΔH = − 152 KCal/mol.

h = 20 kCal/m^{2}hrC

$r = k\,C_H$.

So, to do this what I am going to do is; let us consider a reaction equipment, let us say it has a catalyst, I mean it is a catalyst, I will just put down some numbers just to select say the temperature k at 513 Kelvin, some data I have taken is 1800 per hour. Let us say the activation g for this reaction is 20000 calories per mole. Let us say the delta H for this reaction is minus 152 kilo cal per mole. And, heat gas phase reaction the heat transfer coefficient is 20 kilo calories per square meter hour C. And, the rate function r is sum some k times C H, it is some reaction ok.

We look at this reaction what it is etcetera right now, it may not be so crucial. Now, heat comes in and it goes out so, reaction occurs. And since it is an exothermic reaction very highly exothermic reaction. We need to cool, so there is a coolant which is flowing let us say it is a T c, all right. Now, as usually action takes place lot of heat gets generated and therefore, these gates you know passes on to the coolant. And, therefore the reactor is maintained at temperature that is appropriate for the process, ok.

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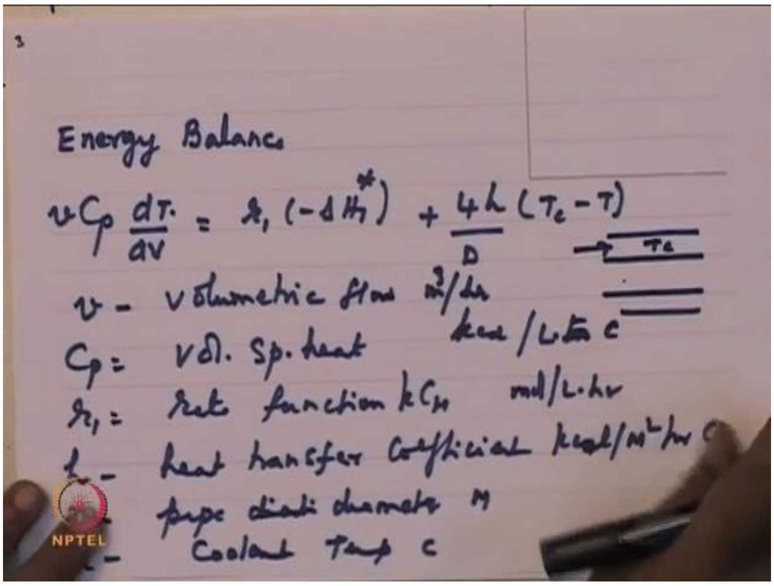

3

Energy Balance

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

v - volumetric flow m^3/hr

C_p = vol. sp. heat   kcal / Liter C

r_1 = rate function $k C_H$ mol/L·hr

h - heat transfer coefficient kcal/m^2 hr C

- pipe dia diameter M

- Coolant Temp C

Go forward a little and then, let us say our energy balance is; I will just write it down C p d T d V equal to some r 1 times minus of delta H 1 star plus 4 h by D T c minus of T. We are just recall what is v? v is volumetric flow, this is volumetric flow at any position. C p is volumetric specific heat then, r 1 is rate function. In this case; we have taken the rate function as C H times k, and h is heat transfer coefficient, and D is the pipe diameter. And, T c is coolant temperature C, meters, k calorie, k calories per square meter, hour degree, C rate function is mole per liter per hour let us say. Volumetric specific heat let us say it is kilo calorie per liter per C. Volumetric flow some say cubic meter per hour, ((Refer Time: 05:05)) these are all the units. Now, when you are running this process; let us say, you have this is the tubular rector, this is the coolant going throw coolant T c. Now, this temperature inside what happens is the temperature inside this reactor if is an exothermic reaction.

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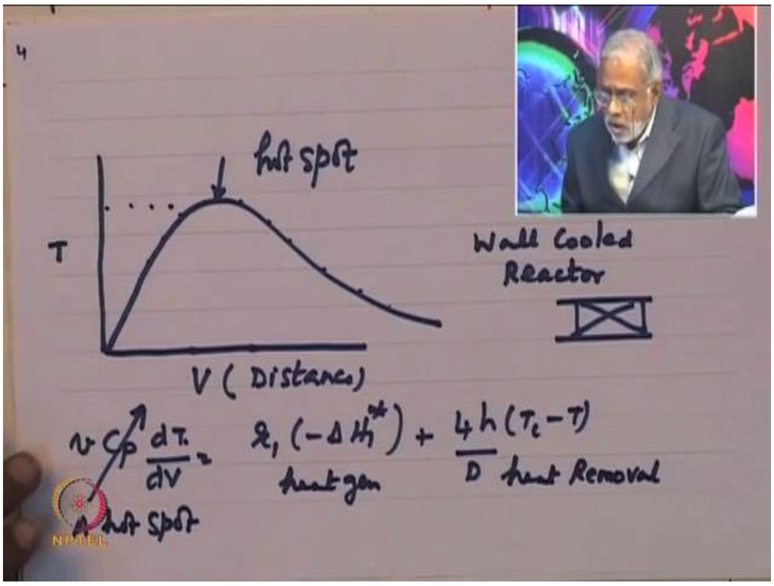

So, an exothermic reaction we should expect that then, we make a plot of say volume of the, or distance whichever is appropriate distance versus temperature. So, if it is a wall cool heat is an instance of a wall cooled reactor that means; this reactor is cooled from the wall. So, we will expect the reactor that go through a temperature like this, it goes through a, this is called as the hotspot, this is a hotspot temperature. Now, we are said earlier and said a once again; hotspot is the highest temperature that is exhibited by the reactor. And, this is because of the fag that the process heat generation and heat accumulations are such that sorry, heat accumulation heat removal research.

Now, this temperature at which this occurs, this temperature may have an important barring on the kind of catalyst that you have using. In many systems there is a specification on the catalyst; that is that you are not supposed to exceed a certain temperature. On other words; hotspot temperature is a faly important temperature from the point of view of controlling the reactor, ok. So, if this is specified saying that this is the maximum temperature that we have willing to permit.

Therefore, and if you can measure temperature along the length of the reactor, which is not so difficult because we can put thermocouples, and measure temperature along the length of the reactor and, this temperature read out and might be continuously available as the process is running. In other words; as you running the process at every point in the reaction equipment the temperature would be continuously measured and then it is available to you from your data. Now, how is it that you can make you good use of this temperature heat to understand the process, to understand how best to control this equipment, ok.

Let us what you would like to do by looking at this energy balance, this is the energy balance. If you want to look at this energy balance and see how best we can do this control. And, to illustrate this we take an example that is what we are trying to do now. What we are said just now is that; if there is a wall cool reaction there is hot spot picture quitted out just now. There is a hotspot, and this hot spot and if you look back at our equation v C p d T d T d V equal to r 1 times minus of delta H 1 star, this is the heat generation due to reaction. And, this is T c minus of T by D, this is the heat remover, the heat generation, this is heat generation, this is heat removal. Now, at the hotspot this must be 0, we know this at the hotspot we should have the left hand side as 0, this is well known.

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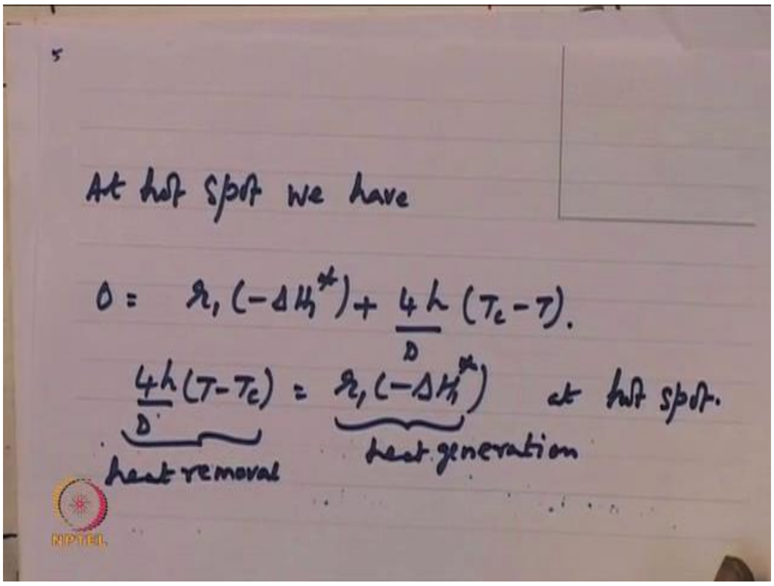

At hot spot we have

$$0 = r_1(-\Delta H_1^*) + \frac{4h}{D}(T_c - T).$$

$$\underbrace{\frac{4h}{D}(T-T_c)}_{\text{heat removal}} = \underbrace{r_1(-\Delta H_1^*)}_{\text{heat generation}} \quad \text{at hot spot.}$$

On other words; what we are saying is that at hotspot, we have 0 equal to r 1 times minus of delta H 1 star plus 4 h by D T c minus of T, or again write this as 4 h by D T minus of T C equal to r 1 times minus of delta H 1 star at hotspot. So, what are we saying this is the heat generation, and what is this? This is heat removal, ok.

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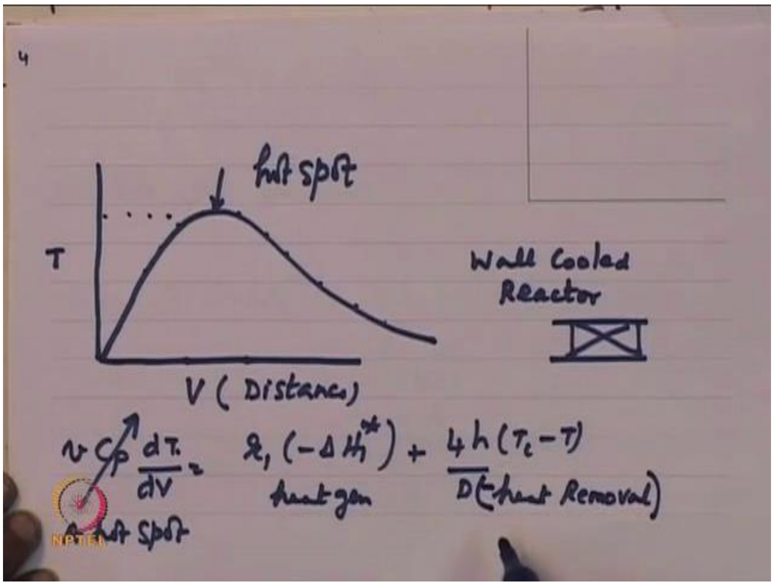

$$v C_p \frac{dT}{dV} = r_1 (-\Delta H_r^*) + \frac{4h}{D}(T_c - T)$$

heat gen

(-heat Removal)

hot spot

Now, please notice that this term; I put a negative sign here, because in first law conversion the heat addition is positive. So, I shall put a negative sign here. So, what we are saying is that heat removal equal to heat generation at the hotspot, these at hotspot.

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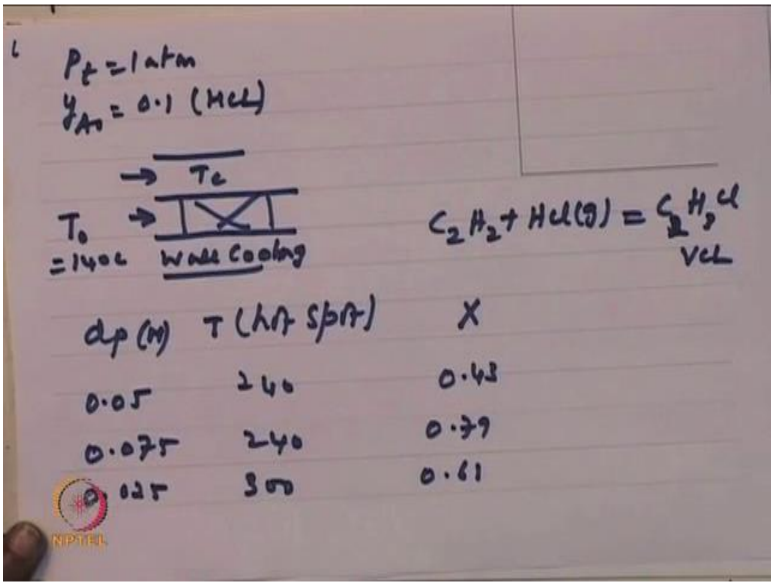

$P_t = 1$ atm

$y_{A0} = 0.1$ (HCl)

$C_2H_2 + HCl(g) = C_2H_3Cl$

VCL

dp (m)	T (hot spot)	X
0.05	240	0.43
0.075	240	0.79
0.025	300	0.61

Now, I have some data this is some data; let me just put down this data what does this says? This data says the following. You have an exothermic reactor is just cool by the wall, cooling from the wall cooling T c and this is T so, wall cooling this is wall cooling. The data says d p T at hotspot, and conversion at hotspot this numbers look like this.

0.05, 0.075, 0.025 and then, you have to 240, you have 240, you have 300, and you have 0.43, 0.79 and 0.61. What are we saying this is a data that is available from the process? What is it that, what are we expected do with this data? We are expected to review this data to see how best we can use this information to control the process. So, that is what we are trying to do.

So, we will try to look at this data so and also, me more information is given that is heat temperature is this is T naught is equal to 140 C. And then, feed y A 0 is coming at 0.1 and pressure is 1 atmosphere. On other words; we have a gas entering a reactor containing a catalyst at 140 C at 1 atmosphere pressure with A at 0.1, the rests so. As an example; so we can look at this reaction acetylene plus hydrochloric acid this is gas both are gas, giving you y net chloride monomer. C 2 H 3 c l this is V C L. So, the rest why use this is H C L let us say, and the balance is acetylene the reaction is taking place. And, in this 1 is 5 centimeter diameter pipe, it is 7.5 centimeter pipe, and this 2.5 centimeter pipe, it 1 inch, 2 inch, and 3 inch pipes. And, this is the x observe data at this temperatures, all right.

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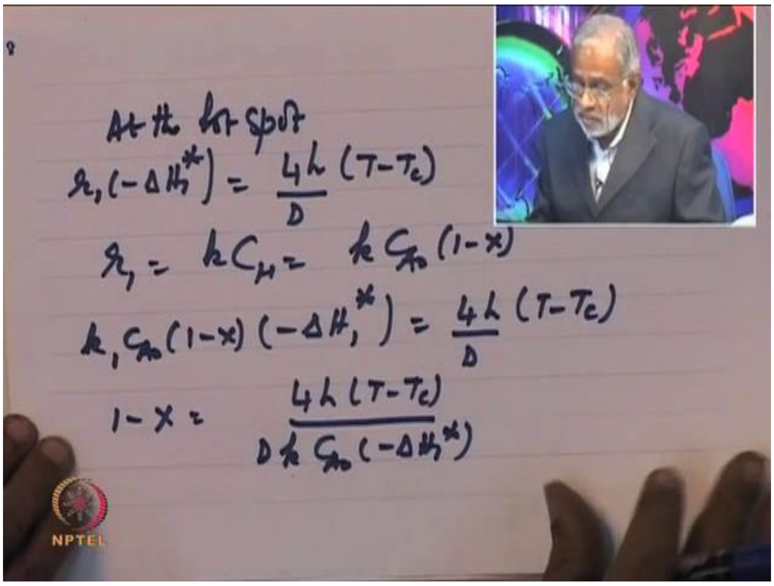

At the hot spot

$$r_1(-\Delta H_1^*) = \frac{4h}{D}(T-T_c)$$

$$r_1 = kC_H = kC_{A0}(1-x)$$

$$k_1 C_{A0}(1-x)(-\Delta H_1^*) = \frac{4h}{D}(T-T_c)$$

$$1-x = \frac{4h(T-T_c)}{D k C_{A0}(-\Delta H_1^*)}$$

Now, that you know that we know that r 1 times minus of delta H 1 star equal to 4 h by D T minus of T c. What is r we can say it is k times C H we said it is k times C A 0 times 1 minus of x, ok. So, I am doing small simplifications, because it is only 10 percent H c l I have not taking into account the volume change due to reaction. So, to as extent it is not such an accurate calculations, but that is not so important for the movement. What we trying to bring out is; how we can understand the data from the point of view of controlling the process. That is why I am not doing the calculations to such data. Let us do this calculations; so r 1 delta H so we can substitute for r 1 so, k C A 0 times 1 minus of x times minus of delta H 1 star equal to 4 h by D T minus of T c, 1 minus of x equal to 4 h T minus of T c divided by k C A 0 D minus of delta H 1 star, is it clear.

So, at the hotspot so what does this equation give us, it tells us; what is conversion at the hotspot 1 minus of x conversion. How it is related to the heat this is the heat I mean cooling the reaction and the heat transfer, you know how it is related h transfer coefficient and so on. Now, we can put all over numbers here, and find out what is the value of x we will at just do that quickly. Let us do that quickly for the 3 sets of data, let us quickly do that.

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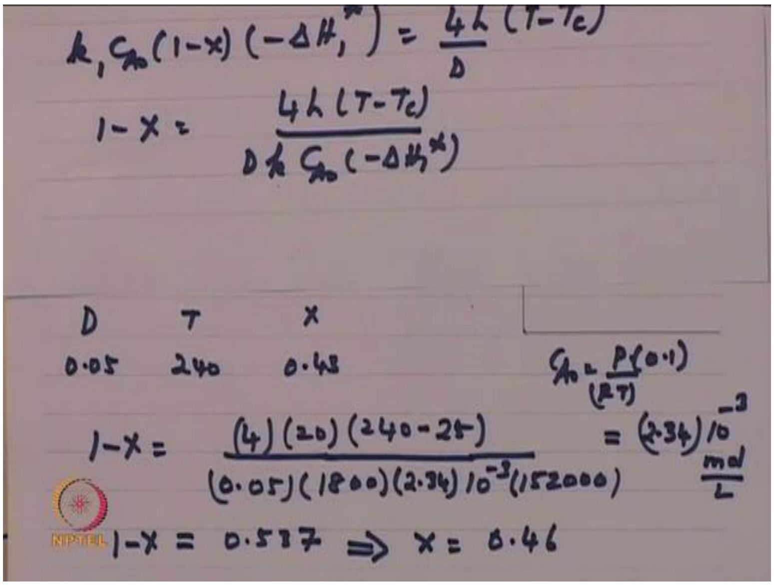

$$k_1 C_{A0}(1-x)(-\Delta H_1^{*}) = \frac{4h}{D}(T-T_c)$$

$$1-x = \frac{4h(T-T_c)}{D\,k\,C_{A0}(-\Delta H_1^{*})}$$

D	T	x
0.05	240	0.43

$$C_{A0} = \frac{P(0.1)}{(RT)} = (2.34)10^{-3}\ \frac{mol}{L}$$

$$1-x = \frac{(4)(20)(240-25)}{(0.05)(1800)(2.34)10^{-3}(152000)}$$

$$1-x = 0.537 \Rightarrow x = 0.46$$

So, set 1, what is set 1? Set 1 is let me just D is 0.05, temperature is 240, x is 0.43. So, 1 minus of x equal to 4 h value is given so, it is 20. And then, our equation is here 4 h T minus of T c, T is what is it this particular case; what is the 240? 240 is the 240 minus what is the cooling temperature coolant temperature T c. Coolant temperature T c I should write it down here, T c is 25 C. So, 25 divided by diameter of pipe is 0.05 rate constant at 513, 240 is 513 is that right, this is 240. So, it is 1800 per hour see data is given at please note that data is given at 513 that is 240 C, correct.

So, it is 1800 so that is what I am substituting here; k is 1800 and what is C A 0, you should calculate C A 0 it is not very complicated C A 0. Let me just do it here for you C A 0 equal to P by R T and then, we have to multiply this by the mole fraction 0.1. So, that is turns out to be 2.34 10 minus of 3 moles per liter. Now, let us put all these numbers here, that is 2.34 into 10 minus of 3 and heat of reaction please note here, it is exothermic so, 152 kilo calories per mole. So, I will put them in 152 I have to make it 1 152000 get all the units, right. So, this is 20000 I have put 20, 20 kilo calories per hour, which can delete foreign height and so on. And, this is 152000 and so on so, if you put all these numbers and then, we get x equal to 0.537. We do this calculation, we find that x equal to point x equal to sorry, 1 minus of x equal to 0.537 implies x equal to 0.46.

Now, please notice from our data here; x is given as 0.43 in the experiment these are experiment, ok. And, from our model we get a value of x 0.46 so, just I want you to remember this we will come back to it as you go along is it ok. Let us do 1 more calculations so, this is for 240, similarly we can do for 1 more calculations let us do it quickly this next data.

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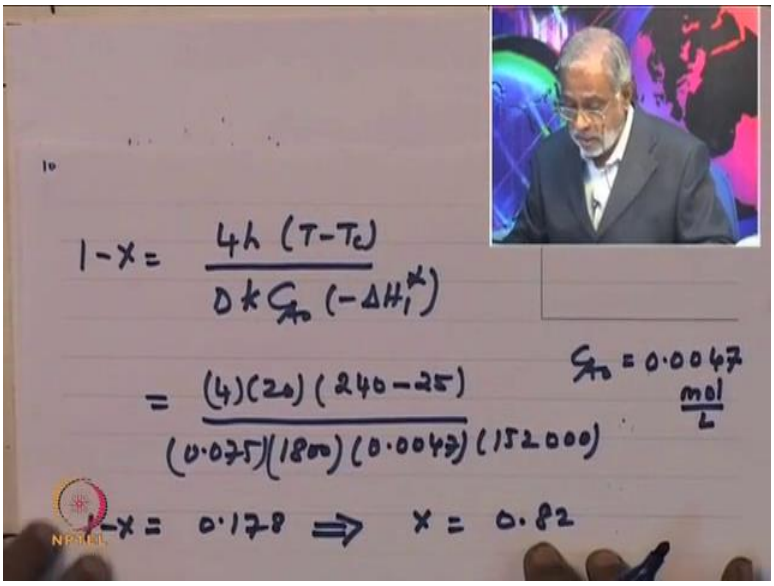

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$$1-x = \frac{4h\,(T-T_c)}{D\,k\,C_{A0}\,(-\Delta H_1^*)}$$

$$= \frac{(4)(20)(240-25)}{(0.075)(1800)(0.0047)(152000)}$$

$C_{A0} = 0.0047\ \frac{\text{mol}}{L}$

$1-x = 0.178 \Rightarrow x = 0.82$

Then, next data once again let me just remember 1 minus of x equal to 4 h T minus of T c divided by D k C A 0 into minus of delta H 1 star. So, let us once again put these numbers here we have the second set of data 0.075 to 240 and 0.79 is experimental value. So, we have to calculate notice here that the temperature here is 0.075 so, we can use this once again, let us do this. I will put all the numbers so, numbers look like this equal to 4 times 20 times 240 minus of 25 divided by our pipe size is 075 temperatures is 240. So, it is 0.075 and, what is C A 0 we have already calculate it C A 0, where is C A 0 at 240.

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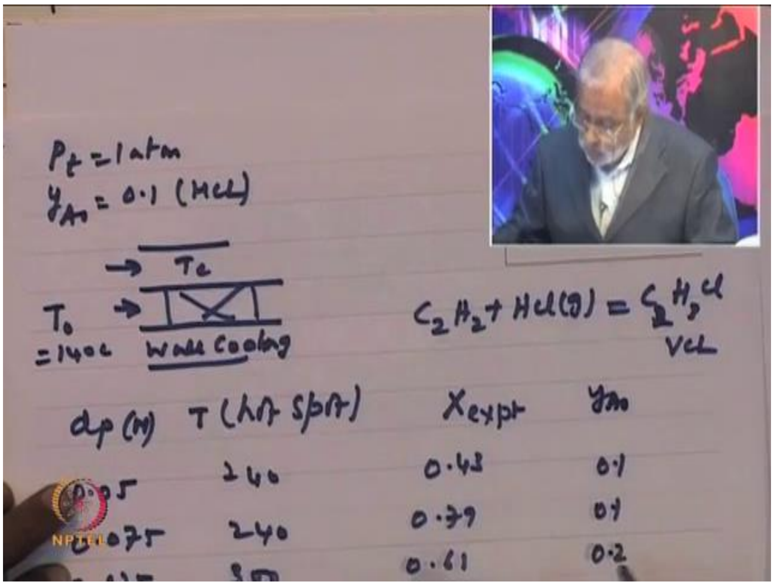

$P_t = 1\,atm$
$y_{A_0} = 0.1$ (HCl)

$C_2H_2 + HCl(g) = C_2H_3Cl$
VCl

d_p (m)	T (hr sphr)	X_{expt}	y_{A_0}
0.05	240	0.43	0.1
0.075	240	0.79	0.1
[illegible]	[illegible]	0.61	0.2

There is 1 more data which is missing y A 0 this is 0.1, this is 0.1, this is 0.2. So, that is what missing so, C A 0 corresponding to y A 0 equal to 0.2, this is 0.2 y A 0 that turns out to be point this turns out to be 0.0047, this is actually double the number. Let me have calculated see here, it was 2.34 so, it is double that because the mole fraction is it is a 0.1 it is 0.2, that is why I use this term 0.07 mole per liter, all right. So, it is k value is 1800 and 0.0047 and then, 152000 so, the whole terms to be 1 minus of x equal to 0.178 implies x equal to 0.82. Notice here that the experimental value is 0.79 and then, our model value is 0.82. Let us do 1 more calculation for this third set of data just bare with me for a little while, because this is important point to be made here. So, I thought of going through these calculations in front of you.

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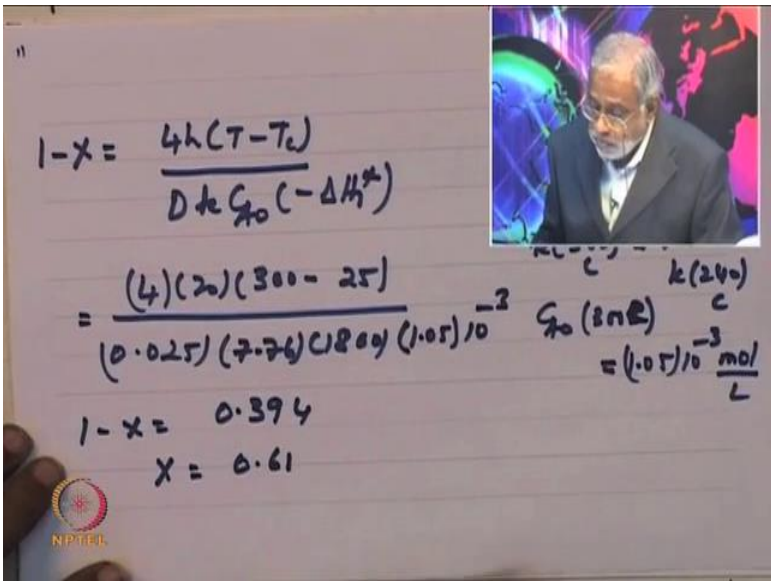

$$1 - x = \frac{4h(T - T_c)}{D k C_{A0}(-\Delta H^*)}$$

$$= \frac{(4)(20)(300 - 25)}{(0.025)(7.76)(1800)(1.05)10^{-3}}$$

$k(240\,C)$

$C_{A0}(300\,C) = (1.05)10^{-3} \frac{mol}{L}$

$$1 - x = 0.394$$

$$x = 0.61$$

Now, we have third set of data once again; 1 minus of x equal to 4 h T minus of T c, this is at hotspot D times k times C A 0 times minus of delta H. So, I am putting this as 4 times 20 and here, the data says that it is 300 minus of 25 divided by 0.025 this size of the, this is 0.25 per take size of the pipe. So, that is why 0.25 k value corresponding to 300; we have to calculate k at 300 of course, since the activation which is are known, I will just write down the number k at 300 is 7.76 times k at 240. This is C 240 C, I would not calculate this because quite obvious I am just putting down the numbers. Since, activation which are known you can do all these things yourselves, ok.

So, we have 0.025 and then, the 7.76 times 1800 that is k value. So, you got D you got k then, you got C A 0 corresponding to 300 C A 0 at 300 Kelvin sorry, 300 C not Kelvin 300 C. That also I have calculated and found it to be 1.05 10 to the power of minus 3 mole per liter, this is at 300 C what it is this C A 0 corresponding to mole fraction y equal to 0.1 which is given, ok. So, all these then I have to put this as 1.05 10 rise to minus 3 so, all these to be put our number comes out to 0.394 therefore, x equal to 0.61.

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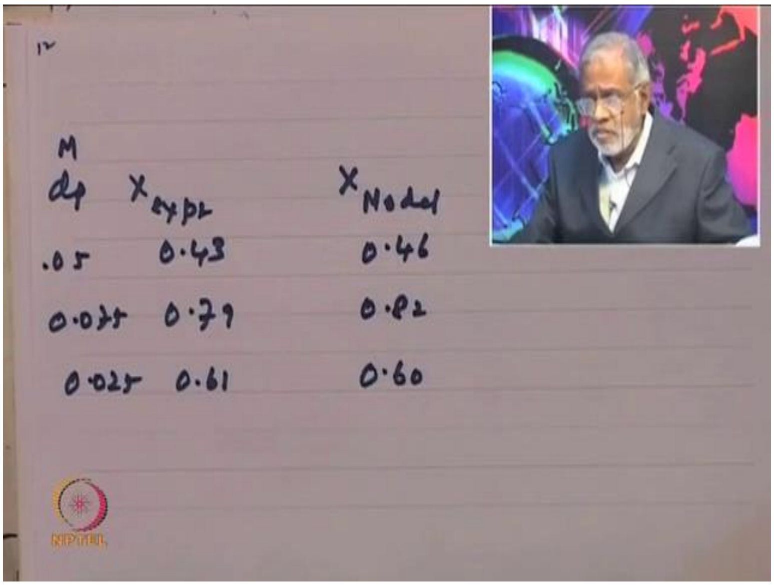

M d_p	X_{expt}	X_{Model}
.05	0.43	0.46
0.075	0.79	0.82
0.025	0.61	0.60

So, let me summarize by saying that we have here; X experimental X model so, we have d p I will write d p here, so that you know 05, 0.075 and 025, it is all meters d p in meters. For the 3 experiments the last 1 the model experimental value, this is the model value is 0.61 and the previous case. Let put me put down previous case; the model value let me just put down on the model values so; it is experimental 0.61, 0.79, 0.43. And then, the model values are this is 0.60 not 61 0.60, ok. Model value of 0.60 and the other one is model value is 0.82 we have got that also, and then model values is 0.46. What in a sense you have done is the following; we have let me reduce this once again.

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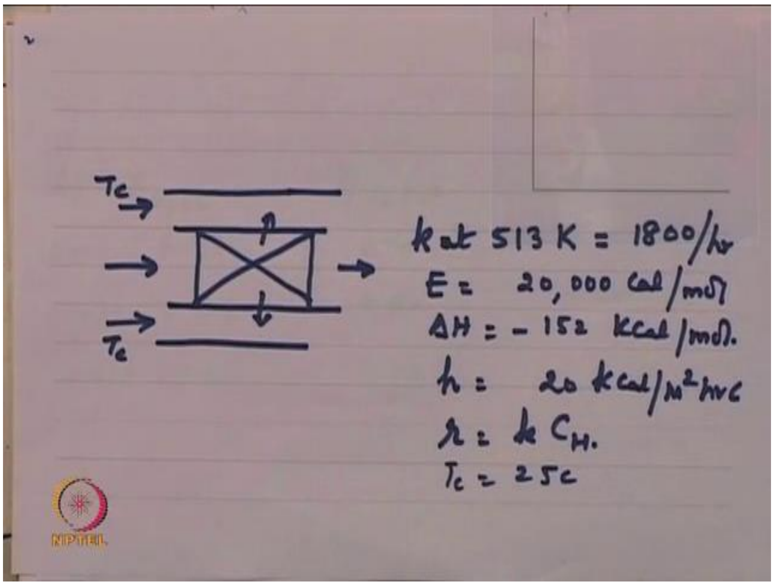

k at 513 K = 1800/hr

$E = 20,000$ cal/mol

$\Delta H = -152$ kcal/mol.

$h = 20$ kcal/m^2 hr C

$r = k\,C_H$.

$T_c = 25$C

What we have got, we started with a tubular reactor which contains a catalyst. We said this tubular reactor is cool from the wall and the coolant temperature is at 205 C. This is the catalyst and we have done experiments with different sizes of the pipe, just to understand how we can regulate or control such a process. So, we have done 3 experiments; one experiment with 5 centimeter pipe, one with 7.7 centimeter pipe, one experiment with 2.5 centimeter pipe. In each case you have find out; what is the hotspot temperature, and what is the conversion at hot spot, this is an experimental data.

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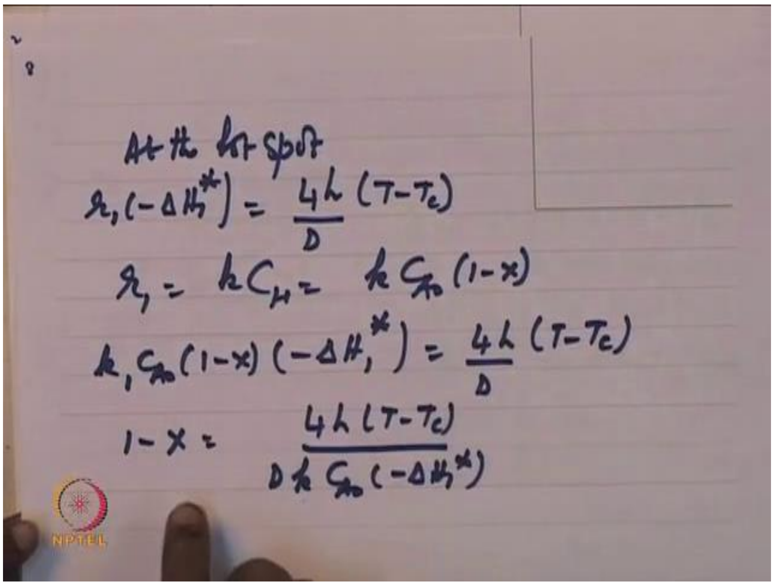

At the hot spot

$$r_1(-\Delta H_1^*) = \frac{4h}{D}(T-T_c)$$

$$r_1 = kC_M = kC_{M0}(1-x)$$

$$k_1 C_{M0}(1-x)(-\Delta H_1^*) = \frac{4h}{D}(T-T_c)$$

$$1-x = \frac{4h(T-T_c)}{D k C_{M0}(-\Delta H_1^*)}$$

Now, based on our model, what is our model? Our model said that; at the hotspot the heat generation must be equal to heat removal, heat generation equal to heat removal. And, therefore we have from this equality; we are able to find out what is the value of conversion at the hotspot. See conversion measurement is more complicated, while temperature measurements are relatively easy. So, you can relate conversion to temperature and use this as a way of controlling your process, it becomes a very valuable tool for the point of view of executing a process control. That is what I am trying to illustrate to you through this example.

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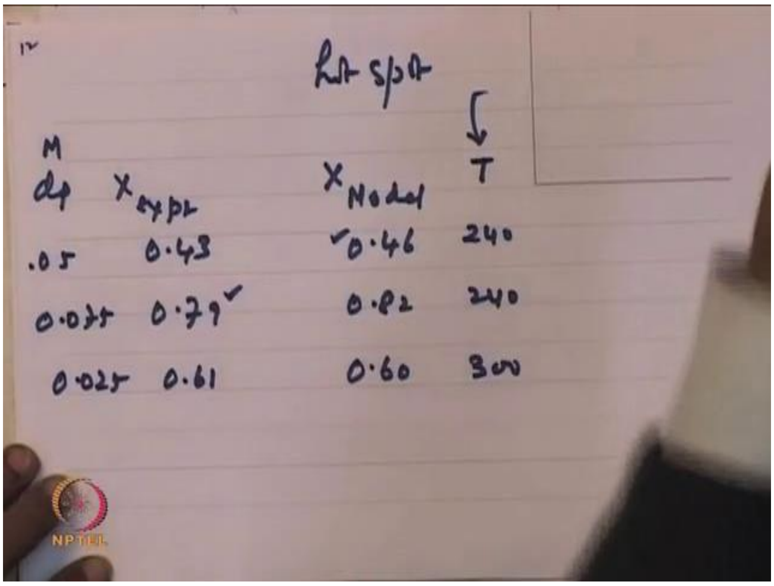

hot spot

M dp	X_{expt}	X_{Model}	↓ T
.05	0.43	✓0.46	240
0.035	0.79✓	0.82	240
0.025	0.61	0.60	300

So, what we have done? We have done 3 experiments, and those 3 experiments they tell us I will write the hotspot temperature here is 240 and 300 this is hotspot temperature. Now, based on these 3 experiments what we find is that; the experimental value of conversion and the model predated value of conversions are nearly pretty good, it is not bad at all. Showing that our way of predicting or in other words; we can know look at this in slightly different way. Now, we are now able to tell that if you know the hotspot temperature then, we can tell what is the conversion? So, alternatively suppose we have a process in which, we want to run the process so that we produce so many tunes of a given product. So, that means the experimental conversion that we are getting it is actually a design that we have to ensure, that we must produce so much.

Therefore, this 0.79 or 0.61 or 0.43 is something that is given as requirement of the process. What is it that we need to do from our side is to see whether ensure that this is actually achieved. Now, what is being said from our model is that; if indeed our model is a right, and we are able to predict the experimental conversion simply we will looking at the hotspot temperature. Now, we can say alternatively that in a process; simply by controlling the hotspot temperature, we can actually get conversion of our interest. So, this is the point of this whole exercise. What we are trying to put across to you is that now, since temperature measurements are relatively easy and very accurate. And therefore, we continuously monitor hotspot temperature, and once that monitoring hotspot temperature and regulate, we can regulate hotspot temperature.

How do you regulate hotspot temperature? You look at this equality, if you want to regulate this you have to control the coolant temperature. Which is also relatively easy in the sense that the coolant flow can be controlled coolant temperature at which is entering can be controlled. Therefore, T c is something that is in your hand, movement you manage T c you are able to get hotspot temperature of your choice and therefore, productivity of your choice. So, this is the important point of this exercise which is a part of our further considerations in energy balance. So, this is the exercise that I want to explain to you this. So, we want to consider then second related issue of what I call as further considerations in a energy balance. So, let us look at that exercise.

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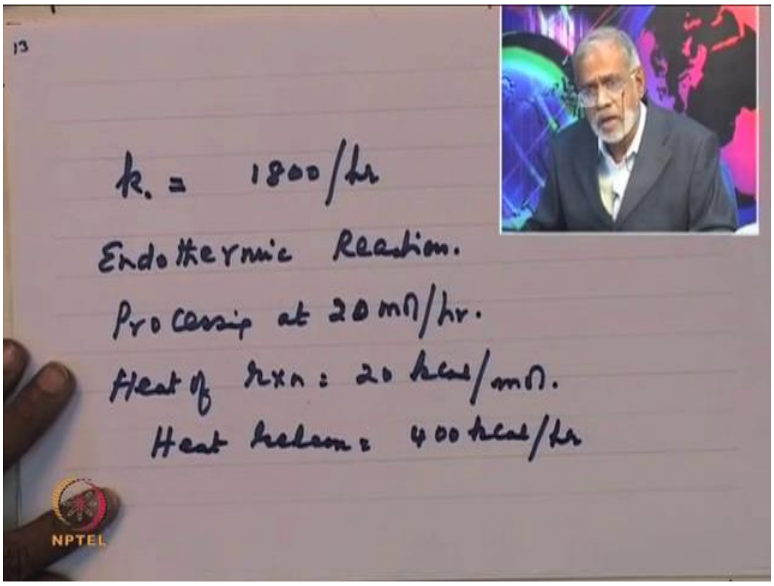

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$k = 1800/hr$

Endothermic Reaction.

Processing at 20 mol/hr.

Heat of rxn: 20 kcal/mol.

Heat release: 400 kcal/hr

Now, let me before we get into this there are few points I want to draw your attention. Let us say, you have a chemical reaction k whose rate constant is let us say 1800 per hour. Let us say you have an endothermic reaction, it is an example; see your processing at let us say 1 mole per hour, and your heat of reaction 21 mole per hours 20 mole per hours, heat of reaction is 20 kilo calorie per mole. Therefore, if you wanted complete conversion you will say that heat release equal to heat to be delivered sorry, 20 into 20 which is 400 kilo calorie per hour. This is 400 kilo cal per hour is what you have to supply is that clear, ok.

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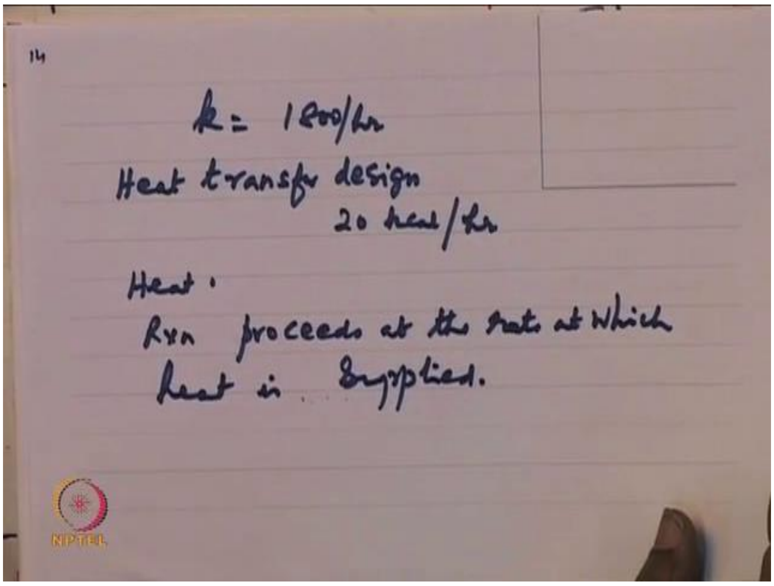

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$k = 1800/hr$

Heat transfer design

20 kcal/hr

Heat :

Rxn proceeds at the rate at which heat is supplied.

Now, let us say you have your heat transfer design; what is your heat transfer design? Your heat transfer design is that you are able to supply 20 kilo calories per hour as an example, 20 kilo calories per hour. And then, what is heat of reaction, what we are saying is that we want to process 20 kilo mole per hour. That means; you must be able to heat supply, you must be able to supply 400 kilo calories per hour to be able to process correct is this clear.

So, what we are saying is that; the amount of heat that you supply is what is going to determine the rated which chemical reaction occurs. Because your chemical reaction itself your k is something like 1800 per hour. And then, this reaction is relatively fast compare to what you are able to supply. What we are saying is that; the rate at which you are able to supply is quite low compare to the rate at which the reaction occurs. On other words; reaction only moves at the rate at which you supply heat, ok. So, we are looking at an instant of a reaction, reaction proceeds at the rate at which heat is supplied. So, if heat is not supplied the reaction does not move. So, we are looking at situations where the rate of heat transfer essentially determines the rate of chemical reaction.

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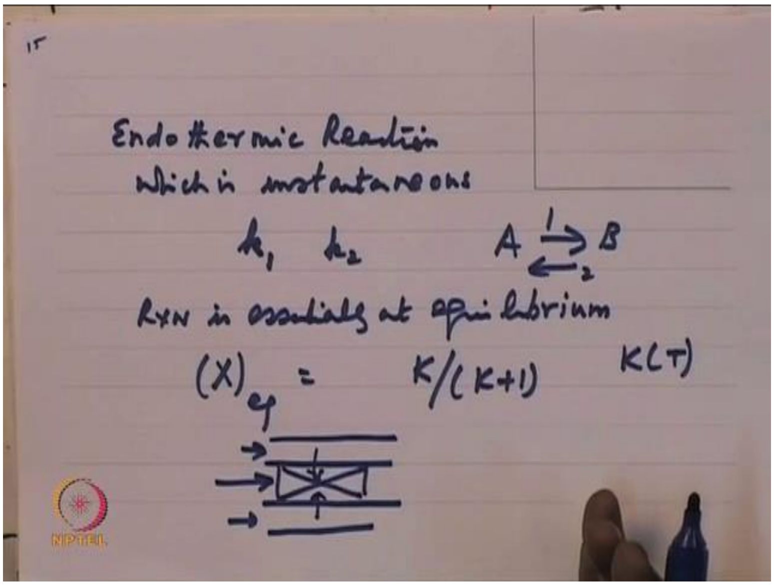

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Endothermic Reaction
Which is instantaneous

k_1 k_2 $A \underset{2}{\overset{1}{\rightleftarrows}} B$

Rxn is essentially at equilibrium

$(X)_{eq} = K/(K+1)$ $K(T)$

Now, what the situations that would be of such situations; let us check an example; an endothermic reaction which is instantaneous. How what do we understand by an instantaneous reaction? By understanding instantaneous reaction is that; if the rate constant k 1 and rate constant k 2 are such there were very large. This is one way of understanding instantaneous reaction. That means; therefore, the reaction is essentially at equilibrium is that clear, because both k 1 and k 2 are very large. Says A going to B, and B going to A this is a reversible reaction, k 1 and k 2 both are very large and therefore, essentially at equilibrium.

So, if a reaction at equilibrium what is the conversion at equilibrium? At equilibrium we have done all these things so, I will write down the answers. If k, equilibrium constant is k then conversion is k by k plus k 1. So, and k is a function of temperature, and this dependence on temperature comes from our van’t hoff’s equation we know all that, ok. We have we have done all that thing we know how k depends on temperature and so on, because comes in van’t hoff’s equation. Therefore, let us say if you have a reaction; let us say this is the jacket through which some fluid circulating this is the reactor, this is some catalyst may be may not be. So, this reaction is able to move forward only because this heat is getting supplied. You have this supply is not there reaction does not move. At every point in the equipment the conversion is as describe by the equilibrium, because the reactions are very fast in relation to the heat of supply. So, that is a example we are considering.

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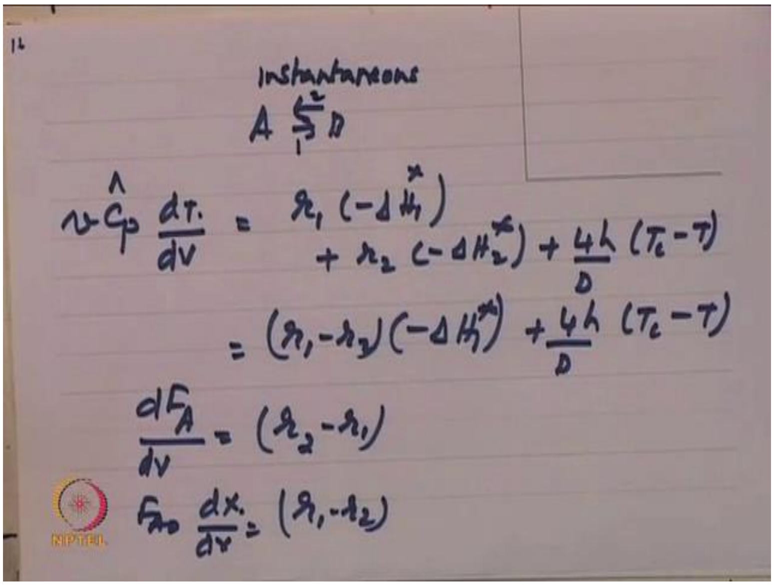

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instantaneous

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

$$v \hat{C}_p \frac{dT}{dV} = r_1(-\Delta H_1^*) + r_2(-\Delta H_2^*) + \frac{4h}{D}(T_c - T)$$

$$= (r_1 - r_2)(-\Delta H_1^*) + \frac{4h}{D}(T_c - T)$$

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

$$F_{A0}\frac{dx}{dV} = (r_1 - r_2)$$

Now, what we would like to do is that; let us say v C p just want to draw attention to our energy balance and sort of draw attention to your delta H 1 star plus r 2 minus of delta H 2 star plus 4 h by d T c minus of T. So, this is our energy balance equation which is also written as r 1 minus of r 2 times minus of delta H 1 star plus 4 h by d into T c minus of T. And, we also know from our material balance, that for a fluke flow reactor it is ok. So, this we know, this is the reaction is A going to B, and B going to A, all right. Or, this is also written as d x d v equal to r 1 minus of r 2.

Now, the question that is A in front of us is; this reaction r 1 and r 2 are given as instantaneous reactions. Now, if r 1 and r 2 was instantaneous which means what r 1 is very large r 2 is very large. So, what is the r 1 minus of r 2? There are 2 quantities both are very large. So, what is the difference between 2 large quantities, it is not easy to tell how large is large we do not know. So, clearly therefore; we not able to make good use of the energy balance equation to solve a problem like this; one of the reason why I am looking at this further considerations in energy balance is to be able to deal with variety of situations; that we made encounter in daily life.

Here, is one such such instants were we have a instantaneous reaction now, when you try to apply this into our energy balance we find that r 1 minus of r 2 which is 1 and 2. Now, r 1 is very large, r 2 is very large and therefore, we do not know what is a r 1 minus of r 2. And, the rate functions themselves are not known, therefore; we do not know what is r

1 minus of r 2. All that we know is that; because r 1 and r 2 are very large therefore, it is essentially at equilibrium at every point in the process. So, we want to use that information to get around the difficulties that we face in using our energy balance, and that is the point of interest to us in this exercise.

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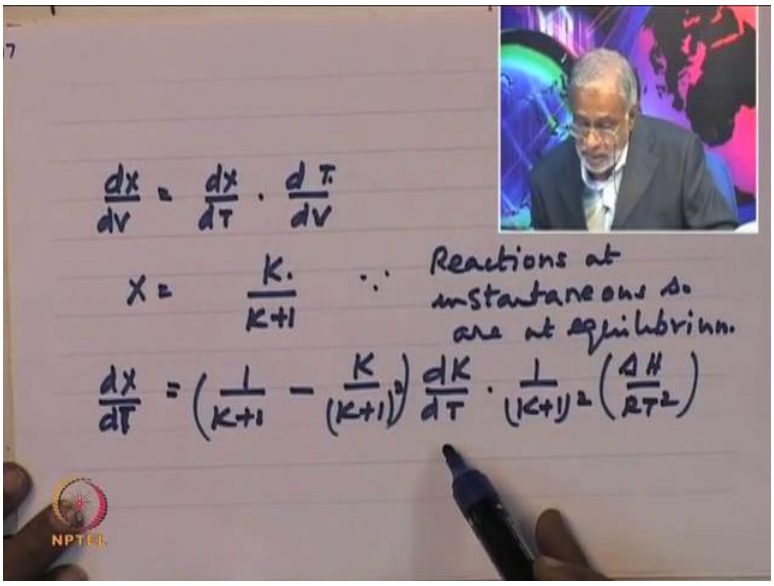

$$\frac{dx}{dV} = \frac{dx}{dT} \cdot \frac{dT}{dV}$$

$$X = \frac{K}{K+1} \quad \because$$ Reactions at instantaneous so are at equilibrium.

$$\frac{dx}{dT} = \left(\frac{1}{K+1} - \frac{K}{(K+1)^2}\right)\frac{dK}{dT} \cdot \frac{1}{(K+1)^2}\left(\frac{\Delta H}{RT^2}\right)$$

Let us see how to do this? To do this we recognize the following. We know that d X d V equal d X d T multiplied by d T d V. Now, we know that X equal to K by K plus 1 this is sense reactions are instantaneous so, are at equilibrium, ok. Now, so what is d X d T now; d X d T equal to we have to differentiate this, I have done that. So, let me write down this K plus 1 minus K by K plus 1 whole square into d K d T multiplied 1 by K plus 1 whole square delta H by R T square. Now, this is I mean you might wonder you know how I have written this without giving you the details so, we can understand this. See when you differentiate this you get let us go through this 1 by 1. So, we get 1 by K plus 1 K by K plus 1 whole square minus sign d K d T and all right.

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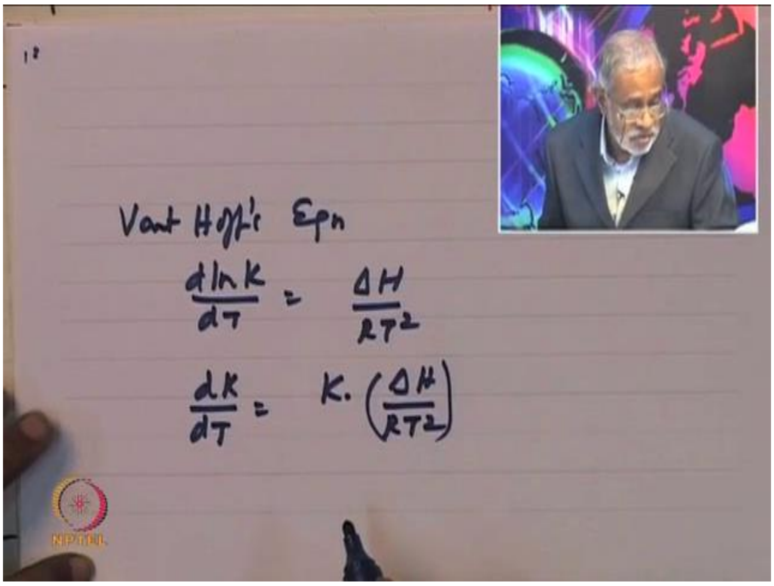

Vant Hoff's Eqn

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

$$\frac{dK}{dT} = K.\left(\frac{\Delta H}{RT^2}\right)$$

And, what is d k d T? Let me write van't hoff's equation here, van't hoff's equation; what does it say d l n K by d T is delta H by R T square correct. Or, d K d T equal to K time's delta H by R T square is it all right, what we are said. So, what we are tried to do is that; we have substituted for all these and got that result. So, let us go through this now substitute and then, simplify I have to simplify it we have got we have got d X d T now, all we have to do is following.

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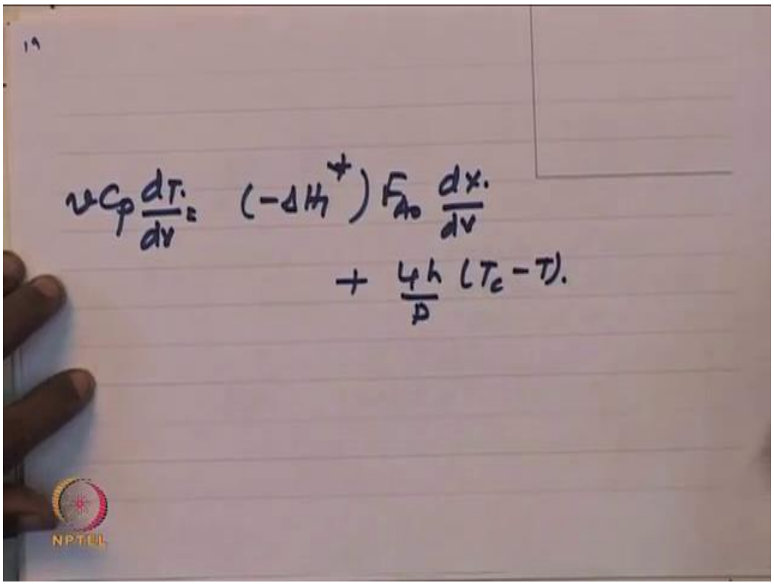

$$v C_p \frac{dT}{dv} = (-\Delta H^{+}) F_{A0} \frac{dx}{dv} + \frac{4h}{D}(T_c - T).$$

So, let us write the energy balance; now, let energy balance is v C p d T d V equal to minus of delta H 1 star F A0 d X d V plus 4 h by d T c minus of T. I hope you understand what we are saying it just look back and recognize all these things.

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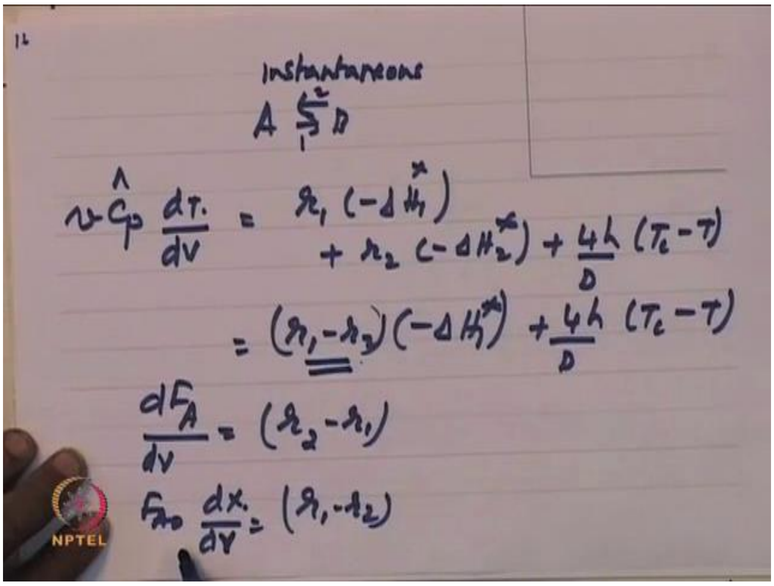

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instantaneous

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

$$\nu \hat{C}_p \frac{dT}{dV} = r_1(-\Delta H_1^*) + r_2(-\Delta H_2^*) + \frac{4h}{D}(T_c - T)$$

$$= \underline{\underline{(r_1 - r_2)}}(-\Delta H_1^*) + \frac{4h}{D}(T_c - T)$$

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

$$F_{A0}\frac{dX}{dV} = (r_1 - r_2)$$

Please, recognize that r 1 minus of r 2 is F A 0 d X d V, correct. Now, since we have difficulty in managing r 1 minus of r 2 what I have done is that; I have replace this r 1 minus of r 2 from material balance and, by F A 0 d X d V. Or, in other words; our energy balance equation is this. So, first term this r 1 minus of r 2 terms I have replaced with d x is that clear.

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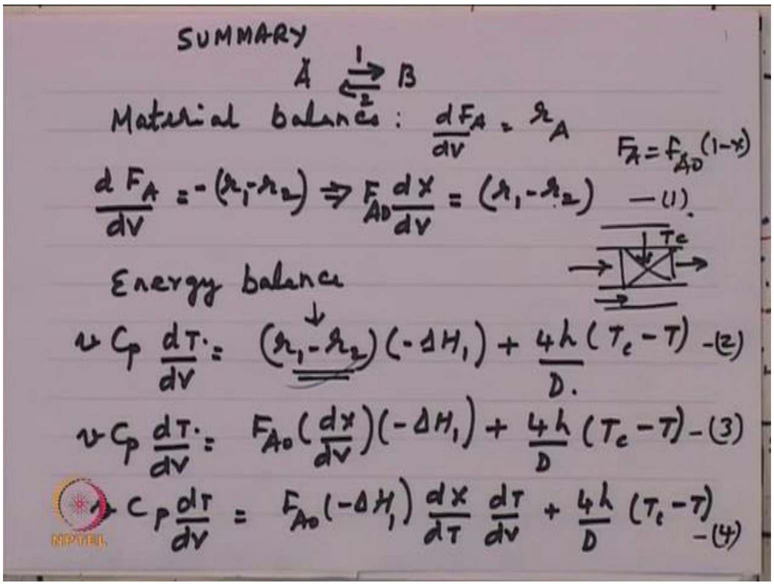
SUMMARY

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

Material balance: $\frac{dF_A}{dV} = r_A$

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

$$\frac{dF_A}{dV} = -(r_1 - r_2) \Rightarrow F_{A0}\frac{dx}{dV} = (r_1 - r_2) \quad -(1)$$

Energy balance

$$v C_p \frac{dT}{dV} = \underline{(r_1 - r_2)}(-\Delta H_1) + \frac{4h}{D}(T_c - T) \quad -(2)$$

$$v C_p \frac{dT}{dV} = F_{A0}\left(\frac{dx}{dV}\right)(-\Delta H_1) + \frac{4h}{D}(T_c - T) - (3)$$

$$c_p \frac{dT}{dV} = F_{A0}(-\Delta H_1)\frac{dx}{dT}\frac{dT}{dV} + \frac{4h}{D}(T_c - T) \quad -(4)$$

So, our reaction of interest is A going to B, and B going to A as an example. Now, we have written material balance which is d F A d V equal to r something we have written for a long time. Now, if you substitute put F A and then, recognizing that r A is what? r A is basically component A is consumed in reaction 1, and it is formed in reaction 2 they have put a negative sign here. Therefore, and if you call F A as F A 0 times 1 minus of x something that we know, if we call F A equal to F A 0 times 1 minus of x based on our understanding of Stoichiometry and so on.

Therefore, we can write the left hand side as F A 0 d X d V equal to r 1 minus of r 2. Something that we know it is not really difficult to understand this so, you have this is the material balance, I call this let us say our equation 1. Now, what is our energy balance? The energy balance is v C p d T d V, we are talking about a fluke flow please understand this fluke flow reactor. That means; our reactor look like this, our reactor looks like this may there is a catalyst here and so on, flow is coming in and flow is going out. So, v C p d T d V is r 1 minus of r 2 delta H 1 plus 4 h by d T c minus of T. This we have written for a long time, you know this heat is getting transferred from T c is the fluid that is flowing in the jacket through which there is a heat transfer fluid flowing.

So, this is a statement of energy balance of for a fluke flow reactor. Where, v C p d T d V is r 1 minus of r 2 minus of delta H 1 plus 4 h this is the heat transfer. What we have done since r 1 minus of r 2 this is very large, because this is very large this quantity is very large what we do. We try and replace this from material balance. So, r 1 minus of r 2 is what F A 0 d X d V so, what is it that we have done v C p d T d V is in the left hand side, if we are knocked out this term and replacing it by from reaction 1. If I call this as reaction 2, what we have done is that; we have replaced r 1 minus of r 2 from reaction 1 in equation 1. In equation 2 so, that this term r 1 minus of r 2 can be now written as F A 0 d X d V ok. Therefore, our energy balance now looks like v C p d T d V which is F A 0 d X d V minus of delta H 1 plus 4 h T c minus of T.

Now, in this formulation what is the advantage that we see; we have got writ of the rate function we have gotten writ of the rate functions. And, they are given in terms of d X d V in principle X is measurable. See the advantage of equation 3 is that; now your quantities are all measurable. Therefore, even though your reaction may be very rapid and therefore, the rate functions is difficult to handle. But X conversions are measurable, positions are measurable. So, we have replaced at difficult situation in to something that we can handle. Now, we want to go further to see what more we can do. So, what we have done here is that; this d X d V we have written as d X d T, and d T d V d X d T and d T d V which something that we can write there is nothing. So, if I call this is equation 4 now, in this form of the equation 4 d X d T and d T d V let us see what benefits that we get.

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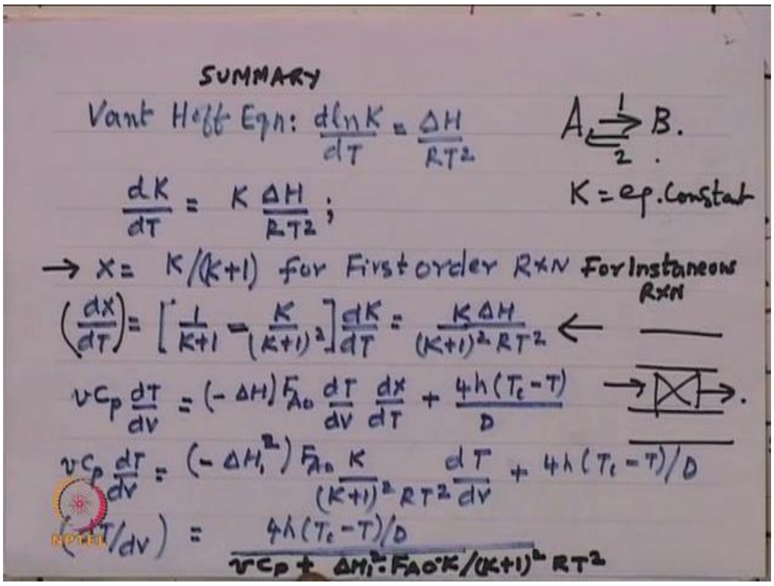

SUMMARY

Vant Hoff Eqn: $\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2}$

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

$\frac{dK}{dT} = K\frac{\Delta H}{RT^2}$;

K = eq. Constat

→ $x = K/(K+1)$ for First order RxN For Instaneous RxN

$$\left(\frac{dx}{dT}\right) = \left[\frac{1}{K+1} - \frac{K}{(K+1)^2}\right]\frac{dK}{dT} = \frac{K\Delta H}{(K+1)^2 RT^2} \leftarrow$$

$$vC_p\frac{dT}{dV} = (-\Delta H)F_{A0}\frac{dT}{dV}\frac{dx}{dT} + \frac{4h(T_c-T)}{D}$$

$$vC_p\frac{dT}{dV} = (-\Delta H_1^2)F_{A0}\frac{K}{(K+1)^2 RT^2}\frac{dT}{dV} + 4h(T_c-T)/D$$

$$(dT/dV) = \frac{4h(T_c-T)/D}{vC_p + \Delta H_1^2 \cdot F_{A0} \cdot K/(K+1)^2 RT^2}$$

Now, let us see what I got here is; let us our reaction is A going to B it is instantaneous. Because it is instantaneous therefore, it is add it is equilibrium and, because it is a equilibrium we can say that extent of reaction X is given by K by K plus 1 where, K is the equilibrium constant. So, k is equilibrium constant and therefore, we can say that X is K by K plus 1. Now, what we are saying now is; that in our previous representation our equation left hand side is related which temperature changes its position or volume. And, the right hand side involves a d X d T and a heat transfer term. This d X d T is a term that we can understand more for the case of an instantaneous reaction, for the case of instantaneous reaction we said K can be given by K by K plus 1 where, K is equilibrium constant.

And, now d X d T which are appears in our equation can be obtained by differentiating X that is what does been done here. So, you notice here is a d X d T from our van't hoff's equation which is well known to you, d X d T is simply K delta H divided by K plus 1 whole square r T square. Let us just understand how it comes. Now, van't hoff's equation says that; d l n K by d T is delta H by r T square that I have written as d K d T equal to K times delta H by r T square, this is nothing very new to you. Now, we know the d K d T is K delta H by r T square. Now, what is d X d T you have to differentiate K by K plus 1 this is what I have done. I have taken the first term 1 by K plus 1 then, I have taken the next term differentiation of this is K plus 1 whole square with a minus sign. And, whole thing multiplied by d K d T is that clear, what we are saying.

So, we can simplify this common denominator is K plus 1 therefore, you get K delta H by K plus 1 whole square r T square. So, on other words; what we are saying here is that; d K d T of our material balance, of our energy balance can now this term d X d T can be represented from this equation here; d X d T is given by k delta H by K plus 1 K plus 1 whole square r T square. Therefore, now I am able to replace that d X d T term of our energy balance equation. I am able to replace this d X d T term and simplify this is what I have done here. So, I have replace the d X d T term here and then, put it as minus.

So, any way you know all that so, I have replaced it I found delta H F A 0 d T d V and then d X d T plus is it all right, what I have done. F A 0 delta H d X d T, d T d V the d X d T I want to replace. I am d X d T is what I want to replace from here, which I have replace here. So, essentially what we have got? What we got is that; because we are able to replace d X d T in terms of d T d V in terms of a equilibrium constant, and so on. So, the equation now looks like this v C p d T d V on the left hand side, and on the right hand side also you have term d T d V and then, heat transfer term, ok.

Now, you can combine this d T d V terms that is what I have done. Now, what it gives you is that the tubular reactor that we have now, that we have this is the catalyst may be. Now, what we have now is that; d T d V that means the rated at which temperature changes with position d T d V can be given as this heat transfer quantity divided by v C p and delta H squared F A 0 K by K plus 1 whole square. The whole thing is denominated I have written it again here.

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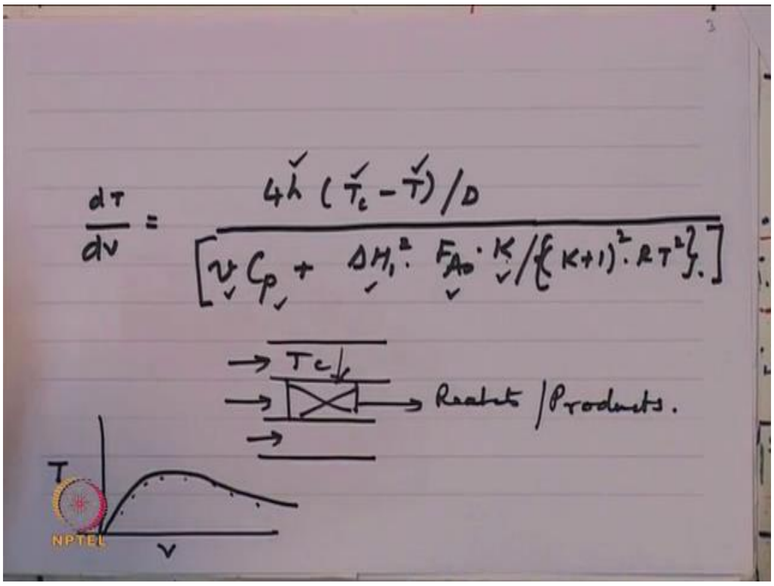

$$\frac{dT}{dv} = \frac{4\overset{\checkmark}{h}\,(\overset{\checkmark}{T_c}-\overset{\checkmark}{T})/D}{\left[\underset{\checkmark}{v}\,\underset{\checkmark}{C_p} + \underset{\checkmark}{\Delta H_1^2}\cdot \underset{\checkmark}{F_{A0}}\cdot \underset{\checkmark}{K}/\{(K+1)^2\cdot RT^2\}.\right]}$$

So, that our tubular reactor let me just show it once again, because this seems to be very important to understand this is; if reagents are going, this is where the heating or cooling medium is going. These are the reactants, and products. So, what we are saying now is that; the rated at which temperature changes with position inside the reaction equipment, it depends upon the heat transfer that means; the amount of heat that you are able to transfer or remove depending upon the in the direction. You know whether it is T is greater than T c or less whatever, it can be this way or the other way. So, heat transfer divided by v C p delta H 1 square F A 0 K by K plus 1 whole square and R T square.

So, what we are now able to do is that; if you have an instantaneous reaction then, this if you want to trace what happens to our temperature, what happens to our temperature with position? Now, you can notice here on the right hand side at position 0, at v equal to

0, h is known T c is known T is known, because T is T 0, v is known which is v 0, C p is known, delta H 1 comes to thermodynamics, F A 0 is known to you, equilibrium constant is known to you, at the temperature. So, or in other words; what we are saying is that d T d V at V equal to 0 is a known quantity.

So, you have a differential equation where, the initial state is known you can do a forward march. Lots of settings are available for you do the integration, and therefore; you are able to tell if it is an exothermic reaction, if wall cooling you might get a profile like this. You can actually do the profiles simply by integration. So, what we are trying to put across to you here is that; even when you have an exothermic reaction which is instantaneous, you are able to handle that reaction, because of the formulation that we have provided. Let us just take this idea a little forward, let us take I mean this is an example that you would like to see whether this applies to you in your practical situation. Rate constant will oppose in the first order reaction, the rate constant k has a units of inverse of time.

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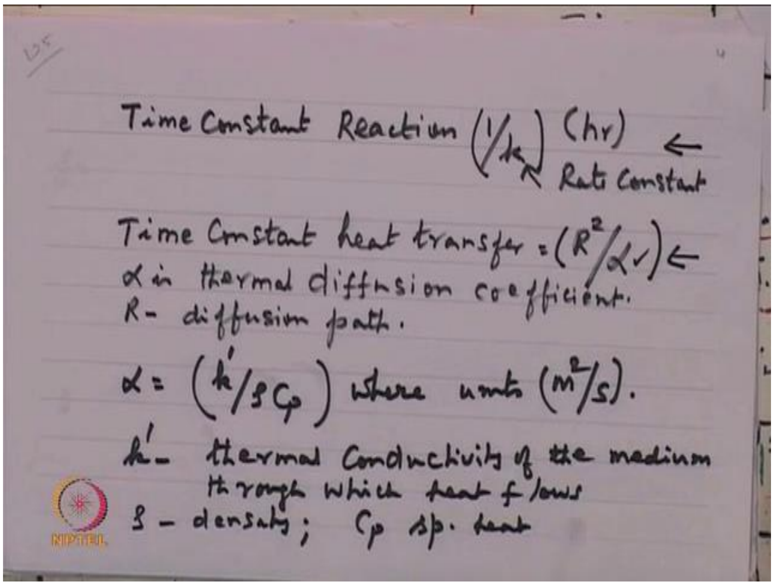

Time Constant Reaction $(1/k)$ (hr) ←

Rate Constant

Time Constant heat transfer $= (R^2/\alpha)$ ←

α in thermal diffusion coefficient.

R- diffusion path.

$\alpha = (k'/\rho C_p)$ where units (m^2/s).

k'- thermal Conductivity of the medium through which heat flows

ρ - density; C_p sp. heat

Or, therefore; time constant for the reaction can be take 1 by K can be sort of as a time constant for reaction, ok. Now similarly, you can look a time constant by heat transfer. So, what is time constant by heat transfer? So, if I know the thermal diffusion coefficient, and if you know the characteristic dimension R squared by d r squared by alpha is the thermal diffusion coefficient. So, R squared by alpha is an measure of the time constant per heat transfer. This is time constant by heat transfer; this is time constant for reaction. Now, if the time constant or inverse of time constant the reaction so, if time constant is very large which means that; that particular step is rate control, ok.

Therefore if in a situation you find that heat transfer rates are very low; it is you know heat transfer coefficients are very low and therefore, essentially the reaction moves only to the extent that you supply or remove heat. Therefore, you can actually design the system simply as heat transfer equipment, because the reaction rates are so fast that everything depends upon the rate at which heat is supplied or removed. This is the point I am trying to put across to you, that every situation you will be able to determine whether. You know; what is that controls your process if heat transfer is controlling? You just look at the heat transfer problem an appropriately if a design your equipment. This is the object of this exercise.