

Chemical Reaction Engineering 1 (Homogeneous Reactors)
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Lecture No 39
Non-Isothermal Reactors Part II

So now what we try to find out is what is the effect of temperature and pressure on these reactions okay first good yes so what do you think I mean how this temperature and pressure is affecting the rates because again here we need rate of reaction right but unfortunately (0:28) rate of reaction depend on temperature as well as concentration, so now you have to find out what is the effect of that temperature on the rate of right okay.

Whether you have if it is Euclidean it is much worse effect will be very drastic, so that is why we have to now discuss those things right, so you just take this equilibrium composition, rate of reaction and product distribution are affected by changes in operating temperature that is 1 point okay what is this product distribution? I think you understand equilibrium composition, will it change with temperature?

Student: Yes.

Professor: Rajesh Shree is thinking.

Student: It is a function of temperature.

Professor: Yes, it is a function of temperature so it affects. Then what about the rate of reaction?

Student: (0:24).

Professor: That should be immediate louder answer like Yes. Okay that is rate of reaction affected by temperature I think it LKG kid will tell okay then what is the product distribution getting affected? What do you mean by product distribution?

Student: (0:40)

Professor: Yes depending on activation energies then you will have some reaction preferred some reaction not preferred and all that, so even your product distribution or multiple reactions is also affected by this temperature. Then what are other things that can get affected? Point number 2 selectivity product distribution will come in selectivity and all that.

Yes product distribution is a general word. Any other thing which can affect temperature effects? Call all files there stored just call and search me files.

Student: (0)(2:22).

Professor: Activation energy is supposed to be independent of temperature, yes something connected to that only we have to tell so search all the files.

Student: (0)(2:34)

Professor: (0)(2:37) rate of reaction affected means that is only.

Student: (0)(2:41)

Professor: Concentration rate of reaction affected means concentration will come, temperature will come.

Student: Heat of reaction.

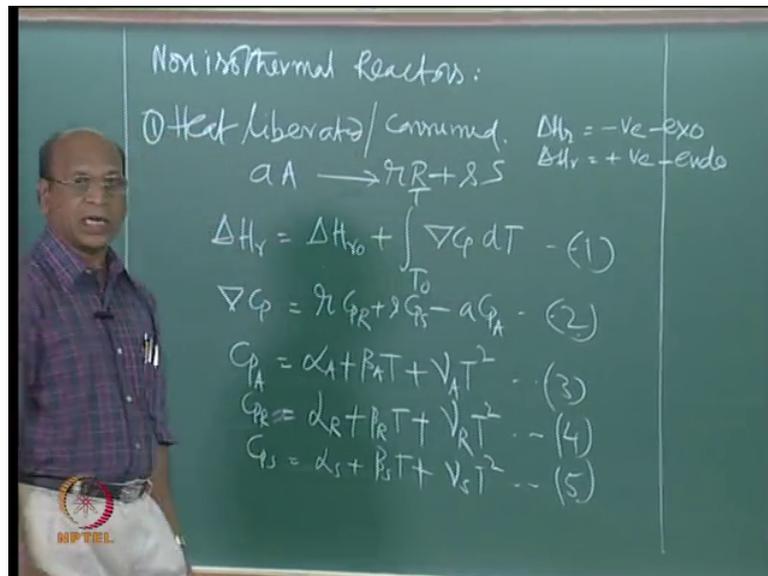
Professor: Heat of reaction ΔH are also will get effected by temperature so the next point is that it affects during reaction which determining heat requirement and exchange of heat okay are also affected by temperature okay so these 2 are most important things and in fact the entire academics depends on these 2 the temperature how it is affecting the rate, equilibrium conversion. You see equilibrium conversion you know one case where equilibrium conversion falls with temperature which case is that? Equilibrium conversion falls or decreases with temperature, which (0)(3:32)?

Student: Reversible exothermic.

Professor: Yes, reversible exothermic, reversible exothermic reactions will have lower and lower conversions and you have higher and higher temperatures. Now you see the academics will depend on that. So if I take okay temperature is very good so I go to very high temperature then conversion will get 1 percent right, so I am not able to convert more the plant will yes it cannot produce more so that is why it may go into the losses or otherwise what you do is you have to put another (0)(4:13) column separator this 1 percent and then remaining 99 percent you have to...yes but not in the sense of recycle reactor that is why you were telling that to increase the conversion to use recycle reactor.

So that is not recycle in fact you are only separating the reactants and products and reactants are again send back to yes for the reaction to be carried out that is all but not as in the sense of recycle reactor. Recycle reactor you are mixing the recycled products with the first stream there you are making this one itself as first stream okay, so that is why many of you get confuse why recycle reactor you know is more efficient than all other reactors because that is the question when I asked you most of you wrote that recycle reactor and when it is used means when you need more conversions. You will never get more conversions there you will always get less conversion than plug flow right okay good, so that is the one then from thermodynamics have to now calculate heat absorbed or heat released and all so we have to now discuss equilibrium conversions these 2 and we have the equation.

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That is why quickly very briefly we will give this equations that is heat liberated or consumed so that means this is exothermic reaction this is endothermic reaction yes that is one case where let us take that I think I know a specific reaction a A go in to r plus R plus s plus S this is the reaction okay, so now I want to calculate Delta H r for this, what is the equation? Delta H r equal to Delta H r not at some standard temperature and then plus T 0 to T del C p into d T okay ((6:30) closed and not writing at all. Why, do you not like equations or what? Okay so this is the equation where del equal to yes r C p R plus s C p S minus a C p A where C p are specific heats I think you know that right, so then here also I have to say that Delta H r negative means what?

Delta H r positive means yes, so this is exo this one is endo that is the conversion means if I give minus Delta H r equal to let us say 10,000 minus Delta H r equal to yes that is

exothermic reaction and on the other hand if I give ΔH_r equal to 10000 that is endothermic reaction that is the convention okay different books may follow differently but that is the convention okay and also we know that C_p also is a function of T all these also functions of temperature $\alpha + \beta T + \gamma T^2$ we are (8:11) only with square okay so then this one is $\alpha R + \beta R T + \gamma R T^2$ this is 4 then this will be $\alpha S + \beta S T + \gamma S T^2$ this is 5 right this is from thermodynamics we know this.

So then actually I have to substitute all this in this and then calculate what is ΔH_r at the required temperature at which I am conducting the reaction? So I may give you ΔH_r not at 25 degree is so much and I can give the temperature is happening maybe around 500 degrees centigrade then if I give all these values we have to substitute here and then integrate and then finally calculate ΔH_r at 500 degrees centigrade okay that is what is the actual heat that is released okay good, so I will also give this integrated expression.

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The image shows a chalkboard with the following equations written on it:

$$\Delta H_T = \Delta H_{T_0} + \int_{T_0}^T (\Delta \alpha + \Delta \beta T + \Delta \gamma T^2) dT \quad (6)$$

$$\Delta H_T = \Delta H_{T_0} + \Delta \alpha (T - T_0) + \frac{\Delta \beta}{2} (T - T_0)^2 + \frac{\Delta \gamma}{3} (T - T_0)^3 \quad (7)$$

$$\Delta \alpha = \nu_R \alpha_R + \delta \alpha_S - \alpha \alpha_A \quad (8)$$

$$\Delta \beta = \nu_R \beta_R + \delta \beta_S - \alpha \beta_A \quad (9)$$

$$\Delta \gamma = \nu_R \gamma_R + \delta \gamma_S - \alpha \gamma_A \quad (10)$$

At the bottom left of the chalkboard, there is a logo for NPTEL (National Programme on Technology Enhanced Learning).

So if I have ΔH_r equal to ΔH_r not plus okay T not to T we have $\Delta \alpha + \Delta \beta T + \Delta \gamma T^2 dt$ which after integration gives me ΔH_r not sorry $\Delta \alpha (T - T_0) + \frac{\Delta \beta}{2} (T - T_0)^2 + \frac{\Delta \gamma}{3} (T - T_0)^3$ yes this is equation number 6 this is equation number 7 okay, so this is ΔH_r where again I have to write $\Delta \alpha$ what is $\Delta \alpha$ equal to $\nu_R \alpha_R + \delta \alpha_S - \alpha \alpha_A$. $\Delta \beta$ equal to $\nu_R \beta_R + \delta \beta_S - \alpha \beta_A$ sorry capital A. $\Delta \gamma$ equal to $\nu_R \gamma_R + \delta \gamma_S - \alpha \gamma_A$ sorry capital A.

$\Delta G = R \ln K$ so this is 8, 9, 10. I am not giving any explanation how you got and all that but anyway it is straightforward you have to substitute there integrate and then group out all those things like this and then you will get the simple form of equation. ΔG are normally used only to minimise the space and minimise the writing okay so that is why this is the one good, so now the next one what we have to also think there is the equilibrium conversions okay,

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Equilibrium Conversion

$$\frac{d(\ln K)}{dT} = \frac{\Delta H_r}{RT^2} \quad (11)$$

$$\ln \frac{k_1}{k_2} = -\frac{\Delta H_r}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (12)$$

So this is one and 2nd one is equilibrium conversion yes. So what is the equation normally we use $d \ln K = \Delta H_r / R T^2$ what is this equation? Yes (13:07) equation and once you integrate this what you get $\ln k_1 / k_2$ because this is equilibrium K so k_1 / k_2 if I have a forward reaction and backward reaction equal to minus $\Delta H_r / R (1/T - 1/T_0)$ not in our sense okay this is equation 12 good. How is this uhh... Equilibrium conversion how do you get here? I have not told anything about equilibrium conversion but I give this equation.

Student: (13:56).

Professor: k_1 / k_2 is related to... because this is nothing but forward reaction by backward reaction so a simplest sense when you have a go into r reversibly so then what is equilibrium conversion?

Student: (14:10)

Professor: In terms of X_a , X_a is by $1 - X_a$ (14:15) I think all that you remember hopefully okay capital K equal to X_a by $1 - X_a$ and you should know how you got it okay very good.

Student: So these are reversible reaction so how can we write ΔC_p as a R product minus reactor there will be some equilibrium conversion also.

Professor: What is it that you talking this is different and that is different.

Student: But H_r you are taken from there.

Professor: Yes this H_r okay yes your problem of this one yes, here when you are doing it we have ΔH_r as constant.

Student: You did from that equation?

Professor: Yes.

Student: So in that equation we assumed it is 100 percent...

Professor: It is a function of temperature.

Student: Over there we assumed it is 100 percent conversion because (15:06) r product minus.

Professor: No 100 percent conversion we have not that will be total ΔH_r , so this is yes that is the truth that at the end I think it is only 100 percent conversion right so you are write for that but in the actual one how do you calculate how much heat released that maximum ΔH_r into minus R_a .

Student: Number of (15:35) present at any time.

Professor: (15:37) anytime when you are...

Student: Will it be valid if the reaction is not going to be completed, whatever...?

Professor: Yes definitely because whatever conversions you get at any point of time is only stoichiometric proportional only stoichiometric proportion only you cannot have any other that is the beauty of stoichiometry it is only the stoichiometric proportion only will react will result finally with the products okay, so that is why that is not a problem but in this equation what we have assumed is that ΔH_r is not a function of temperature not only in this in

most of the chemical engineering calculation we assumed that ΔH_r is not a function of temperature that is justified...

Student: Function of temperature integrate the (ΔH_r) (16:21)

Professor: Yes mathematically it will be very complicated and normally in engineering we do not do that at all because our reaction in any reactor happening over a small range even if you have a non-isothermal come inlet to the outlet maximum you may have some 100 degrees centigrade or 50 degrees centigrade okay over that how much it is affecting that is what you have to check? At means at inlet temperature what is the ΔH_r ?

At outlet temperature what is the ΔH_r if that variation is not much then you assume that ΔH_r is constant but as an engineer what we also do is even if there is not a very substantial change but reasonable change then what do I do? I will take the arithmetic average of these 2 and then say that my ΔH_r is reasonable over this and constant over this range of operation otherwise it is only mathematically complicated if you want to do you can do it right but the only thing is mathematically complicated so that is why, okay Abhishek. So that is why ΔH_r is calculated for final one only right and then ΔH_r multiplied by minus R_a what are the units of ΔH_r ?

Student: (kJ/mol) (17:34)

Professor: Kilojoules or kilocalories per mole then I have to find out what is the rate of release, how do I calculate that? Multiplied by minus R_a what you will get?

Student: (kJ/mol) (17:54)

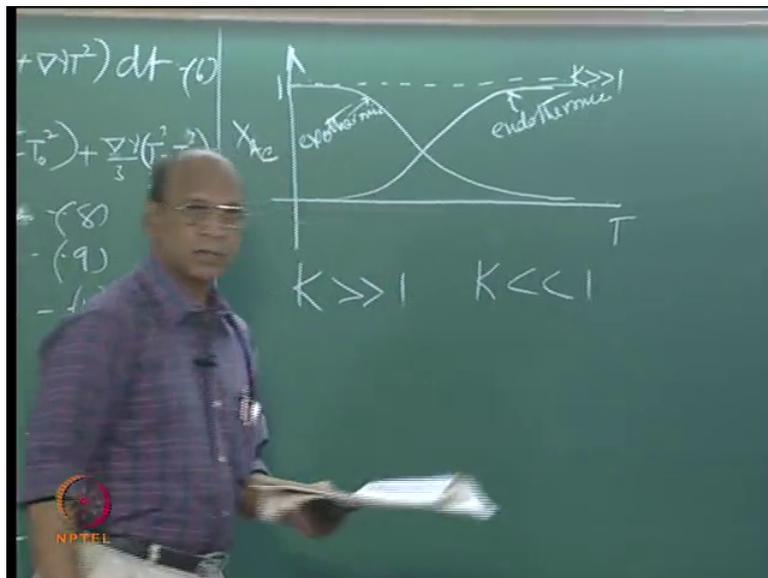
Professor: Kilojoules or kilocalories per second per (m^3) (18:01) so now that is why that volume element will also (kJ/mol) (18:04) minus R_a into $D v_{\text{small } v}$ if I take plug flow reactor or if I take mixed flow reactor it is total V so that will tell me how many calories or how many kilojoules per second released okay that is the rate of heat released right, good. So if it is exothermic reaction knowing that this much heat is released now my process requirement tells me how much I have to remove out of that okay. If you completely remove the temperature will fall and then again conversions may be less now depending on the reaction I am telling okay sometimes less sometimes more.

So that is the reason why I also told you in the beginning you know academics will depend on these how much you have to cool how much you have to heat and also ΔH_r also we need

that information because that will also determine what is the temperature in the system correct. If there is too much ΔH_r definitely temperature is going to increase it is exothermic reaction if it is too much endothermic also ΔH_r then temperature will fall very rapidly then you will have very low conversion rate of reaction equal to almost 0 okay so this is additional parameter which automatically comes into picture when you talking about temperature effects okay, good.

So that is the one and now we will just summarise you points about the thermodynamic information that is required for reactor design, thermodynamic information required for please write that thermodynamic information required for reactor design. In terms of points will go one by one (0)(19:42) beautifully summarised all of these. Now let us take those points and discuss point number 1 thermodynamic equilibrium constant is unaffected by a pressure of the system, by the presence or absence of (0)(19:58), or by the kinetics of the reaction, but is affected by the temperature of the system. How it is also affected also we will draw here.

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So this is X_{Ae} saying that that means a is our key component okay, so this is temperature this is maximum conversion that is one, so now if it is exothermic you will have like this, if it is endothermic that will have like this okay. This is exo exothermic and this is endothermic okay. Point number 2 though the thermodynamic equilibrium constant is unaffected by pressure or (0)(21:07), the equilibrium concentration of materials and equilibrium conversion of reactants and be influenced by these variables point number 3 we will discuss once you note down one by one will discuss later okay.

Point number 3 K for greater than 1 indicates that practically complete conversion maybe possible and that the reaction can be considered to be reversible. Excellent, we will stop there. Okay K for less than 1 next sentence okay for less than 1 indicates that reaction will not proceed to any appreciable extent that is in the direction what we want okay. Number 4, for an increase in temperature equilibrium conversion raises for endothermic reactions and drops for exothermic reactions. I am telling all this because this can be one of my (22:03) yes all this 6 points you have to write you know 2 more will come.

Yes next one number 5, for an increase in pressure in gas phase reactions conversion raises the number of moles decreases with reactions; conversion drops when the number of moles increases with reaction okay good. Number 6 is a decrease in K for all reactions at in the way that an increase in pressure \times reactions. Now what are the meaning of point number 1 because in fact all these things is beautiful summary of thermodynamics that is required for reactions. There are many other things for energy and all that but for reactions wonderful point wonderful summary.

The thermodynamic equilibrium constant is unaffected by the pressure okay and also the kinetics, kinetics also but only thing is it is a function of temperature okay that we should know that is number 1. Number 2 is though the thermodynamic constant is unaffected by pressure and K but the equilibrium compositions will change that is why we add sometimes you know Q and all that to shift the reaction for conversion from one side to the other side right so temperature effects only thermodynamic equilibrium but compositions that means the conversions okay yes the actual composition that is C_A C_B C_R C_S those things will be affected by again K okay yes that is point number 2 good. What is point number 3? Very simple K is for greater than 1 it is almost irreversible reaction that means yes so almost here K you may almost get 100 percent reaction okay this is K for greater than 1.

Student: Does this mean if you give me Gibbs free energy I can tell it as reversible or irreversible without conducting experiment.

Professor: That is what in our 1st class we discussed okay depending upon you know how do you know that 1st of all the reaction is occurring and depending upon Gibbs free energy... because Gibbs free energy again is connected with K , so if ΔG is very large you calculate...

Student: (24:21)

Professor: Exactly now that is what I think you know the 1st few questions what we have discussed there how does a chemical process (24:29). In that the 1st step is to find out whether the reaction is feasible not, how? Go to Delta G Gibbs free energy, calculate Delta G from you know how to calculate we should know the stoichiometric equation if you have stoichiometric equation like that you have the tables where for the components that free energy G is listed okay from there calculate delta G I think that is very good once more I can repeat because some of you still would have not got that idea right calculate Delta G that is equal to minus R t ln K but we have to assume T for a particular T what is K, Right?

So depending on that K value you can say that whether it is reversible, irreversible or kinds of things we can interpret from that okay good. So that is the one and the next one is we are now trying to discuss about the graphical design of non-isothermal reactors, the graphical design that means from we are not going to get exactly the quantitative numbers like okay volume of this is 10 meter cube but the procedure for you know the graphical analysis that is what what we are going to discuss now.

Student: Provided the times is infinite any reacting system provided the times is infinite, can I do that?

Professor: Please repeat again.

Student: Can I write the equilibrium...say time equal to infinity so reaction will eventually...

Professor: Where is time K is coming here because if I know the K value is very large then it is irreversible okay if the K is may be...

Student: So the reaction will go to completion ultimately?

Professor: That is all what you can get from that... the time will not come here.

Student: I am asking about the model if I write (26:12) model for a reacting system.

Professor: What is equilibrium? Is it reaction equilibrium or you are talking about something else.

Student: Reaction equilibrium.

Professor: Reaction equilibrium you do not talk about...

Student: For irreversible reaction also can I write.

Professor: For irreversible reaction what do you want to write tell me, what is that you want to write?

Student: Model of the...

Professor: What model?

Student: Either a kinetic model or equilibrium model.

Professor: What kinetic model?

Student: Kinetic model is conversion of given type... Sir I will ask you separately.

Professor: Now, what kinetic model you are telling for example I have a batch reactor first order reaction and I know the equation, what is the equation for design? Because I have written my model equations and then got okay, for plug flow $K \tau$ equal to...

Student: (())(27:04)

Professor: Yes $K \tau$ equal to let me write that $K \tau P$ equal to $-\ln(1 - X_a)$, so which one you are talking here? Because this equation I got only by writing the model equation that means what is entering, what is leaving and all that but this is for isothermal system what you are writing.

Student: Irreversible reaction...

Professor: You cannot make equilibrium expansion for the reactor.

Student: No, considering the reaction is very fast.

Professor: Yes.

Student: And irreversible.

Professor: Okay.

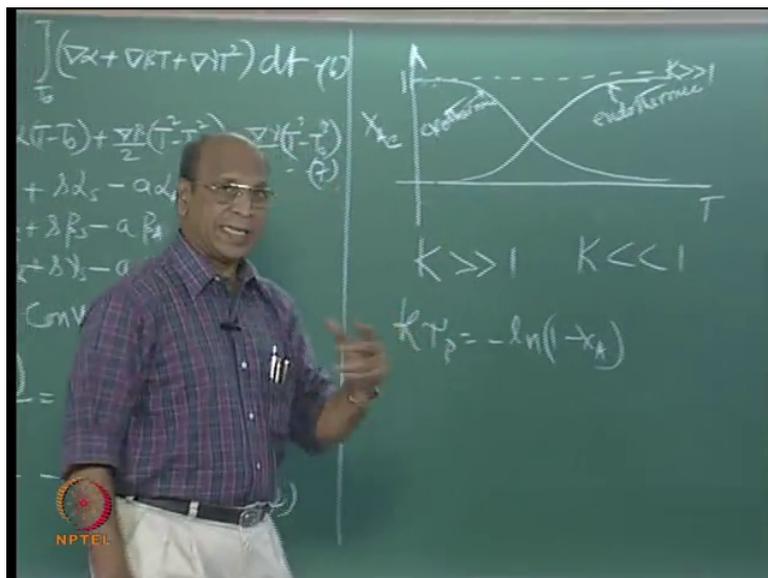
Student: Still I can work for (())(27:36).

Professor: What is the use? Because...

Student: (())(27:41) in kinetics I can go...

Professor: Because x anyway for irreversible you can get 90 percent conversion 99 percent conversion, right but when you have reversible reaction that will limit it will tell you fellow you cannot go to 99 percent you can only go to 60 percent at that temperature, so it is always associated with the temperature, so that is why in the Gibbs free energy you will get temperature versus conversion graph also you can plot that is what is the meaning of this in fact.

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When I am operating exothermic reaction at very low temperatures this is the conversion I can get equilibrium conversion but the disadvantage of operating at very low conversion here the rate of reaction itself will be very low X a you can get that much but the rate is very low this is thermodynamic information okay, so equilibrium conversion almost 1 means I can also get actual conversion almost one but how much time I have to wait because there it is not equilibrium coming it is only the rate of reaction coming when the temperature is very low then the rate of reaction is not very fast right.

So that is why my reaction will be very big because I have to provide that much residence time for the reaction to take place okay, so I think that question of writing a model for equilibrium model for irreversible reaction it will not come into picture at all as far as I know it will not come into picture. What is exactly you are not able to understand because something must be worrying you, something must be bothering you, so what is that point?

Student: () (29:20)

Professor: Okay. So you see I think maybe some of you also may have the same doubt there where we will do here is that if I know from Gibbs free energy I will find out K value that will decide whether I have irreversible or reversible right. Irreversible I can go to any conversion but only thing is depending on the temperature and what conversion that means volume of the reactor maybe more sometimes I told you that sometimes from 0.9 to 0.95 the volume maybe triple or it may be 4 times from 0.95 to 0.96, 97, 98 the volume maybe tremendously increasing so academics will tell you fellow do not go beyond this otherwise all money will go only for constructing the reactor so then I think it is a problem do not go like that again academic analysis that is one thing but that is irreversible.

The moment I have reversible reaction now I know at what temperature I am going to conduct that we should know at what temperature we are going to conduct the reaction, no let us say 150 degrees I am going to conduct the reaction that will automatically fix my equilibrium conversion. If 150 is somewhere here that is what is the equilibrium conversion for reversible exothermic reaction? Beyond that no one can do that is why I feel many a times thermodynamics is guard because that tells you, you cannot go beyond this that is what guard also tells you he will not directly tell you but through other some other system he will tell okay that I think only you can get maximum this degree beyond that you cannot get whatever you try you cannot get that degree I tell you okay.

If your life is written only like okay M. Tech is the maximum degree you may (())(31:06) PHD something will happen you have to leave and then go back that is the guard's law that is all that is the point beyond that you cannot cross. Exactly with thermodynamics so will tell you X a e here only 60 percent you can never cross that but sometimes we cheat we have what is called process intensification. If it is reversible reaction than what we do is we will take out the product so that only always it is forward reaction, so for reaction alone means very good I mean I can increase the conversion so that is cheating also is there you also cheat sometimes so you may not get degree from IIT Madras you may buy one from any place. Correct as there are many places who are selling PHD degrees yes and then you are very happy I got the degree okay even though God said you cannot do it, he said only you cannot do it not get it. Okay

Student: (())(31:59)

Professor: Range of K for reversible reaction around 1, 2, 3 you cannot tell even 0.5 okay so that again automatically that K value whatever you get from the reaction itself that depends

on the temperature it will be fixed by temperature limit right beyond certain temperature slightly that flexibility is there with you, you can conduct the temperature over 50 degrees okay or maybe 100 degrees depending on each case but we cannot generalise that K must be only this well for reversible reaction you can never, right and the example which I gave early asked you know $k = \frac{X_a}{1 - X_a}$, if K is equal to 1 what is the equilibrium conversion?

Student: 0.5

Professor: 0.5 that is all you cannot go beyond that, so like that okay but that is also fixed at one temperature right because K changes with some other temperature, so that is how...that is only you cannot fix exactly what is this value must be like this. That depends on the process, type of reaction, materials of construction many things will come into picture. Okay Abhishek, not able to get...?

Student: (0)(33:18)

Professor: That (0)(33:28) will be 10000.

Student: (0)(33:30)

Professor: That K only I am telling that K is 10000 that you got already K but only thing is that $K = \frac{k_1}{k_2}$. This $K = \frac{k_1}{k_2}$, so what is the meaning of 10,000? The backward reaction is almost 0 that is why you were telling that it is irreversible it is only going for one direction you got already that, right. The K value, are you talking about the equilibrium constant or red constant?

Student: (0)(34:08)

Professor: There is equilibrium constant which is a very large value because Gibbs free energy when you calculate and then get very large value that means there is a K value. If you have stoichiometry and if you have the components those components have that G values you can calculate and then when you calculate you will get let us say 20,000, so your idea is okay my forward reaction is very large very fast and my backward reaction is very small so this is theoretically reversible reaction but practically it is irreversible you have K value, you got K value.

Student: (0)(34:45) till (0)(34:56)

Professor: There is no purely irreversible.

Student: (0)(35:00)

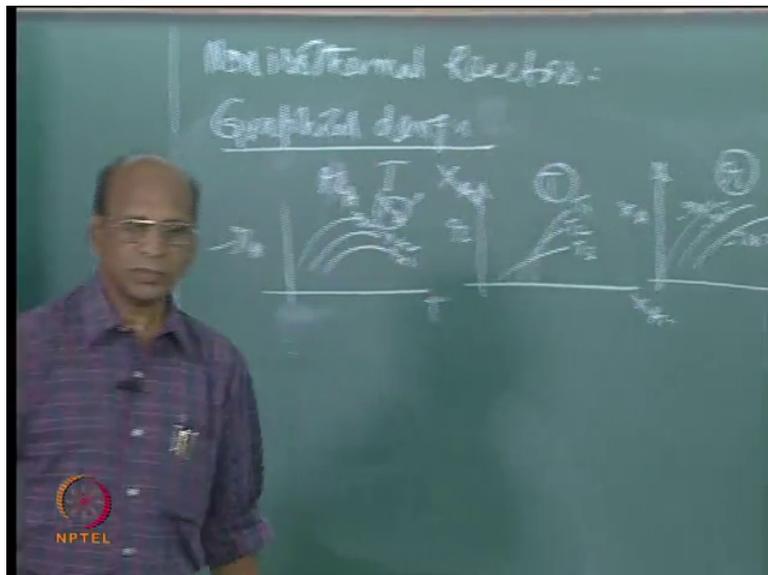
Professor: Yes that means you know you will have purely irreversible (0)(35:05) equal to 0 you will get infinity yes okay that is purely theoretically. So that is why what you are taking there is that a forward reaction is very large when compared to backward reaction that is why you know there is one statement that all reactions are reversible, correct? So then depending on the value of K you decide whether you have yes and as Abhishek asked we cannot fix what is the value for capital K right but you can specify temperature automatically capital K is fixed because k_1/k_2 , you can also get in a different way you can actually conduct kinetic expressions get k_1 value get k_2 value and also...at a given temperature again you can also get K there is to check your thermodynamics as well as kinetics not able to understand?

Student: (0)(35:56)

Professor: Okay good. So the next one is the graphical design for isothermal reactors what is the graphical design?

Student: (0)(36:09)

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Professor: Okay I think (0)(36:17) reactions are there graphical design yes for isothermal you tell me non-isothermal is just above.

Student: 1 by minus R a.

Professor: Yes so 1 by minus R a versus?

Student: X a.

Professor: But what is the problem here or what is the problem that is going to be here?

Student: More than 1

Professor: You want now another variable.

Student: Temperature.

Professor: Now you have 2 (())(36:38) actually three-dimensional okay so again we cheat there instead of drawing 3 dimensional graph what you do? We fix 1 parameter and then draw the other 2 that is all so because I have 3 here what are the 3 I have rate, temperature, X a these are the 3, so for isothermal is easy for me because I think this fellow will be sleeping so these 2 only will be active so we plot, so because there are 3 now you can draw a 3 dimensional graph, 3 dimensional graph we cannot understand okay so that is why we better go for two-dimensional graph by fixing yes many a times we say parameter. What is the difference between a parameter and the variable?

Student: (())(37:39)

Professor: Parameter will be constant variable will be variable that is what the meaning is? So what is the meaning?

Student: (())(37:47)

Professor: So parameter is a constant.

Student: (())(37:57)

Professor: Yes tell me what is parameter then.

Student: (())(38:06)

Professor: Yes variables are shown in X and Y parameters are shown as fixed numbers and then only for that particular value you see the behaviour and then again increase or decrease and then see how the behaviour is changing that is only for cheating you know because we cannot understand three-dimensional graph that is why what we are doing here? Now we can also plot here the graphs like this is minus r A versus okay temperature I can plot, good.

Similarly I can also plot r versus X_a and we can also plot X_a versus temperature so here r will be parameter and here temperature will be parameter and here X_a will be parameter.

So any one of these things we can choose okay but normally what we choose is yes in fact if you brought minus r_A versus temperature general graphs you may have like this, like this. This may be X_{a1} , X_{a2} , X_{a3} so in this case r versus X for different temperature you may get something like this yes something like this. This is T_1 , T_2 , T_3 just I am showing some general graphs or otherwise if I plot X versus T you may get okay like this, so this will be minus r_{A1} , minus r_{A2} , minus r_{A3} these are the 3 different graphs you get but what actual type of graph you get we can also derive that is what, what I am going to do okay good anyway I think tomorrow we will meet and see actually we have not covered much in non-isothermal, so that is why this also can be included in the examination.