Chemical Reaction Engineering

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Module No. # 02

Lecture No. # 04

Thermodynamics of Chemical Reactions: Part II

Friends, let us continue our discussion on thermodynamics and chemical reactions. And to recap what we saw in our last session, if you have a reaction of the kind, let us say summation u j a j equal to 0.

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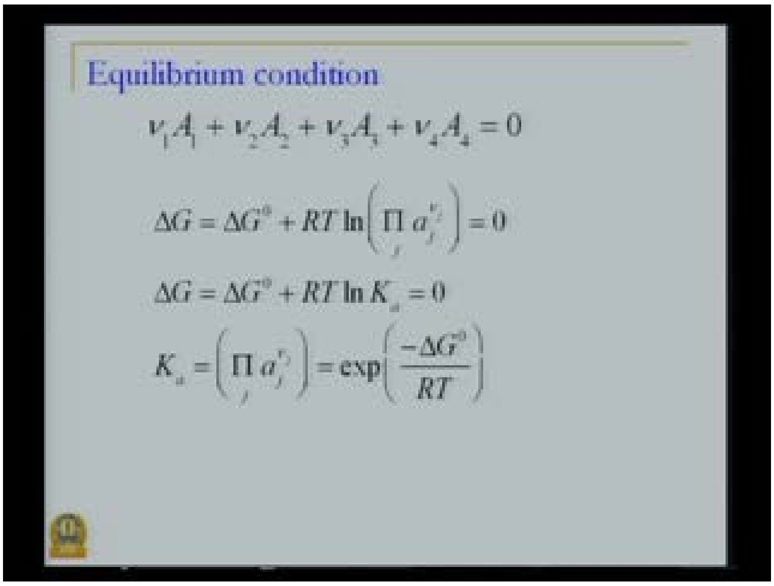

Equilibrium condition

$$\nu_1 A_1 + \nu_2 A_2 + \nu_3 A_3 + \nu_4 A_4 = 0$$

$$\Delta G = \Delta G^0 + RT \ln\left(\prod_j a_j^{\nu_j}\right) = 0$$

$$\Delta G = \Delta G^0 + RT \ln K_a = 0$$

$$K_a = \left(\prod_j a_j^{\nu_j}\right) = \exp\left(\frac{-\Delta G^0}{RT}\right)$$

Then, the condition of equilibrium works out to be summation nu j mu j, where mu j is the chemical potential equal to 0. And from there, we saw that, we can define the equilibrium constant K a as product of activity of species j raise to nu j and product over all species j. So, before we proceed further, let us take few examples and see how this information is useful.

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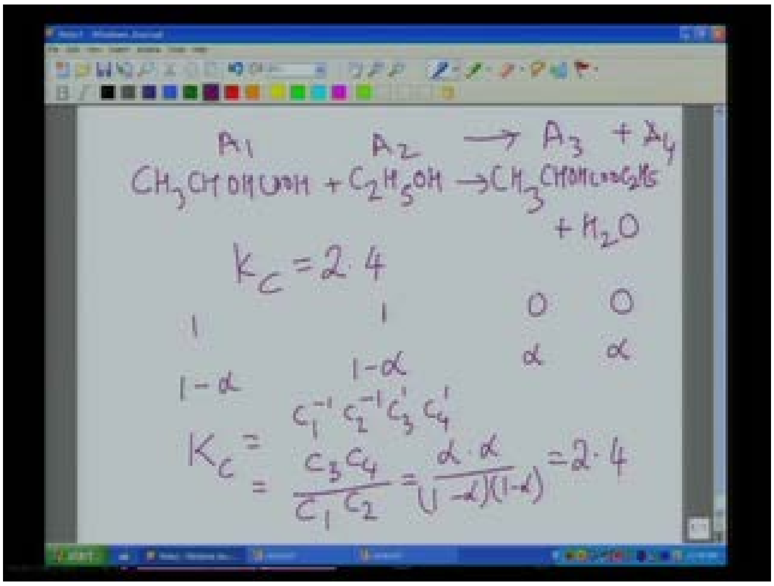

$A_1 \quad A_2 \rightarrow A_3 + A_4$

$CH_3CHOHCOOH + C_2H_5OH \rightarrow CH_3CHOHCOOC_2H_5 + H_2O$

$K_c = 2.4$

$1 \quad 1 \quad 0 \quad 0$

$1-\alpha \quad 1-\alpha \quad \alpha \quad \alpha$

$K_c = C_1^{-1} C_2^{-1} C_3^{1} C_4^{1} = \frac{C_3 C_4}{C_1 C_2} = \frac{\alpha \cdot \alpha}{(1-\alpha)(1-\alpha)} = 2.4$

So, let us say that we have a reaction in which reaction in which lactic acid reacts with ethanol to give ethyl lactate plus water. So, we have a reaction esterification of lactic acid, this is lactic acid, ethanol giving ethyl lactate and water. Ethyl lactate is one of the important components of making biodegradable polymers and it has several other uses as well.

The equilibrium constant K C from thermodynamic considerations comes out to be 2 point 4. So, now we would like to find out, how much of ethyl lactate can we get, and remember this is the maximum ethyl lactate that you can get, because you cannot go beyond equilibrium, equilibrium is the upper limit. So, to do this calculation, let us say that we started with 1 mole of ethyl, 1 mole of lactic acid, 1 mole of ethyl alcohol or ethanol and 0 moles of ethyl lactate and water. And our extent of reaction is, let us say alpha, so at any given time, 1 minus alpha is what lactic acid is remaining, 1 minus alpha is what ethanol is remaining and alpha each of ethyl lactate and water is formed. So, let us label this species A 1, A 2, reaction is A 3 plus A 4.

So, now we can define our equilibrium constant, since note here that, I have said our equilibrium constant with superscript or rather subscript C, which denotes I am working with concentrations, so liquid phase reaction so easy to work with concentrations. So, this we can define as product of C 1 stoichiometric coefficient minus 1, C 2 stoichiometric coefficient minus 1, C 3 and C 4 each with stoichiometric coefficient 1. This, we can conveniently write as C 3 C 4 divided by C 1 into C 2.

So, now let us put our compositions or concentrations of all these species. So, this is alpha into alpha divided by 1 minus alpha into 1 minus alpha and as per our thermodynamics, this is 2.4.

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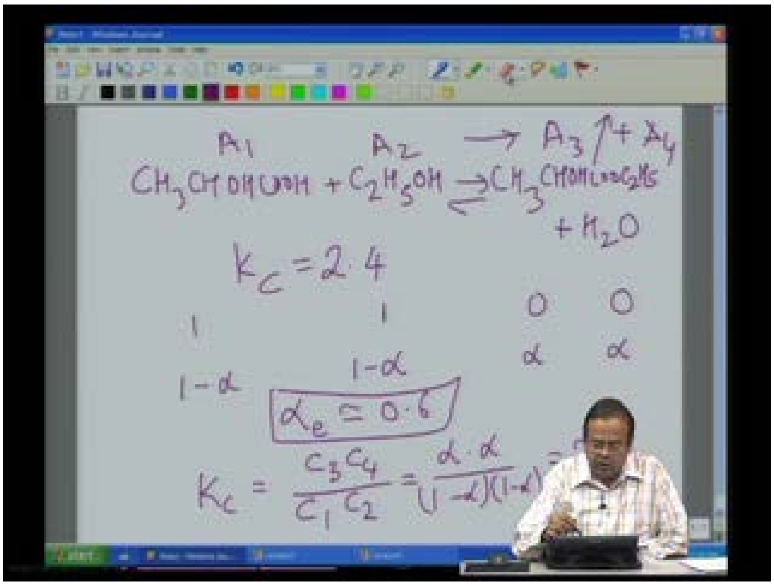

$$\overset{A_1}{CH_3CHOHCOOH} + \overset{A_2}{C_2H_5OH} \rightleftharpoons CH_3CHOHCOOC_2H_5 + H_2O \qquad \longrightarrow A_3 \uparrow + A_4$$

$$K_c = 2.4$$

$$\begin{array}{cccc} 1 & 1 & 0 & 0 \\ 1-\alpha & 1-\alpha & \alpha & \alpha \end{array}$$

$$\boxed{\alpha_e \simeq 0.6}$$

$$K_c = \frac{C_3 C_4}{C_1 C_2} = \frac{\alpha \cdot \alpha}{(1-\alpha)(1-\alpha)} =$$

I can now, so this is my this is my equilibrium value; so, there is only one unknown alpha and I can solve it and I get alpha equilibrium approximately 0.6. What this implies is that, at equilibrium if we start with 1 mole of 1 mole of lactic acid, at best you can get 0.6 moles of ethyl lactate, and reaction cannot proceed beyond that, roughly 60 percent conversion.

So, now that raises a question, should we just stop here or are there any ways we can overcome this limitation. Indeed, there are ways and as you can you can think in the following manner. For example, while this reaction is going on, suppose I remove this ethyl lactate by some means, let us say distillation. So, if I remove this https://www.google.com.np/search?q=one+mole+of+ethanol+lactic+acid&spell=1&sa=X&ei=Pr-UUYbyLoPxiAeF4oGgAg&sqi=2&ved=0CCQQvwUoAA&biw=1280&bih=895ethyl lactate by some means, then what will happen? The reaction will go from lactic acid lactic acid and ethanol to ethyl lactate, but ethyl lactate has been removed from the system. So, these reactions will continuously keep going from left hand side to right hand side because, equilibrium will will will not be reached now, because we are continuously removing this, mathematically what will happen is the following. Suppose that I say that, I remove some quantity of ethyl lactate, so what is beta is the quantity that I am continuously removing.

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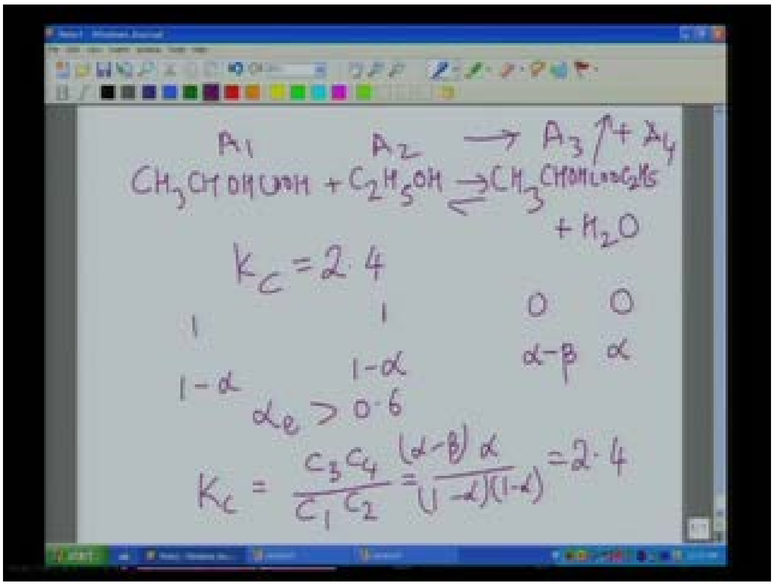

$$A_1 \qquad A_2 \longrightarrow A_3\uparrow + A_4$$

$$CH_3CHOHCOOH + C_2H_5OH \rightleftharpoons CH_3CHOHCOOC_2H_5 + H_2O$$

$$K_c = 2.4$$

$$1 \qquad 1 \qquad 0 \qquad 0$$

$$1-\alpha \qquad 1-\alpha \qquad \alpha-\beta \qquad \alpha$$

$$\alpha_e > 0.6$$

$$K_c = \frac{C_3C_4}{C_1C_2} = \frac{(\alpha-\beta)\alpha}{(1-\alpha)(1-\alpha)} = 2.4$$

So, now what we have to change in this equation is that, our definition of equilibrium constant and the value is same, but this is now, alpha minus beta into alpha. So, alpha minus beta into alpha divided by 1 minus alpha into 1 minus alpha and this will be now 2.4. If beta is 0, I got our, we got our, alpha equilibrium as 0.6, but for any non zero value of beta and of course, we are looking for positive values of beta. You can see that these equations will lead to a solution where, now alpha e will be greater than 0.6 depending on what is this value of beta.

In other words, we are able to overcome the limitations of thermodynamics by combining reaction with distillation. So, we have reactive distillations and thereby we are overcoming this limitation. So, the point is that, thermodynamics therefore tells us a whole lot about how we should operate our reactor.

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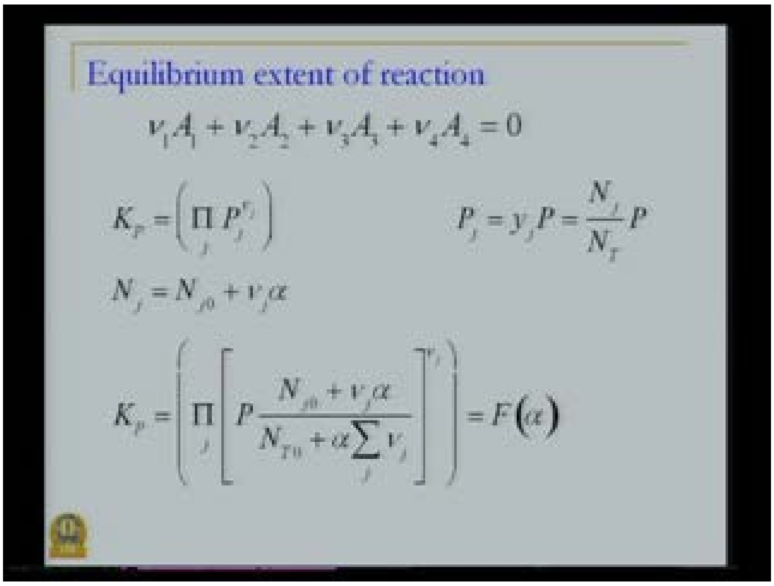

Equilibrium extent of reaction

$$\nu_1 A_1 + \nu_2 A_2 + \nu_3 A_3 + \nu_4 A_4 = 0$$

$$K_p = \left(\prod_j P_j^{\nu_j}\right) \qquad P_j = y_j P = \frac{N_j}{N_T} P$$

$$N_j = N_{j0} + \nu_j \alpha$$

$$K_p = \left(\prod_j \left[P \frac{N_{j0} + \nu_j \alpha}{N_{T0} + \alpha \sum_j \nu_j}\right]^{\nu_j}\right) = F(\alpha)$$

Let us go little further and these are some of, last time we stopped here, this is this is basically the equation we just not used for calculating F, calculating the value of alpha, that is what equilibrium value we will we will get. Now, a close examination of this function reveals some interesting interesting property, although we would not go into the mathematical details of this, but you can you can believe me when I say that, if remember our our equation is K p equal to F of alpha, so that value of alpha which satisfies these equation is my equilibrium value.

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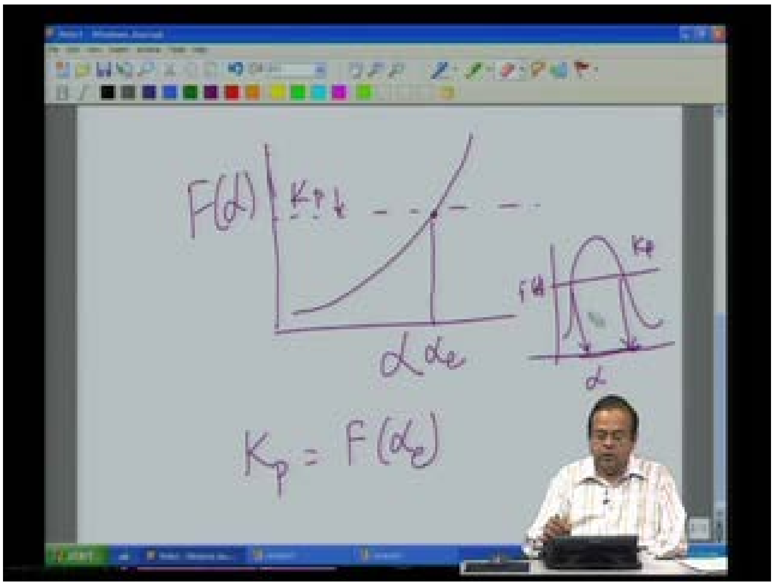

Now, it turns out that, if you look at this function F of alpha versus alpha, it is always a monotonic function. That means, it is continuously increasing as alpha alpha increases and we are looking for solution alpha e such that F of alpha is equal to K p, so graphically, I can put some value K p. So, suppose this is my K p value, then wherever K p becomes F of alpha, that is this particular point, this is my alpha alpha equilibrium; this leads to several interesting observations.

Firstly, F of alpha is a non-linear function, but it is a monotonic function. So, there is a unique value of alpha, see what is, it is a monotonic function, what is a non monotonic function? This is a non monotonic function, it goes up and down. So, now if this was my, for some reason if this was my alpha and if I had my K p value over here, there are two possible possible solutions. However, real thermodynamics, one can actually show it, this never occurs; so, this is the only possibility. There is another interesting observation which we will use to see some properties of equilibrium.

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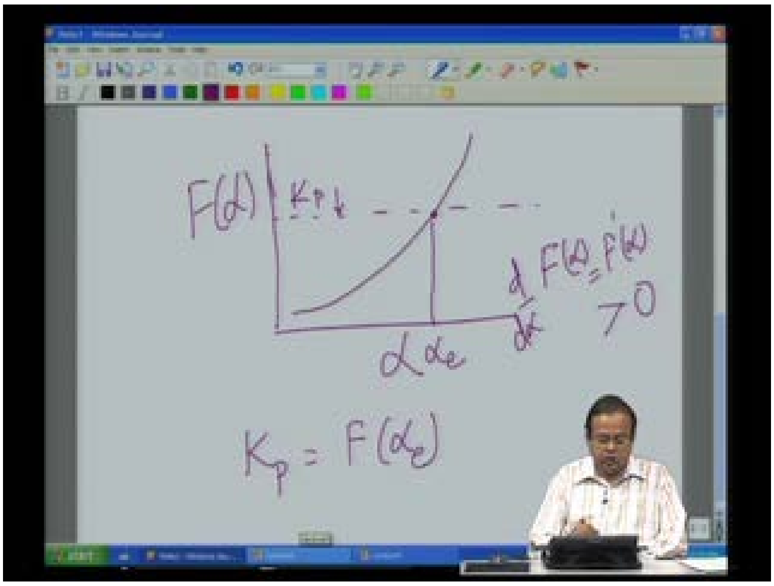

If you look at this function, it is monotonic, which implies that the derivative of F of alpha with respect to alpha or F prime alpha is always positive. So, F prime alpha is always positive, that means the derivative of this function is always positive.

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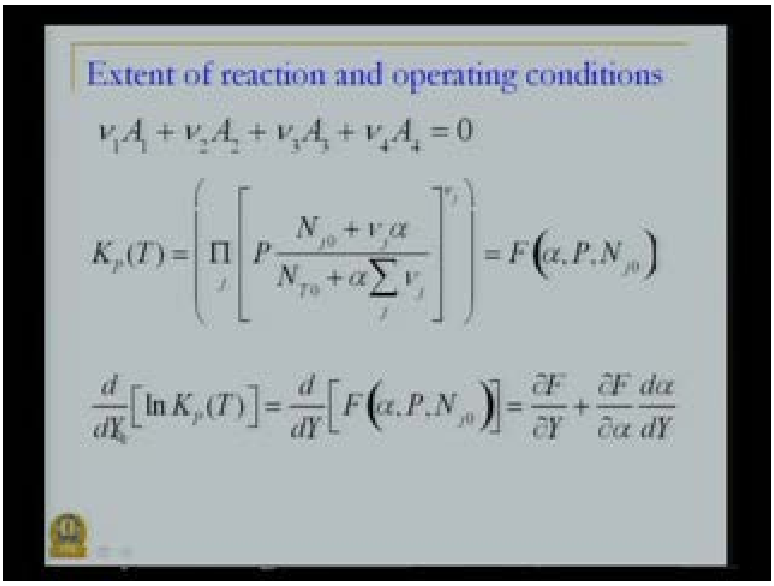

Extent of reaction and operating conditions

$$\nu_1 A_1 + \nu_2 A_2 + \nu_3 A_3 + \nu_4 A_4 = 0$$

$$K_p(T) = \left(\prod_j \left[P \frac{N_{j0} + \nu_j \alpha}{N_{T0} + \alpha \sum_j \nu_j} \right]^{\nu_j} \right) = F\left(\alpha, P, N_{j0}\right)$$

$$\frac{d}{dX_k}\left[\ln K_p(T)\right] = \frac{d}{dY}\left[F\left(\alpha, P, N_{j0}\right)\right] = \frac{\partial F}{\partial Y} + \frac{\partial F}{\partial \alpha}\frac{d\alpha}{dY}$$

Now, why is this interesting? Let us go back to our our condition of equilibrium and re-examine re-examine this, let us say, for these general reaction nu 1 A 1 plus nu 2 A 2 and so on equal to 0, we got our equilibrium constant K p as a function of alpha, extent of reaction and solution of this for a given condition whatever is the value is my value of alpha e. Now, let us examine this F of alpha, we see several things here. Let us start with nu j, these are the stoichiometric coefficients and there is there is nothing much we can do about it, given reaction, this conditions are conditions are fixed.

So, if we look at this function, this function is dependent on alpha and we saw its behaviour just few minutes back, but it also depends on pressure p. So, it is a function of pressure, it is also a function of how many moles of species that we start with. That is, in our lactic acid example, depending on whether I start with 1 mole of lactic acid or 2 moles of lactic acid, I will get different value of N j 0 and so, this is a function of N j 0. And from our thermodynamic considerations, for a perfect gas mixture, assuming perfect gas mixture, K p is a function of temperature.

So, now examination of this equation allows us to look at what happens to the extent of reaction under different operating conditions. Under different operating conditions, what happens to the extent of reaction? If I know that, then I can decide what operating conditions I should be using. The choice is obvious, whatever that leads to increased value of extent of reaction is the condition we are looking for, and so how do we how do we find out?

Slight slight algebraic algebraic manipulation of this gives us, that is, we take derivate of this function with respect to any operating condition, operating condition Y can be any operating condition, temperature, pressure, or even the moles and so on. Then we can take a derivate of F and since F depends on operating, because operating conditions are appear also in F. So, we can express it as del F del Y, the partial plus how F depends on alpha and how alpha depends on Y.

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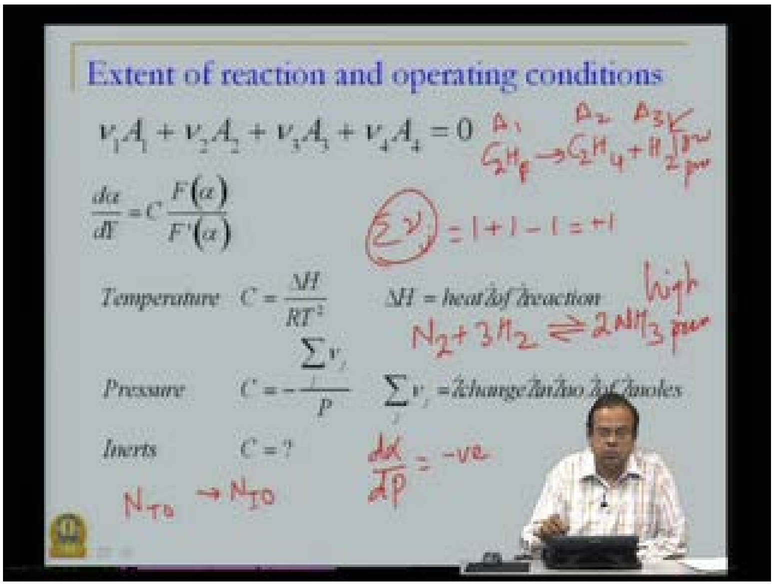

Extent of reaction and operating conditions

$\nu_1 A_1 + \nu_2 A_2 + \nu_3 A_3 + \nu_4 A_4 = 0$

$\frac{d\alpha}{dY} = C\frac{F(\alpha)}{F'(\alpha)}$

Temperature $C = \frac{\Delta H}{RT^2}$ ΔH = heat of reaction

Pressure $C = -\frac{\sum_j \nu_j}{P}$ $\sum_j \nu_j$ = change in no of moles

Inerts $C = ?$

So, if we now take this two together, we get the following. For this reaction, how alpha changes with operating condition is given in a form of some constant C multiplied by F of alpha divided by F prime of alpha. Now, F prime is always positive, F is also positive. So, how alpha depends on a given operating condition that is this derivate, its sign will be determined by sign of this constant C and let us look at look at some of the operating conditions. For example, if you, if our y is temperature T, then this constant C is delta H by R T square; what is delta H, delta H is the heat of the reaction.

So, C depends on, the the the sign of C depends on sign of delta H, because R is a universal gas constant, T is the temperature, these are all positive. So, if delta H is positive, that means we are looking at endothermic reactions, then del d alpha d T is positive or in other words, alpha will increase as temperature increases, if the reaction is endothermic. If del H or heat of reaction is negative, that means, we are looking at looking at exothermic reaction, then del alpha del T will be negative, that means alpha will decrease as the temperature is increased.

So, we now know that endothermic reactions are favored or the equilibrium constant or equilibrium extent of reaction is higher, if temperature is higher and for exothermic reactions, the reverse is true. What happens if if if we change pressure? Now, it turns out the constant C, if in this case is summation nu j of this stoichiometric stoichiometric coefficient. Now, what do we what do we mean by that? Let us let us let us take this reaction of ethane formation.

So, what do we have here? Let us say A 1, A 2, A 3, so what is summation nu j? That is addition of stoichiometric coefficient, 1 plus 1 from the product side minus 1, that is plus 1. So, what is happening in these reactions? This reaction is accompanied by increase in number of moles and that is reflected in summation nu j value, which is positive. So, if nu j summation nu j is positive, that means, there is increase in number of moles, then then what will what will happen to our d alpha d p? That will be negative or in other words, for cracking of ethane as we increase pressure, the equilibrium extent of reaction decreases.

So, this now explains why pressure should be low for this reaction, because if you have high pressure, then the extent of reaction or equilibrium is adversely affected, because there is increase in number of moles. If there is a decrease in number of moles, what can you expect now? The converse, that is if the reaction is accompanied by decrease in number of moles, that means, this summation nu j is this one over here is negative, then C will be positive or in other words, in that reaction, d alpha d p will be positive. So, those reactions in which there is a decrease in number of moles, we have to carry them at high pressures, if there is an increase in number of moles, we have to carry it at low pressures.

Now, tell me what should happen with this kind of reaction? Ammonia synthesis, 2 minus 3 minus 1, again summation nu j 2 minus 3 minus 1, so minus 2, that means there is a decrease in number of moles, so ammonia synthesis has to take place, it is a high pressure reaction, this is a low pressure reaction; this is how the operating conditions are determined. Same thing for temperature, we will come look at temperature once again, but let me just leave it for you to figure it out. What happens if there are inerts in the system? Now, how does inerts affect the equilibrium? Recall that, F of alpha has N T 0, N T 0 has inerts in it, so if we change inerts, N T 0 will change, therefore alpha will change, I will I will I will I will leave it for you to work it out, that what what happens if you increase the inerts. Let me give you a hint, in this reaction we add steam as inerts, I think you should be able to able to take it forward from there.

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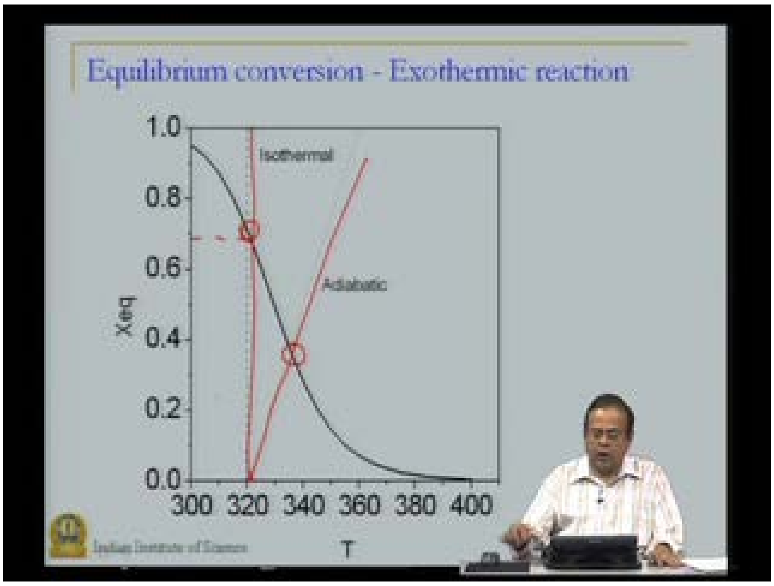

Equilibrium conversion - Exothermic reaction

Let me just complete the discussion by looking at what happens to equilibrium conversion or extent of reaction for exothermic reaction. We just now said a few minutes back that, as temperature is increased as temperature is increased for exothermic reactions, the extent of reaction decreases; so at lower temperature, our extent of reaction is high, at higher temperatures, the extent of reaction is reaction is low.

This raises several interesting questions; for example, let us say that we carry out a reaction in an isothermal manner. Now, if you carry out reaction in an isothermal manner, let us say, this particular temperature, then we can get this value of our equilibrium extent of reaction roughly, let us say, whatever numbers do not matter, but qualitatively, this is my extent of reaction if I do isothermal process.

Now, if I do a process adiabatic process, from thermodynamics you would have learnt what is an adiabatic process, where there is no heat added or removed from the system; and remember that we are looking at an exothermic reaction. So, if you have exothermic reaction and we do not add or remove any heat, there will be a natural tendency for temperatures to go up as reaction proceeds. Now, we can show that pictorially on this equilibrium conversion or conversion versus temperature diagram by following the trajectory of adiabatic reaction and this is what conversion that we can we can expect, because temperatures are increasing, the equilibrium conversion compared to an isothermal process will be lower in an adiabatic process.

Now, why is this why is this interesting? This is interesting because, look at it this way. For a reaction or for a for a reaction to progress satisfactory, there are now two constants on us; one, we should carry out reaction as fast as possible and we should also worry that reaction are reversible. So, there is a constraint on how much maximum conversion you can get, which thermodynamics has put on us. So, exothermic reactions lower temperatures, higher the equilibrium conversion; but lower temperatures also means lower rates, so if even though conversion is very high, the time required to reach that conversion will be low and we will discuss that as we proceed.

But, I just want to introduce this concept at this point. On the other hand, for adiabatic process temperatures are higher, so reaction rates will be faster, but equilibrium conversion will be low. So, that is that's the dilemma that we somehow has to have to resolve.

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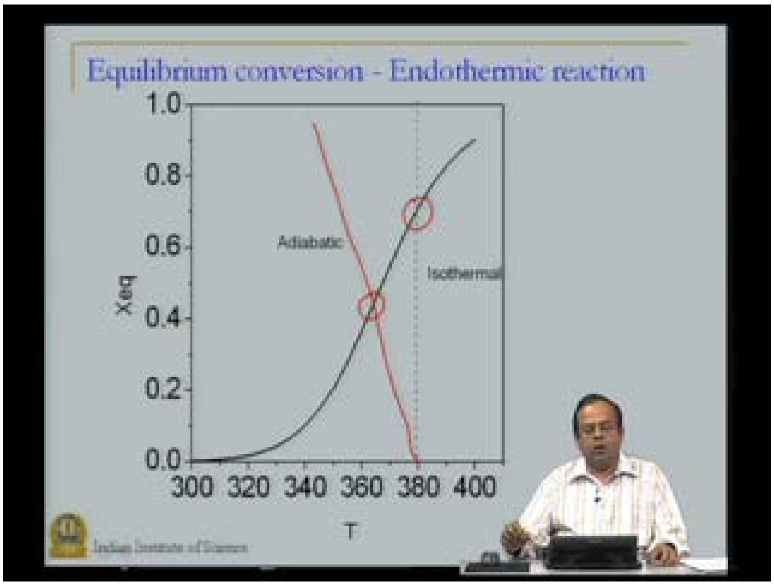
Equilibrium conversion - Endothermic reaction

Endothermic reactions, the equilibrium conversion increases as temperature increases and this is what we see, as we are increasing the temperature, the equilibrium conversion is increasing; y axis is our equilibrium conversion.

So, if we are doing reaction at let us say, this particular temperature, we can get in an isothermal process, this conversion, whereas for adiabatic process, we can get only this much conversion. So, for endothermic reactions, what happens in an adiabatic process? Because there is absorption of heat, the temperatures naturally tend to decrease if we do not add or remove anything that means adiabatic operation. So, we have not only we have lower temperatures, lower temperatures mean lower rates of reaction, but in this particular case, it also means, lower equilibrium, extent of reaction or conversion; a situation which is completely unfavorable, so higher temperatures, higher rates, higher conversions.

But, the story does not end here, as we will see when we design non-isothermal reaction. You have an endothermic reaction, you want high temperatures, naturally the system has tendency to absorb heat; that means you will have to continuously keep on supplying supplying energy to maintain those high temperatures, again a dilemma when it comes to design of design of reactors.

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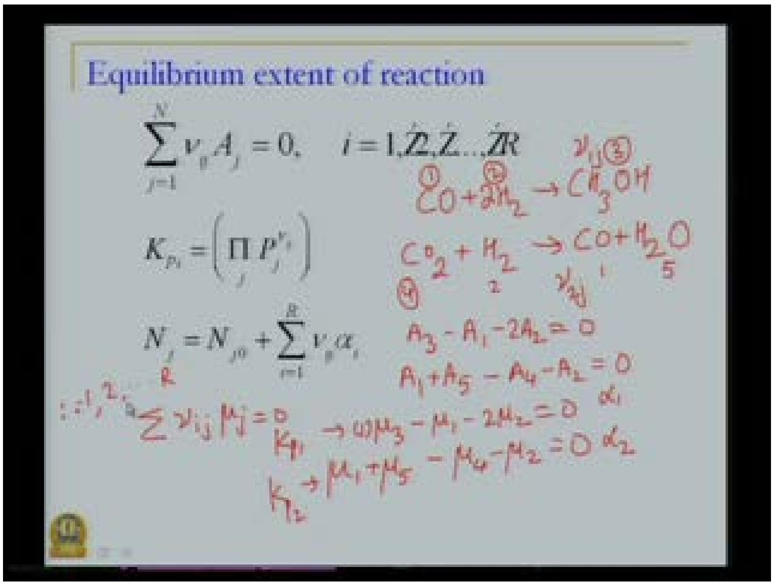

Equilibrium extent of reaction

$$\sum_{j=1}^{N} \nu_{ij} A_j = 0, \quad i = 1, 2, 2 \ldots R$$

$$K_{p_i} = \left(\prod_j P_j^{\nu_{ij}} \right)$$

$$N_j = N_{j0} + \sum_{i=1}^{R} \nu_{ij} \alpha_i$$

ν_{ij}

$CO + 2H_2 \rightarrow CH_3OH$

$CO_2 + H_2 \rightarrow CO + H_2O$

ν_{2j}

$A_3 - A_1 - 2A_2 = 0$

$A_1 + A_5 - A_4 - A_2 = 0$

$\sum_{i=1,2,\ldots}^{R} \nu_{ij} \mu_j = 0$

$K_{p_1} \rightarrow \mu_3 - \mu_1 - 2\mu_2 = 0 \quad \alpha_1$

$K_{p_2} \rightarrow \mu_1 + \mu_5 - \mu_4 - \mu_2 = 0 \quad \alpha_2$

Now, let us just extend these arguments, for multiple multiple reactions. So, suppose we have more than one reaction, for example, the example of carbon monoxide, carbon dioxide and so on; so, if you have R reactions, let us say summation nu i j a j equal to 0, then we can write for each of those R reactions corresponding equilibrium constant K p i. Now, it turns out that, when the system is at equilibrium, all reactions individually are at equilibrium. So, let us say that we have we have these reaction, so let us take an example, let say that C O plus 2 H 2 gives rise to methanol, that was one of the reactions and we also had another reaction, let us say H 2 O, so now we have two reactions. Now, for multiple reactions, it turns out that, each of these reactions is at equilibrium. So, as before, we had defined nu 1 j as stoichiometric coefficient of all the species; for this particular reaction, nu 2 j as stoichiometric coefficients of all species for this particular reaction, so we can write equilibrium condition as follows.

Let us define this species as 1, 2, 3, 4 and let us say, this is the fifth one. So, what is my first reaction? My first reaction is A 3 minus A 1 minus 2 A 2 equal to 0, what is my what is my second reaction? This is my species 2 and this is my species 1; so A 1 plus A 5 minus A 4 minus A 2 equal to 0 is my two reactions, and remember, we are talking only independent reactions. So, these are, if you add them and create a third reaction, that that is not going to count. So, if this reaction is at equilibrium, then the equilibrium condition is summation nu i j mu j equal to 0, for all these reactions i going from 1, 2, up to R. So, let us try to write down the equilibrium condition for first reaction. So, that one will be 1 into mu 3 minus 1 minus 2 mu 2 equal to 0, I am just picking up corresponding stoichiometric coefficients and the second one would be mu 1 plus mu 5 minus mu 4 minus mu 2 equal to 0. So, I have two conditions, I can use the same same logic as before, express this chemical potentials in terms of operating conditions and partial pressures.

For example, if we assume perfect gas law, both these conditions individually, so for this condition, for example, I will have equilibrium constant K p 1 for this reaction, K p 2 for this reaction; so, we have our equilibrium constant K p s and K p 1 K p 2, then again come to mole balance. Now, what I do is, I define extent of reaction alpha 1 for first reaction, alpha 2 for second reaction, so my unknowns all alpha 1 and alpha 2; but I have two equations K p 1 and K p 2. So, I can find alpha 1 and alpha 2 value, that is how far this reaction will go, how far this reaction will go, that is these two separate reactions, when we reach when we reach equilibrium. So, this is how we extend the thermodynamic considerations to multiple reactions, which incidentally will be the most general case to consider.

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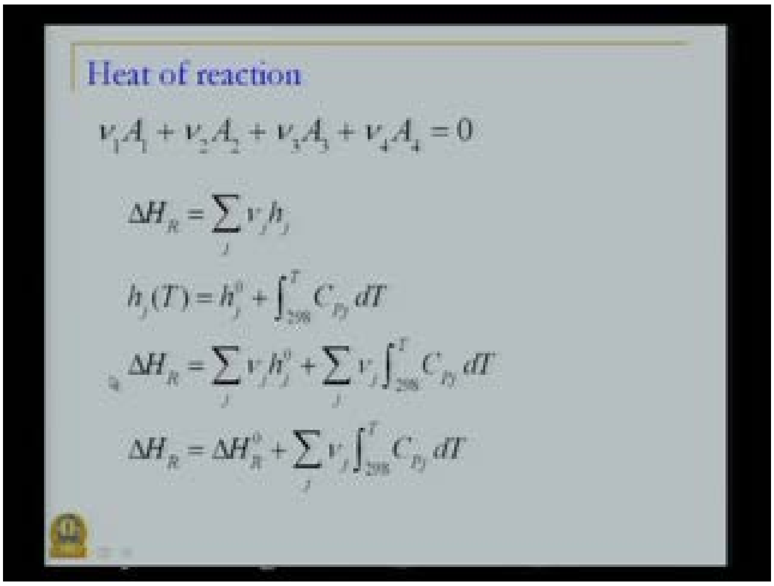

Heat of reaction

$$\nu_1 A_1 + \nu_2 A_2 + \nu_3 A_3 + \nu_4 A_4 = 0$$

$$\Delta H_R = \sum_j \nu_j h_j$$

$$h_j(T) = h_j^0 + \int_{298}^{T} C_{Pj}\, dT$$

$$\Delta H_R = \sum_j \nu_j h_j^0 + \sum_j \nu_j \int_{298}^{T} C_{Pj}\, dT$$

$$\Delta H_R = \Delta H_R^0 + \sum_j \nu_j \int_{298}^{T} C_{Pj}\, dT$$

Before we close our discussion on thermodynamics and chemical reactions, this you have seen before, but just a recap of, how do we calculate the heat of reaction. We talked about heat of reaction either positive, that means an endothermic reaction or negative, as an exothermic reaction. Incidentally, steam cracking is an endothermic reaction; ammonia synthesis is an exothermic reaction. So, now, you can you can consider what temperatures other condition should be, but how do we calculate this heat of reaction. This is simply done based on again going back to our reaction and calculating the heat of reaction, delta H R as summation nu j h j, where h j is the partial molar enthalpy of the species j. So, if this is a reaction, for this reaction, it will be simply mu 1 H 1 plus mu 2 H 2 plus mu 3 H 3 plus mu 4 H 4, it will be my heat of reaction.

Now, what is partial molar enthalpy? If you recall definition of specific heat, C P del h j del t. So, partial molar enthalpy is a function of temperature, which we can relate to reference condition h j 0 plus integral from reference conditions typically, 298 to any temperature C P j d T, C P j is the specific heat, which again is a function of function of temperature. So, if you now take this equation and put it back into this, we can combine the reference conditions together as a summation series of nu j h j 0 and these integral as summation nu j integral C P j d T and then, we get heat of reaction at any temperature is the reference condition heat of heat of reaction plus summation nu j integral 298 between the limits 298 and temperature T C P j C P j d t.

So, this gives me the gives me the idea about how heat of reaction is computed. In many calculations, if you want to do a quick estimate of what what what is happening, you can actually look at reference condition heat of reaction to see whether reaction is exothermic or endothermic. It is true that there will be some contribution from this particular function, the second part but, suppose we make an assumption and engineering is all about making assumptions, but right kind of assumptions. And it is a reasonable assumption, at least in many cases, that C P is a constant, it is not a function of function of temperature then, this reference condition and the actual temperature heat of reactions are not very far from each other. It is true, numerically they will be different, but it is not significant significantly different.

So, with this, we now close our discussion on thermodynamics and chemical reactions. But, before we before we conclude, just few key words that we came across in this particular session. Firstly, thermodynamics is about finding out the equilibrium conditions and how those conditions are influenced by various operating conditions; that is as far as the reaction engineering is concern. So, what we would like to know is, for example, given temperature and pressure, what is the maximum conversion I can get in my reaction? And then, as the follow up question, what happens if I change temperature? What happens if I change pressure? So, in order to answer this question, what did we do? We went in a systematic manner that is starting with Gibbs equation for free energy change. We got a condition of equilibrium, that condition of equilibrium involved chemical potential; we got some models which will relate chemical potentials to the operating conditions, including temperature, pressure and composition. And then, using this equilibrium condition and the model for chemical potential, we calculated what will be the equilibrium extent of reaction or equilibrium Equilibrium conversion.

We then also saw how this equilibrium conversion will be influenced by operating condition. For example, in case of operating conditions being temperature, it depends upon the heat of reaction, whether it is positive, that is endothermic reaction, the temperature increase will lead to increase in conversion; if heat of reaction is negative, that means an exothermic reaction, the increase in temperature will lead to decrease in decrease in conversion. We can also find out what happens to pressure, for example, increase in number of moles favored by decrease in pressure and vice versa. Incidentally, you probably have done this for quite some time, right from your high school days probably, le hotelier’s principle, we saw more formal part of it.

So, with this, we will conclude our discussion on thermodynamics. And now, let us move into the next topic namely, the rates of reaction or the kinetic aspect of reactions. And this is of course is what what what will be of concern to us, when we talk about reactor design and so on. So, let us let us continue our review of undergraduate material and let us talk today, about today about the kinetics.

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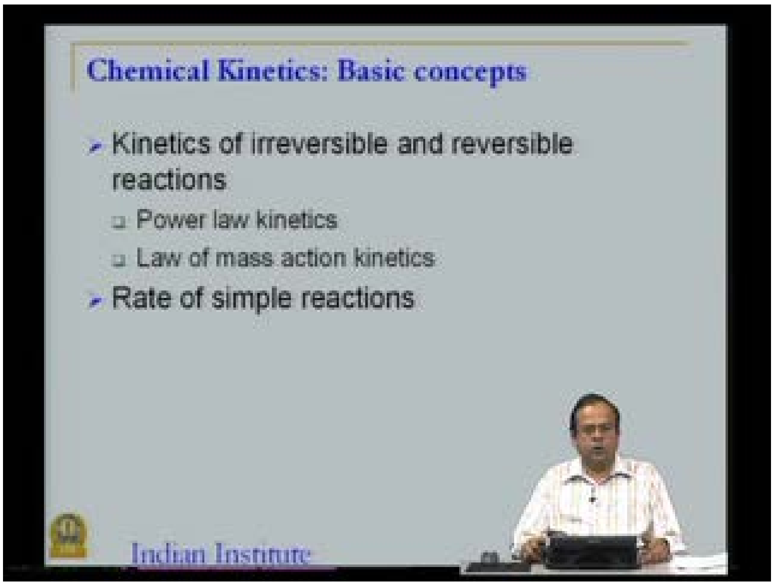

Chemical Kinetics: Basic concepts

- Kinetics of irreversible and reversible reactions
  - ❑ Power law kinetics
  - ❑ Law of mass action kinetics
- Rate of simple reactions

So, when it comes to kinetics, what are what are what are the basis ideas or basic concepts? What we are going to just review quickly over here is kinetics of different types of reactions, a power law kinetics which is quite often used, law of mass action kinetics, which is a specialized case of power law kinetics and we will also see few simple rates of few simple simple reactions.

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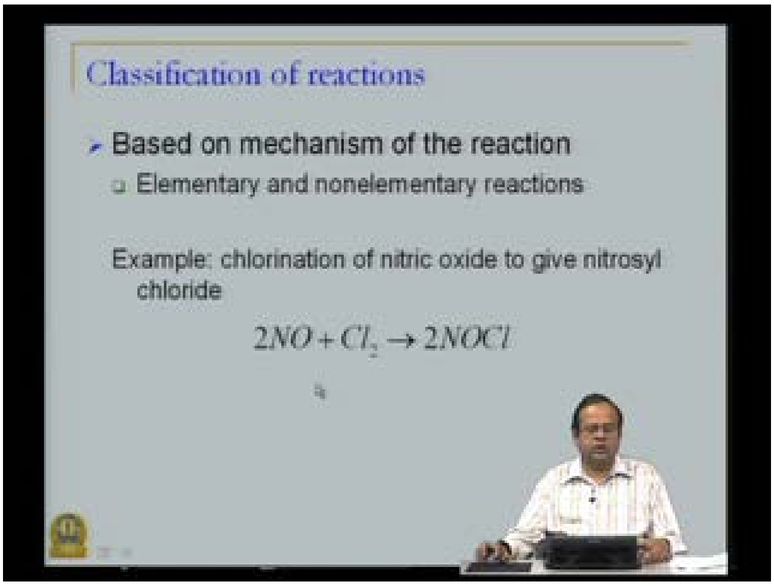

Classification of reactions

- Based on mechanism of the reaction
  - Elementary and nonelementary reactions

Example: chlorination of nitric oxide to give nitrosyl chloride

$$2NO + Cl_2 \rightarrow 2NOCl$$

Before we go into rates of reactions, we will we will just briefly go over various different ways in which reactions are classified. Reactions are classified based on three different things, starting with let us say mechanism of the reaction; that is whether the reaction is elementary or non-elementary. For example, if you consider this chlorination of chlorination of nitric oxide to give nitrosyl chloride, this reaction is an elementary reaction. We call reaction as elementary reaction, if the reaction takes place the way, it is actually written down. For example, here the formation of 2 moles of nitrosyl chloride is a result of direct single step interaction of 2 molecules of nitric oxide and 1 molecule of chlorine; just single step interaction and hence we call these reactions as elementary reactions.

Of course, very few reactions of commercial importance are elementary, they are all non elementary; that means, these are not single step reactions, but there are several steps proceed from when you proceed from reactant side to product side, but for an elementary reaction, for example, in this example, the molecularity of the reaction is 2 plus 1, 2 from nitric oxide, 1 from chlorine, so 3, so this is a example of termolecular reaction. Similarly, there are several examples of unimolecular reactions, bimolecular reactions, that is molecularity 1 unimolecular, molecularity 2 bimolecular, unimolarity 3 termolecular.

Thing to remember is, there are no known reactions of molecularity higher than 4 that is elementary reactions. So, moment you see the molecularity of a reaction is 4, one can strictly say or one can immediately come to a conclusion, reasonable conclusion, that this cannot be an elementary reaction.

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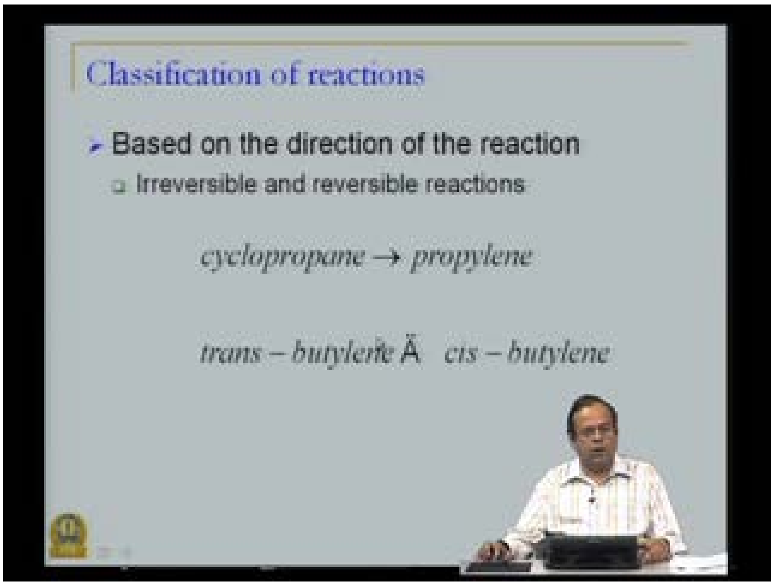

Classification of reactions

- Based on the direction of the reaction
  - Irreversible and reversible reactions

cyclopropane → propylene

trans – butylene Ä *cis – butylene*

Reactions are also classified based on direction of reaction; strictly speaking, no reaction is irreversible; all reactions are reversible. But, thermodynamic consideration tells us, for all practical purposes, some reactions, such as cyclopropaneto propylene always proceed from left hand side to right hand side.

That is almost 100 percent conversion of conversion of cyclopropane to propylene. So, essentially irreversible reaction, but the reaction like trans-butylenes to cis-butyleneisan reversible reaction, this arrow is missing, but take it from me, it is going from left hand side to right hand side and right hand side to left hand side; something we talked about in our equilibrium and thermodynamics, so this is reversible and irreversible reactions.

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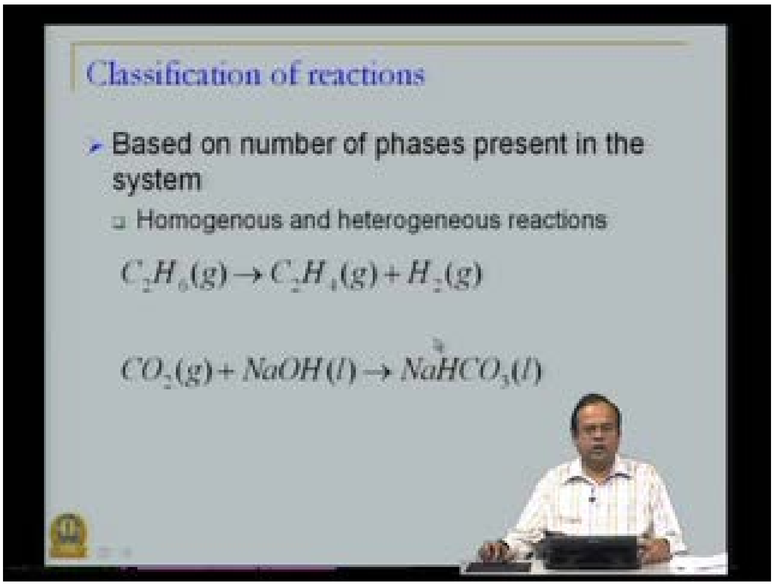

Classification of reactions

- Based on number of phases present in the system
  - Homogenous and heterogeneous reactions

$$C_2H_6(g) \rightarrow C_2H_4(g) + H_2(g)$$

$$CO_2(g) + NaOH(l) \rightarrow NaHCO_3(l)$$

And then we can also classify reactions based on how many phases are present in the system; that is whether it is a homogenous or heterogeneous reaction. For example, take this cracking of ethane, ethane which is in the gas phase gives rise to ethylene which is also a gas and hydrogen which is also a gas; and in the reactor, there are no other phases except gas gaseous phases and hence, we call these reaction as homogenous reaction.

On the other hand, the reaction of carbon absorption of carbon dioxide into alkali, into hot alkali, in fact this is one of the ways of getting rid of carbon dioxide from the gaseous emissions coming out of the reactor. This reaction to give bicarbonate, this reaction is a heterogeneous reaction, because one of the reactant C O 2 is in a gas phase, another reactant N O H in the liquid phase, the product is also in the liquid phase. So, more than one phase and there are all kinds of catalytic reactions. For example, where both gas reactant and product can be in the same phase, but reaction does not occur, unless there is a catalyst that is in the phase separate from separate from the reaction phase.

So, we also called these reactions as heterogeneous reactions. To begin with, we will focus on homogenous reactions and make suitable modifications as we as we proceed.

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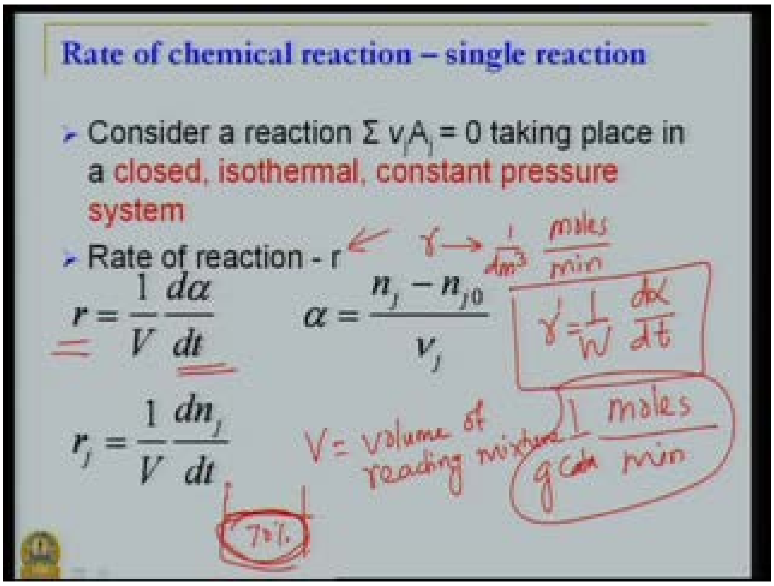

Rate of chemical reaction – single reaction

- Consider a reaction $\Sigma \nu_j A_j = 0$ taking place in a closed, isothermal, constant pressure system
- Rate of reaction - r

$$r = \frac{1}{V}\frac{d\alpha}{dt} \qquad \alpha = \frac{n_j - n_{j0}}{\nu_j}$$

$$r_j = \frac{1}{V}\frac{dn_j}{dt}$$

$r \rightarrow \frac{1}{dm^3}\frac{moles}{min}$

$\boxed{r = \frac{1}{W}\frac{d\alpha}{dt}}$

$\frac{1}{g\ cat}\frac{moles}{min}$

V = volume of reacting mixture

7%

So, just few terminologies to set the background for different kinds of kinds of reactions, for example, we first start as usual with single reaction. Let us say that, we have a reaction summation nu j a j equal to 0 taking place in a closed isothermal constant pressure pressure system. Then, we define the rate of reaction r Rate of reaction r as rate of change of extent of reaction alpha with time d alpha d t normalized by the volume of the reacting mixture.

I will repeat again, for a closed isothermal constant pressure system, and this is important to realize, later on we will talk about reactions in the open systems, such as continuous stirred tank reactors, for that we have a definition of rate of reaction which is slightly different. But, for closed isothermal constant pressure system, the rate of reaction is given as rate of change of extent of reaction d alpha d t normalized by the volume of the reacting mixture.

We saw earlier that alpha is an extensive of property, has a unit of moles, let us say. So, alpha is units of moles, time let us say is in units of minute and the volume of the reacting mixture, let us say in decimeter cube and hence, rate is in the units of moles per d n cube per minute. You could use different units for mass, time and volume but what is important is presence of all these three quantities in the in the expression, so rate is always in moles per minute per d n cube. Now, I mentioned few minutes back about heterogeneous reactions and homogenous reactions. Now, if a reaction is heterogeneous or rather homogenous, then this V that we are talking about is the volume of the reacting mixture not the reactor, there is a distinction to be made here.

For example, if we have a reactor and there is a liquid phase reaction, and this is only 70 percent feed, then this volume we are talking about is the volume of this reactor, volume of this reacting mixture and not the volume of the entire reactor, these two are different things. But for example, later on we will also see that, when it comes to the heterogeneous reactions, we sometimes define rate in terms of extent d alpha d T per unit normalized by weight of the catalyst, these are in fact used for catalytic reactions. So, in this case, the rate is expressed in terms of moles per minute per gram of catalyst; so for catalytic reactions, we have this particular particular definition.

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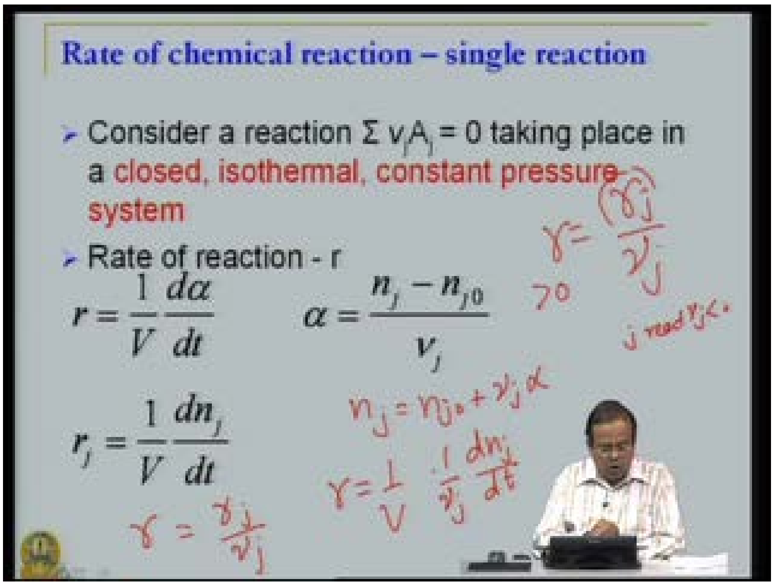

Rate of chemical reaction – single reaction

- Consider a reaction $\Sigma \nu_j A_j = 0$ taking place in a closed, isothermal, constant pressure system
- Rate of reaction - r

$$r = \frac{1}{V}\frac{d\alpha}{dt} \qquad \alpha = \frac{n_j - n_{j0}}{\nu_j}$$

$$r_j = \frac{1}{V}\frac{dn_j}{dt}$$

$r = \frac{(r_j)}{\nu_j}$

70

j read r_j<.

$n_j = n_{j0} + \nu_j \alpha$

$r = \frac{1}{V}\frac{1}{\nu_j}\frac{dn_j}{dt}$

$r = \frac{r_j}{\nu_j}$

Now, we have we have we have this extent of reaction d alpha d t and how did we define alpha? We had define alpha based on n j is n j 0 plus nu j into alpha or alpha is n j minus n j 0 divided by nu j. So, if you substitute for alpha in this particular particular expression, then we will get r equal to 1 over V 1 over nu j d n j d t d alpha d t as 1 over n j, which we can write 1 over V d n j d t as r j and write r equal to r j by nu j. What is the difference between r and r j? Unit wise they are same, but r j is the rate of change of species j and r is the rate of the reaction of this particular reaction. So, r j is for the species r is for the reaction and these of course are related, that is r j by nu j is equal to equal to r.

Few things before we stop for the for the day; remember alpha always start with 0 and is always positive. So, d alpha d t is always positive or in other words, r is always positive, at best it can be 0, but it is always a positive quantity. So, r is always positive, but nu j can be positive or negative depending upon the stoichiometric, whether it is a reactant or product. So, if we have r equal to r j by nu j, this is always positive, this if j is reactant, nu j is negative, that means r j is negative. That is for a reactant, the rate of change is negative or reactant gets consumed; for product, it gets formed, it is always positive, so these are all related to related to each other.

So, we will stop here, and in the next session, we will look at what are different ways and in which we define the rate of reaction, how does is depend on the operating conditions and then, how we use this information in the design of reactors, that will be in the subsequent lectures. Thank you.