

**Chemical Reaction Engineering**  
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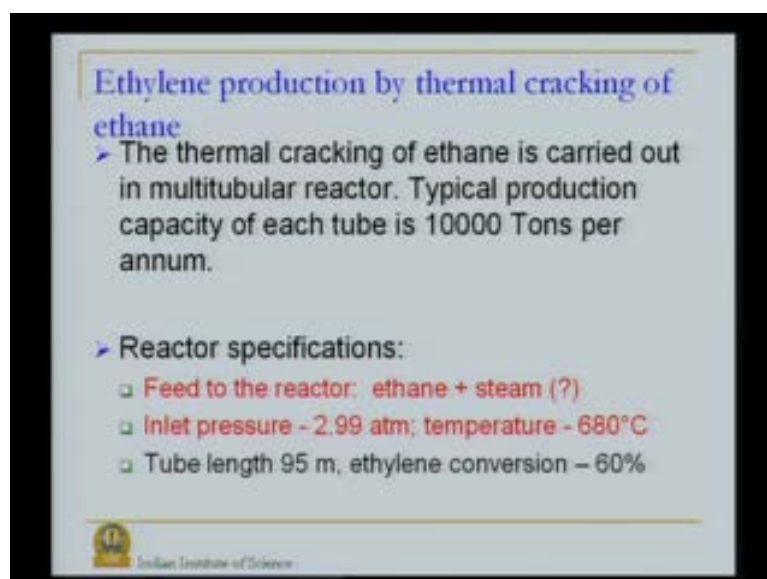
**Lecture No. # 03**  
**Thermodynamics of Chemical Reactions: Part I**

Friends, let us continue our discussion on chemical reaction engineering and in particular reviewing some of the material that you would have already seen in your undergraduate class. Last time we reviewed about stoichiometric of the reaction.

So for example, we saw how we can represent a chemical reaction, a single reaction or a multiple reaction. How we can monitor the progress of these reaction, by way of representing the extent of reaction or conversion of a reaction. And we also saw the idea that in a reaction there may be one component, which will get exhausted first or in other words it will become stoichiometrically limiting.


Let us now continue our discussion bringing in thermodynamics in the domain of reaction engineering. Now, let us go back to the example that we considered in the last class namely steam cracking of ethane. And look at what are the conditions which we operate these typical this reactor is typically operated.

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**Ethylene production by thermal cracking of ethane**

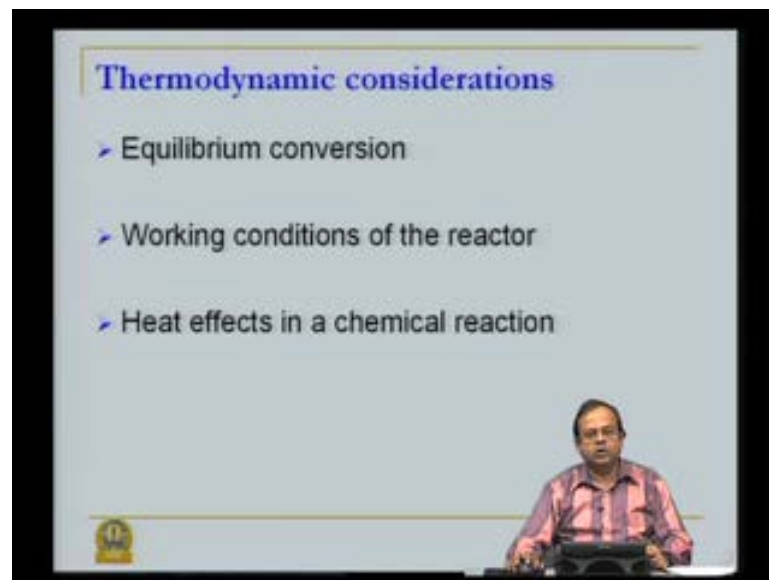
- The thermal cracking of ethane is carried out in multitubular reactor. Typical production capacity of each tube is 10000 Tons per annum.
- Reactor specifications:
  - ❑ Feed to the reactor: ethane + steam (?)
  - ❑ Inlet pressure - 2.99 atm; temperature - 680°C
  - ❑ Tube length 95 m, ethylene conversion - 60%

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We have a tubular reactor, on one end of it we feed in ethane and we get unreacted ethane, ethylene, and hydrogen and so on outside the reactor. Now, two things we had noted last time. that in this reactor, we feed ethane and steam and also the inlet pressure is specified at three atmospheres fairly low atmosphere process and temperature of about 700 degrees centigrade.

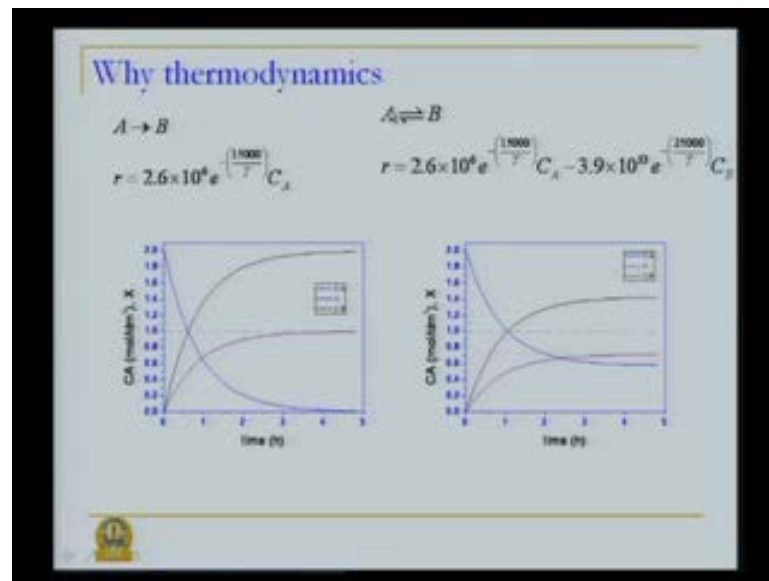
Now the question arises, why these conditions? Why steam in the reactor? Or why for that matter pressure is only fairly low temperature is high and so on. And this is where thermodynamics comes into the picture.

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Let's take an example and see how thermodynamics plays a role. So, let us take a... We will look at equilibrium conversions in a reaction. We will work look at how working conditions of the reactor are dependent on this equilibrium conversion and therefore, on the thermodynamics of the reaction. And we also will look at heat effects in chemical reaction. So, these are the broad topics that we are interested in when we talk about thermodynamics of chemical reaction.

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Let's take an example to illustrate, why thermodynamics is important. Let us say that we have these reactions A going to B or A 1 going to A 2, if you like to call and it proceeds with certain rate as represented over here. And we can carry out these reaction in a batch reactor and monitor the concentrations of A, that of B and also the conversion in the reactor. We will recall the conversion in the reactor will be for this particular case, will be defined in terms of species A, because that is the only species as a reactant so that is our limiting species. Whatever A we had in the beginning  $C_A$  not minus, whatever is present at any time T that is  $C_A$  divided by  $C_A$  not will give us the conversion. Let us closely look at look at the progress of this reaction. So, on the x axis we have time. So, we are doing batch reactions. We are taking, let us say sample at various times and on y axis is conversion and concentration of species A. Let us start with species A first and shown in the blue line is the concentration of A, as it changes as the reaction proceeds. And you can see that we in this particular example, we have started with 2 mole per d m cube of A and as the time progresses this concentration slowly drops down as per the rate given by this expression. And after sufficiently long time **sufficiently long time** in this case is about 4 hours, the concentration of A goes to practically 0, that means A is completely utilized.

Concentration of B on the other hand increases from initial value of 0 to a maximum value of 2. Recall that the strychometric relation between these two is 1 is to 1, 1 mole of

a gives 1 mole of B and therefore, when 2 moles of A are consumed, 2 moles of B are generated. We also have conversion which we calculated as I explained just now. And this conversion again increases from 0 value to value 1 or 100 percent, if you are talking in terms of percentage conversion.

This is how typically reaction of the type A going to B is expected to behave and indeed it does behave in that manner. But now, let us try to look at how a reaction which can proceed from left to right as well as from right to left or in other words we have now looking at we are now looking at a reversible reaction. So, it can go either way depending upon the conditions in the reactor. And we would like to know, what those conditions are? We will come that little later.

This rate of this reaction now consists of two parts, one which represents A going to B. this is my term that that is same as before, but in addition now, we have B going to A which proceeds at this particular rate. And therefore, our rate of reaction is the rate at which A goes to B minus rate at which B goes to B goes to A. And let us look at how these reaction proceeds.

The terminology and everything else is else is same. We have A of 2 moles per d m cube add or 2 moles per liter at the beginning of the reaction. And as time progresses, it decreases, qualitatively similar to what happened to in these reaction. However, after a has decreased to about, let us say 0.6 mole per liter there is no further decrease in the in the concentration of A. And in fact, however you may run these reaction beyond let us say this 3 hour time period, we always have about same value of concentration of A. That means A is no longer consumed. Something is reflected in value of B also and that of conversion. Conversion is increasing from 0, but it is not saturating at value of 1 as is was the case over here. It is saturating axiom intermediate value roughly about 0.6, 0.7, 0.72 or something of that order of magnitude.

No matter what we **what we** do, that means, continue the reaction for longer times, nothing is going to change. The concentrations are going to be at these respective levels conversion is going to be same or in other words now, we have saturation not at the complete consumption of the reactant, but saturation at some partial consumption of the of the reaction. And why has this **why has this** occurred? This has occurred because this

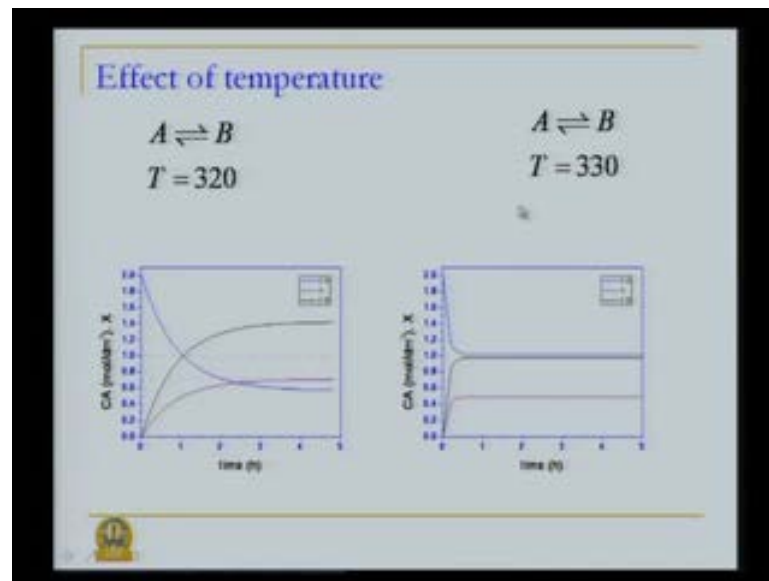
reaction is reversible. So, we have A going to B, B going to A and therefore, we have possibility that at these times has this time has the reaction completely stopped in a sense yes and no.

**Yes**, because we see that there is no more consumption of consumption of A. it has reached a saturation value, but also no in sense that what is really happening at this time at 4 hours, 5 hours and so on. That rate at which A is going to B is counter balance by rate at which B is going to A. So, there is a reaction taking place, A is getting converted to B and B is getting converted to A, but the rate at which they are getting converted are at the same value. And hence there is no net change in the concentrations.

Or in other words these reactions have reached equilibrium. Thermodynamics tells us lot about equilibrium and hence we need to know at what conditions such saturation will occur. Now, operationally this is important, because for example, if you are design your reactor to run for 3 hours, you are getting certain conversion.

Now, it is natural to expect that if you run these reaction for a longer time, you will get little better, but that is not what is happening over here. Whether it is 3 hours or 4 hours or 5 hours practically, the conversion is same. Any investment that you do in running these reactor for a longer period, such as 4 hours or 5 hours, in this particular case is not going to give you any additional returns. That means it is not a wise thing to do.

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Let's continue this same example and say that what we did discussed just now. Is what was happening at temperature, if you maintain the temperature in your reactor of about 320 degrees Calvin? I should point out that these numbers are not that critical this could have been any, but whatever example I have taken these are the numbers that are used. The behavior will be same even if those rates are different and so on.

Once again we see that, that is the saturation in the in the rate. But what if I do these reactions at 330 degree centigrade? That is same conditions, but reaction is now carried out at 330 degree centigrade. And let us compare these two now starting with A. here the saturation is occurring at around 4 to 5 hours and the value of concentration of a remaining in the reactor is about 0.6. But look at what is happening when we do the same reaction at 330 degrees, only 10 degree temperature difference.

We noticed that once again the saturation in concentration of A is occurring, but it is now concentrating the saturation levels are about 1 mole per liter not 0.6 as was the case here. And if similar change is reflected in concentration of B also which is going from a 0 value to a high value or in other words qualitatively behavior is same. It is taking sometime, but after some time there is no more change in the concentrations. So, behavior qualitatively same, but quantitatively that is number wise, the behavior is now different. Whereas, we got conversion of about 0.7, when temperature was 320 degrees

centigrade, we get now conversion of only about 0.5 when temperature is 330 degrees centigrade.

In other words, this conversion is dependent on what temperatures we use. This conversion is therefore, can be said to be dependent on the operating conditions in the reactor. And these could be temperatures, pressures, what concentrations you start your reaction with and so on. We would like to know all these factors, when we try to design the reactor, because clearly any decision for this particular example to run a reaction at higher temperature 330 degrees centigrade is not a wise decision, because you are getting lower conversions.

It is a good decision, if you look at how fast we are achieving those conversions. We are achieving it much faster in only about half an hour compared to our 3 hours over here. And this example therefore, illustrates another interesting aspect in design of reactors that is how temperature influences your reaction.

On one hand, if you carry it out at higher temperature, your reactions are apparently progressing very fast, very rapidly. However, they are progressing only to a limited extent which is not favorable, because you are getting lower conversions. So, there is a balance to be struck. Do you want higher reaction rates or do you want higher conversions. We will come to this aspect of design during the course of my subsequent lectures, but at this point, I want you to keep in mind that there is always a tradeoff, when you try to design a reactor particularly this kind of reaction. What is that kind of reaction?

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**Chemical Equilibrium**

- Consider a reaction  $\sum v_j A_j = 0$  taking place at constant temperature  $T$  and pressure  $P$ . The system will spontaneously change in the direction of increasing entropy, reaching equilibrium when entropy can not increase further.
- Free energy and Gibbs equations  
 $dG = V dp - S dT + \sum_{j=1} \mu_j dn_j$

Chemical Potential  $\mu_j = \left( \frac{\partial G}{\partial n_j} \right)_{T,P,n_k}$

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Let us now formally look at some of developments that we formulations that we use in a chemical reactions in the form of equilibrium. We start out with our general reaction and at this point I will consider only a single reaction, that is taking place summation  $V_j A_j$  equal to 0. Taking place at constant temperature  $T$ , pressure  $P$ . Now, thermodynamics tells us that for any process to occur spontaneously there is always a increasing entropy. Such that the entropy keeps increasing reaches an equilibrium value or the maximum value, when entropy can no longer increase further. This is a broad understanding we all have from our thermodynamics one over one courses. Now, when it comes to using this information in form of for the case of reaction engineering, working with entropy is not an advantageous thing.

we go to free energy and use Gibbs's equation, which tells us that the change in free energy represented here as  $dG$  is  $V dp$  minus  $S dT$  plus summation  $\mu_j dn_j$ .  $V$  is the volume of the system,  $P$  is the pressure,  $s$  is the entropy,  $T$  is the temperature,  $n$  is the number of moles of species in the system and there is a quantity  $\mu$  of  $j$  which is nothing but the chemical potential of the of the species.

Formally what is the definition of  $\mu_j$ ?  $\mu_j$  is nothing but partial of free energy with respect to the moles of the species concerned  $n_j$ . So,  $\partial G$  by  $\partial n_j$  at constant temperature pressure and composition of all species except  $j$  remaining same. On in other



words, it is an amount by which the capacity of the phase to do work changes by incremental addition of small quantity of species  $n_j$ , everything else kept the same.

So, we have this chemical potential  $\mu_j$  which comes in this Gibb's equation. The question now is how do we use this information? Let me step back and what are what information are we looking for. The example which we saw a few minutes back show does that as reaction proceeds. First there is a change in number of moles of various species, but after sometime saturation is reached. So, we want to know what is that level of saturation. In other words to what extent my reaction will proceed? I want to know what will be the conversion when my equilibrium is attained.

We are using thermodynamic equation to gather that that information and with that we have started with Gibb's free energy.

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**Chemical Equilibrium**

Gibb's Equation  $dG = Vdp - SdT + \sum_{j=1}^N \mu_j dn_j$   $A \rightleftharpoons B$

Progress of reaction  $n_j = n_{j0} + \nu_j \alpha$  or  $dn_j = \nu_j d\alpha$

$\Rightarrow dG = Vdp - SdT + \sum_{j=1}^N \nu_j \mu_j d\alpha$

➤ Equilibrium condition

$$\left( \frac{\partial G}{\partial \alpha} \right)_{T,p} = \sum_{j=1}^N \nu_j \mu_j = 0$$

The slide also features a hand-drawn graph of Gibbs free energy  $G$  versus extent of reaction  $\alpha$ . The curve shows a minimum point, indicating equilibrium. A red arrow points to this minimum, labeled  $\alpha_{eq}$ . The reaction  $A \rightleftharpoons B$  is written in red above the graph.

So, let us come back to this Gibb's equation. Same equation  $dG = V dp - S dT + \sum_{j=1}^N \mu_j dn_j$ ,  $j$  going from 1 to 1 to  $n$  that is all species put together.

Now, from our yesterdays or last discussion of stoichiometric of the reaction, we know we have a measure to monitor the progress of reaction, namely the extent of reaction. And according to that definition of extent of reaction, the number of moles  $n_j$  at any point of time is number of moles  $n_{j0}$  that we started with plus  $\nu_j$  into extent of reaction  $\alpha$ . This we had seen in our last session. This now implies that incremental

change in number of moles is directly proportional to incremental change in the extent of reaction. I am just taking a derivative of both sides  $n_j$  is constant; because that is a fixed value  $\mu_j$  is constant stoichiometric. So,  $dn_j$  is  $\nu_j d\alpha$ .

Now, if we now substitute  $dn_j$  equal to  $\nu_j d\alpha$  into our Gibb's equation. Now, we get free energy change  $dG$  is equal to  $V dp$  minus  $S dT$  equal to summation  $j$  equal to 1 to  $n$   $\nu_j \mu_j d\alpha$ .

Now, what happens when reaction proceeds? So, let us say that we have let us say that we have some measure of how the free energy changes as the reaction proceeds. Recall that we said that entropy increases the free energy of the system decreases. Let us say on y axis we have some measure of free energy and on X axis I have my extent of reaction. So, this is my starting point that is some free energy. As reaction proceeds my free energy changes reaches a minimum value and this is the point at which my reaction will stop, because that is a minimum value. So, on the other side I expect that free energy will increase.

For my reaction A going to B **A going to B** my free energy is going to decrease reach a minimum and if you are looking at from this side it is minimum at this point. If you are looking from B going to a then same thing will happen the reaction will reach a minimum. This is the point at which my reaction will come to a halt or come to an equilibrium state. And this extent of reaction at which my G free energy is minimum, I call it as  $\alpha_e$  that is extent of reaction at equilibrium condition.

So, what is that equilibrium condition? We have this Gibb's equation which we have represented in this particular form. We have  $dG$  equal to  $\sum \nu_j \mu_j d\alpha$ . So, if we are looking for that value of  $\alpha$ , at which free energy change is minimum, then mathematically this condition can be expressed as  $\frac{dG}{d\alpha}$  at constant temperature and pressure. We take derivative of this with respect to  $\alpha$  partial derivative by maintaining pressure and temperature constant. And we get that condition now as summation  $\nu_j \mu_j$  this quantity over here. Summed over all species  $j$  equal to 1 to  $n$  must be 0. And this is my condition of equilibrium. That is product of stoichiometric equation into chemical potential of a species and combining contributions from all the species summation that must be equal to 0 and this is my condition of equilibrium.

So, we now know what from our Gibb's equation, what is my free energy? What is my condition of equilibrium? We are only a step closer to getting, what is this value of alpha at equilibrium. we are on our way. What do we now need, we need how is this condition related to the extent of reaction alpha. If you look at this condition as it stands now  $\nu_j$  is the stochiometric coefficients. So, that is given for a reaction there is nothing changing there.

So, it implies that, if this condition is to give me this value of alpha e, then that alpha must be somehow influencing this chemical potential  $\mu$  of the species. In other words, to take this discussion forward we now need another set of equations which relate chemical potential of the system to the progress of reaction.

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**Chemical potential**

- Perfect gas mixture
 
$$\mu_j(T, P, y) = \mu_{j,r}(T, P^r, y^r) + RT \ln \frac{P y_j}{P^r}$$
- Non-ideal gas mixture
 
$$\mu_j(T, P, y) = \mu_{j,r}(T, P^r, y^r) + RT \ln \frac{f_j}{f_j^r}$$

*Denbigh*  
 $y$  = composition,  
 $T$  = temperature,  
 $P$  = pressure  
 superscript  $r$  = reference  
 $P^r = 1 \text{ atm}$   
 $y^r$  = pure  $j$   
 $f_j$  = fugacity

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So, let us proceed in that direction now. And I will be discussing only few illustrative possibilities. There are many more possibilities of this kind and excellent discussion on this appears in a book by Denbigh called chemical equilibrium. This book is fairly old, but the material is classic. The author is Denbigh, his book name chemical equilibrium. Let us look at how we move forward. So, let us say that we are carrying out a reaction and all components of these reactions are in the gaseous phase. And this gaseous phase behaves as a perfect gas mixture.

Then the chemical potential of the component  $j$  at given temperature, pressure and composition. So,  $T$  is temperature,  $P$  is pressure and  $y$  is the composition. We have  $n$  components, so in terms of mole fractions  $y_1, y_2, y_3$  mole fractions is equal to or is related to some reference condition chemical potential  $\mu_j^0$  at given temperature or temperature of interest reference pressure and reference composition, plus  $RT \ln P y_j$ ,  $P$  is the total pressure,  $y_j$  is the mole fraction of component  $j$ . So,  $P y_j$  is nothing but the partial pressure of component  $y_j$  divided by reference pressure.

What is reference pressure? Reference pressure is typically taken as one atmosphere and reference composition is taken as pure  $j$ . So, reference composition  $y$  are will have components all 0 except  $j$  th component unity. That means, mole fraction of  $j$  is one that means, we are looking at pure  $j$ . This is how chemical potential is related to temperature and pressure and the composition. That is a model that we use, but what if gas is not behaving as a perfect gas mixture. Then we have non-ideal gas mixture behavior, where we define the chemical potential for given temperature, pressure and composition. Once again relating it to its reference pressure, plus  $RT \ln$  fugacity of  $j$  by reference fugacity. Reference fugacity is again taken as one atmosphere or pressure reference pressure of one atmosphere and we have fugacity.

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**Chemical potential**

➤ Solution

$$\mu_j(T, P, x) = \mu_j^0(T, P^*, x^*) + RT \ln \gamma_j x_j$$

$\sum \nu_j \mu_j = 0$

$x$  = composition  
 $T$  = temperature  
 $P$  = pressure  
 superscript  $r$  = reference  
 $\gamma$  = activity coefficient

What if reaction is taking place in a solution liquid solution. let us say, we have a similar

definition chemical potential as a function of temperature, pressure and composition  $x$ , as related to the standard condition chemical potential plus  $R T \ln \gamma_j x_j$ .  $\gamma_j$  is the activity coefficient,  $x_j$  is the composition or in other words, we have different models depending upon how we view our solution the reacting mixture is. Whether it is a perfect gas mixture or it is a non ideal gas mixture or if it is a liquid solution and so on.

In a compact or more simpler form, we can write  $\mu_j$  equal to some reference condition chemical potential  $\mu_j^0$  plus  $R T \ln$  activity of  $j$ . And these activity of  $j$  for example, when the gas is perfect mixture is partial pressure of  $j$ . It is fugacity of  $j$  when it is a non ideal mixture, it is  $\gamma_j x_j$ , when we are looking at solution and so on. This is just a simplified representation of our chemical potential  $\mu_j$  equal to  $\mu_j^0 + R T \ln A_j$ . We have the equilibrium condition summation  $\sum \nu_j \mu_j$  equal to 0, we have appropriate model of how chemical potential depends upon the properties of the reacting mixture namely temperature pressure and its composition.

So, now next step would be putting these two pieces of information together. Remember our ultimate goal is to find what is the maximum or equilibrium extent of reaction  $\alpha_e$ ? So, we have equilibrium condition, we have a model for a chemical potential. Yet it is not apparent that  $\alpha_e$  is appearing anywhere in the picture or for that matter  $\alpha$  is appearing anywhere in the picture. So, let us try to bring that in now and complete this discussion to get  $\alpha_e$ .

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Free energy change

$$v_1 A_1 + v_2 A_2 + v_3 A_3 + v_4 A_4 = 0$$

$$\mu_j = \mu_{j0} + RT \ln(a_j)$$

$$\sum_{j=1}^N v_j \mu_j = \sum_j v_j \mu_{j0} + RT \sum_j v_j \ln(a_j)$$

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

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

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$$v_1 \ln a_1 + v_2 \ln a_2 + \dots$$

$$\ln a_1 + \ln a_2 + \dots$$

$$\ln a_1^{v_1} a_2^{v_2} \dots$$

Let us take a specific example now, let say that we have four components A 1, A 2, A 3, and A 4. And let us say that we have strychometric coefficients nu 1, nu 2, nu 3, and nu 4 and this is my reaction. I know my chemical potential as related to these operating conditions temperature pressure is given in this particular form.

Let me now, multiply this chemical potential by nu j and add it up for all the species. So, what do we have here, nu j mu j summed over all n species is nu j 0 nu j summed over all species, that is all reference chemical potentials put together, plus R T the real terms will be nu 1 l n A 1 plus nu 2 l n A 2 plus nu 3 and so on. So, nu j l n A j and we know summation of l n with nu j l n A j is nothing but l n of product of A j raise to nu j or all we are trying to do here is, we have nu 1 l n A 1 plus nu 2 l n A 2 and so on.

So, this I can write it as A 1 raise to nu 1 plus l n A 2 raise to nu 2 and **and**. So, on or this l n A 1 raise to nu 1 l n plus l n A 2 raise to nu 2 is nothing but l n of A 1 nu 1 into A 2 nu 2 and so on. And that is nothing but this product term. So now, I have my equation for free energy change by summing it up for all species in terms of reference conditions and in terms of all the activity of all the species, or in other words now, we look we represent it in a slightly different form that. This is my free energy **free energy** change delta G, as it relates to the standard condition free energy change, which is summation nu j mu j 0, standard condition free energy change plus R T l n product of A j raise to nu j and

product carried over all the terms of this equation. This free energy change what should happen to this free energy change at equilibrium.

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**Equilibrium condition**

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

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

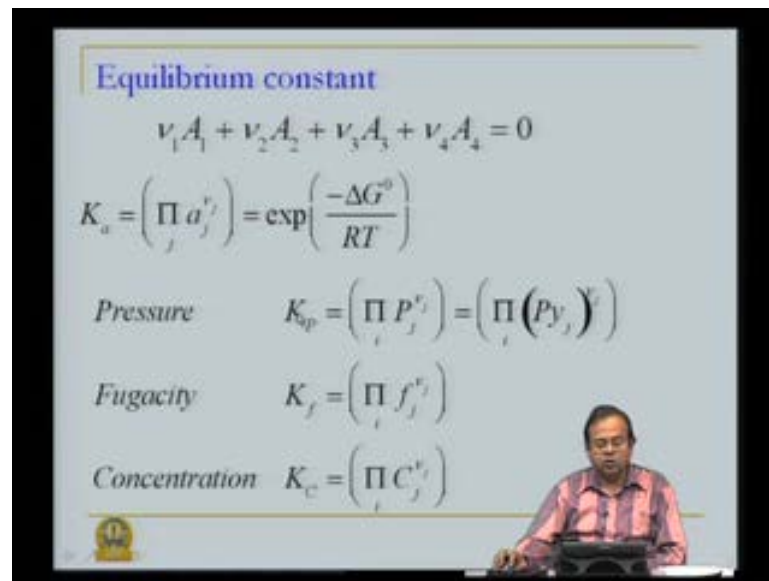
$$\Delta G = \Delta G^0 + RT \ln K_a = 0$$

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

Let us move little further. We have our free energy change, as free energy change delta G 0 R T ln a j nu j a j nu j a j raise to nu j summed over all this. So, this free energy change at equilibrium must be 0. Free energy change delta G at equilibrium is 0. So, this is my condition and I express this product of a j raise to nu j, as a constant equilibrium constant K a. Write this condition as delta G 0 R T ln K a which is must be equal to 0 or K a is nothing but this product, which is exponential minus delta G 0 by R T from this from this equilibrium condition.

So, my equilibrium constant K and this subscript a is devoted to say that I am expressing all my activities as a j. My composition is expressed in terms of a j. So, I am referring to this equilibrium constant with a subscript a. So, this is my equilibrium constant. Related to the standard condition free energy change delta G 0 divided by R T and standard condition free energy change is nothing but summation of product of nu and chemical potential at standard condition.

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**Equilibrium constant**

$$\nu_1 A_1 + \nu_2 A_2 + \nu_3 A_3 + \nu_4 A_4 = 0$$
$$K_a = \left( \prod_j a_j^{\nu_j} \right) = \exp\left( \frac{-\Delta G^0}{RT} \right)$$

*Pressure*  $K_p = \left( \prod_i P_j^{\nu_j} \right) = \left( \prod_i (P y_j)^{\nu_j} \right)$

*Fugacity*  $K_f = \left( \prod_i f_j^{\nu_j} \right)$

*Concentration*  $K_c = \left( \prod_i C_j^{\nu_j} \right)$

We can actually choose to express our compositions in various different forms depending upon how we view our mixture. So, this constant if for example, if I use partial pressure for activity that is pure gas perfect gas mixture then I use term  $K_p$  subscript P denoting we are now referring to equilibrium constant in terms of pressure, as product of partial pressure of j raise to  $\nu_j$ . Or fugacity  $f_j$  raise to  $\nu_j$  product of all those terms as  $K_f$  or if we choose to express composition of the reacting mixture in terms of its concentrations then we have equilibrium constant  $K_c$  which is this product. So, depending upon how we choose to represent our composition, we will have different definitions or different equilibrium constant. But important to remember, this thermodynamic property that is that equilibrium constant is  $-\Delta G^0 / RT$  and one can actually show a definite relationship between all these different kinds of relationships.



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Equilibrium extent of reaction

$$v_1 A_1 + v_2 A_2 + v_3 A_3 + v_4 A_4 = 0$$

$$K_p = \left( \prod_j P_j^{\nu_j} \right)$$

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

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

Handwritten notes:

- $K_p = \exp\left(\frac{-\Delta G^0}{RT}\right)$
- $\Delta G^0 = \sum \nu_j \mu_j^0$
- $P_j = y_j P = \frac{N_j}{N_T} P$
- $K_p = F(\alpha)$

So now, let us try to now, see how we bring in our equilibrium composition from our free energy chain. Let me reiterate that our equilibrium constant and let us say we are measuring in terms of pressures is exponential minus delta G 0 by R T. This is a thermodynamic property **this is a thermodynamic property**, because all these quantities delta G 0 in particular thermodynamics gives us that information.

Again what is this delta G 0? Is nothing but summation nu j mu j 0. So, this is my thermodynamic property and its function of temperature alone, because our mu j 0 is function of temperature. This is my thermodynamic quantity, my next job now, is to having known these equilibrium constant from thermodynamics. How do I calculate my equilibrium extent of reaction? And that is what we will quickly do it going step by step by step.

Let us say that my equilibrium constant is K p defined in terms of partial pressure of j raise to nu j over product. But what is partial pressure after all? Partial pressure is nothing but the mole fraction into total pressure. And what is mole fraction? Mole fraction is nothing but number of moles of N j divided by the total moles in the reacting mixture. So, y j is nothing but N j by N T, P j is nothing but N j by N T into pressure. Now we are a step closer almost there.

What is our  $N_j$ , as per our definition of extent of reaction; it is  $N_{j0} + \nu_j \alpha$ . So now, if I put and what is if I put this  $N_j$  over here, I have my top term over here. For instead of  $N_j$ , I have put  $N_{j0} + \nu_j \alpha$ . And what is  $n_T$ ? Number of moles total number of moles is nothing but summation  $N_j$ . So, summation  $n_j$  is nothing but summation  $N_{j0}$ . Which I have called  $N_{T0}$ , total number of moles initially present plus summation  $\nu_j \alpha$ . I can write it as  $\alpha \sum \nu_j$ . my equilibrium constant, now is partial total pressure  $P$  into this function over here which is nothing but representing the mole fraction.  $N_j$  by  $N_T$  raise to  $\mu_j$ , because that is my definition of equilibrium constant.

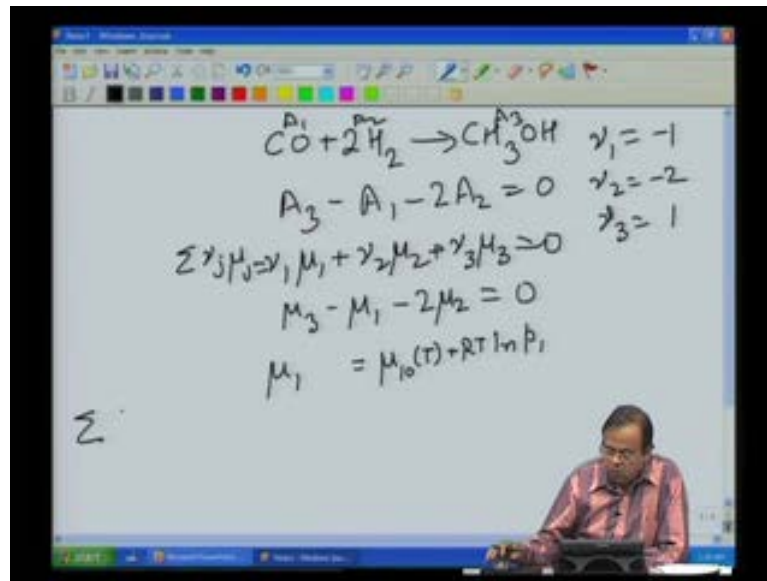
So, now we see my equilibrium constant  $K_p$  is equal to this value. And here, we have  $\alpha$  now appearing for the first time. Or in other words, now my equilibrium information that is  $K_p$  is  $-\Delta G^0 / RT$ . So, knowing the value of  $K_p$  **knowing the value of  $K_p$**  from thermodynamics, I can now solve this equation. I am representing this whole function as some function  $F$  of  $\alpha$  for sake of simplicity.

Knowing this value, we can we can solve this function for  $\alpha$  and get that value of  $\alpha_e$ . Or in other words what will be our  $\alpha_e$ ? Our  $\alpha_e$  will be  $K_p$  equal to  $f$  of  $\alpha_e$ . That is  $K_p$  is known independently from my thermodynamics or let me write it over here,  $K_p$  is equal to  $f$  of  $\alpha_e$ .

I know  $K_p$  independently from my thermodynamic information **I know  $K_p$  independently from my thermodynamic information**, I have this function, I know what is the function this function  $f$ . So, that value of  $\alpha$  which satisfies these equations is my equilibrium extent of reaction.

Let us work out a simple example to make this idea clear. So, let us consider our example of, **let us consider the example of** our carbon monoxide formation.

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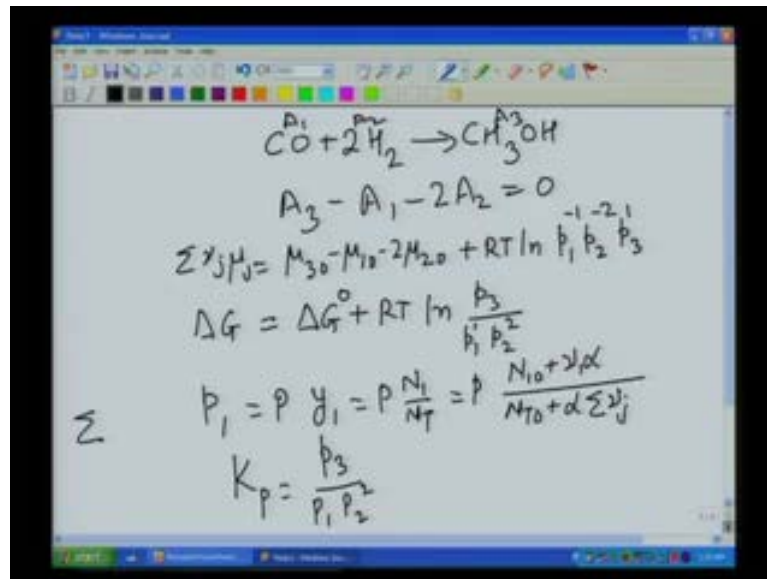


So, I am going to repeat this whole example. Carbon monoxide plus 2 moles of hydrogen gives rise to 1 mole of methanol. Let me call this species as A 1, this as A 2 that is carbon monoxide is A 1, hydrogen is A 2 and methanol is A 3. So, we can quickly write this reaction as A 3 minus A 1 minus 2 A 2 equal to 0. So, my stoichiometric coefficient  $\nu_1$  is minus 1,  $\nu_2$  is minus 2, and  $\nu_3$  is plus 1. What is my condition of equilibrium? My condition of equilibrium is  $\nu_1 \mu_1 + \nu_2 \mu_2 + \nu_3 \mu_3 = 0$ . That is summation  $\nu_j \mu_j$  which is this. So, this is my condition of equilibrium.

Which means, if I have substitute values of  $\nu_1$ ,  $\nu_2$  and  $\nu_3 \mu_3 - \mu_1 - 2\mu_2 = 0$ . Let us come to  $\mu_1$ , what is my  $\mu_1$ ? I am going to use perfect gas mixture behavior. So,  $\mu_1$  as a function of temperature, pressure and all the other quantities,  $\mu_1$  is  $\mu_1^0$ , which is a function of temperature plus  $RT \ln p_1$  partial pressure of one, that is my  $\mu_1$ . So, that is my perfect gas mixture model.

Similar quantities for  $\mu_2$  and  $\mu_3$ . So, now if I substitute these individual values over here, I will get summation  $\nu_j \mu_j$ . So, let me clear some.

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I am just substituting the values of  $\mu_1$ ,  $\mu_2$ ,  $\mu_3$  in this equation. and what I will get is,  $\mu_{30} - \mu_{10} - 2\mu_{20}$  from this first terms over here, plus  $RT \ln \frac{p_3}{p_1 p_2^2}$ . So,  $p_1^{-1} p_2^{-2} p_3^1$ . That is product of  $p_j^{\nu_j}$  in of that so, this is that product.

Now, let me continue this discussion further. So, my free energy change **free energy change** which I had earlier defined as summation  $\nu_j \mu_j$  will be free energy change at standard conditions. And these values you know from **these values you know from thermodynamics**, plus  $RT \ln \frac{p_3}{p_1 p_2^2}$ . What is my partial pressure  $p_1$ ? Total pressure into  $y_1$ , total pressure into  $n_1$  by  $n_T$ , and similarly all other species. And this is now will give me my, what is  $n_1$ ?  $n_1$  is  $n_{10} + \nu_1 \alpha$  and  $n_T$  is  $n_{T0} + \alpha \sum \nu_j$ .

This is what gives me, how I get my equilibrium composition. So now, if I put it over here my  $K_p$  equilibrium is  $\frac{p_3}{p_1 p_2^2}$  and each of this  $p_3$ ,  $p_1$ ,  $p_2$ , will have this term  $\alpha$  and that is how  $K_p$  is related to  $\alpha$ . We will stop here and continue these discussions on how thermodynamics gives us more information in our next session. But before we do that let's try to recap what we saw today. We first of all demonstrated or saw for first hand, why thermodynamics is important? It is important, because it tells us about the equilibrium conditions. It tells us about what operating conditions one

should follow. To get that information, we started with Gibb's equation essentially the idea being that if entropy of the system progressing spontaneously is increasing the free energy decreases.

So, we made use of Gibb's equation got the condition of equilibrium which is summation  $\nu_j \mu_j$  equal to 0 and then brought in by using appropriate model for chemical potential. The composition, temperature, pressure, dependency of chemical potential that is, if it is a perfect gas mixture we have in terms of partial pressures and so on. And then use these conditions to get my equilibrium constant  $K_p$  and relate it to my extent of reaction. How we use this information will be the subject of discussion in my next session. **thank you**