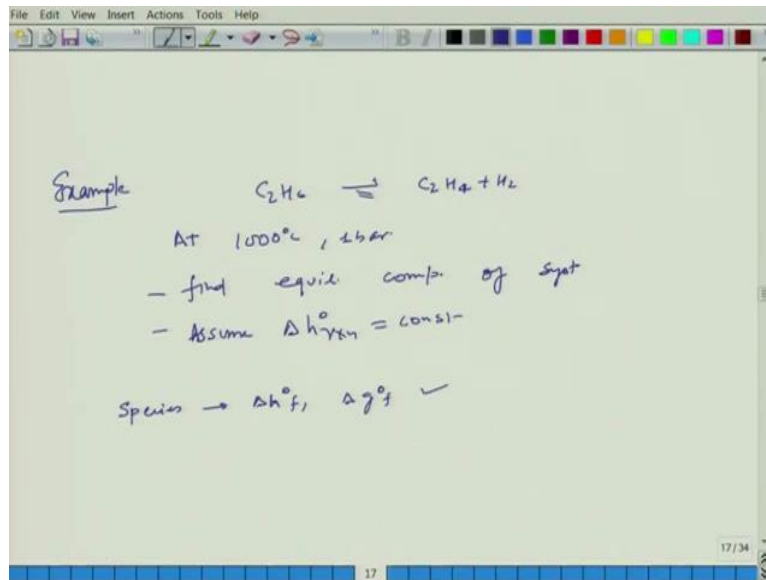


**Chemical Engineering Thermodynamics**  
**Professor Jayant K. Singh**  
**Department of Chemical Engineering,**  
**Indian Institute of Technology Kanpur**  
**Lecture 63**  
**Chemical reaction equilibria - IV**

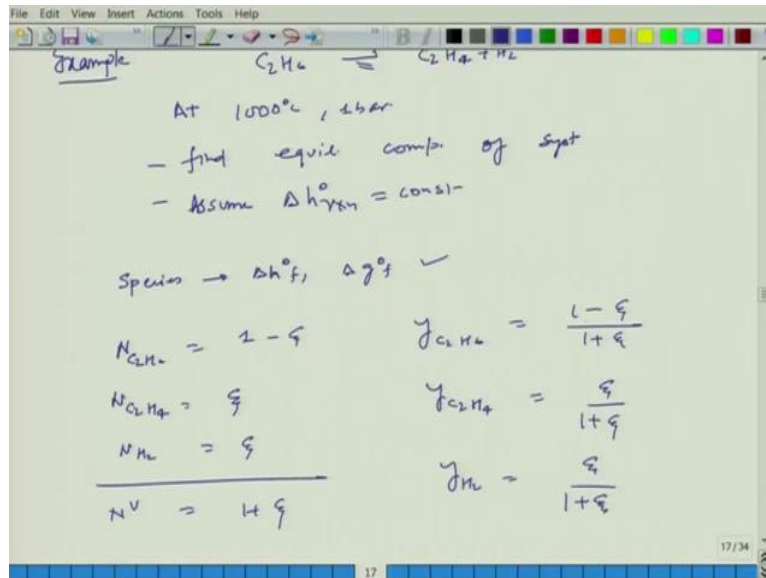
Welcome back. In the last class we discussed about relation of  $K$  as a function of temperature, we also developed an expression where we can find out the  $H$  of reaction at a given temperature with reference to that  $H$  of reaction at 298 that is a standard condition.

(Refer Slide Time: 00:44)



Now, what we want to do is to use an example to illustrate some of our learning which we have did. So, this is an example where basically you have production of ethylene from a decomposition of ethane, so this is your ethane and this is ethylene and the question is at thousand degree Celsius and one bar find the equilibrium composition of the system. Assume that the heat of reaction is constant. Now, what is available for us is the  $\Delta H_f^0$  and  $\Delta G_f^0$  that means the standard heat of formation you know enthalpy of formation and the Gibbs free energy of formation is available to us.

(Refer Slide Time: 01:22)



So, the first foremost important question is that what we need to do in order to find out the equilibrium composition? So, we start from our basic understanding of this  $N$  that given that initially we will be considering that only one, I mean the presence of ethylene and hydrogen initially they were not present and hence I can consider  $N_{\text{C}_2\text{H}_6}$  as simply  $1 - \zeta$  and then  $N_{\text{C}_2\text{H}_4}$  as simply  $\zeta$  and  $N_{\text{H}_2}$  as simply  $\zeta$ .

So, if you sum it up the total  $N^V$  in the vapour phase is  $1 + \zeta$  and this is only as vapour phase reaction.

So, given this your  $y_{\text{C}_2\text{H}_6}$  is going to be  $\frac{1 - \zeta}{1 + \zeta}$ ,  $y_{\text{C}_2\text{H}_4}$  is  $\frac{\zeta}{1 + \zeta}$ ,  $y_{\text{H}_2}$  is  $\frac{\zeta}{1 + \zeta}$ . So, this is a composition which relates to the extent of reaction.

(Refer Slide Time: 02:40)

$$N_{H_2} = 3$$

$$N^V = 4 \cdot 3$$

$$J_{H_2} = \frac{3}{1+3}$$

$$K \rightarrow \Delta G^0_{rn}$$

$$K = \prod (y_i)^{\nu_i} P^{\nu} = \frac{y_{C_2H_4} y_{H_2}}{y_{C_2H_6}} P^{2-1-1}$$

$$= \frac{y_{C_2H_4} y_{H_2}}{y_{C_2H_6}} P$$

$$a) \phi_i = \phi_{i,pure}$$

$$b) \phi_i = 1 \text{ ideal gas}$$

$$a) K = \prod (y_i)^{\nu_i} \prod (\phi_{i,pure})^{\nu_i} \frac{\prod (P^{\nu_i})}{P^{\nu}}$$

$$b) K = \prod (y_i)^{\nu_i} P^{\nu} \text{ ideal gas}$$

Example  $C_2H_6 \rightleftharpoons C_2H_4 + H_2$

Now, we need to find out the equilibrium composition, so essentially that is related to K to your delta  $\Delta G_f^0$  or  $\Delta G_R^0$ . So, let us look at how we can write K. K is nothing but summation sorry K nothing but this  $\prod$  times what we have written here. Now, in this case we are going to consider it to be ideal gas, so assume it to be the ideal gas so this is a very gross approximation, but if you consider  $(y_i)^{\nu} P^{\nu}$  that means we are considering ideal gas and now I can write this why I all the terms here which is available to us.

So, this is going to be  $y_{C_2H_4}, y_{H_2}$  divided by  $y_{C_2H_6}$  and P times  $\nu$ ;  $\nu$  total is  $2-1=1$ , so it is like  $1+1-1$ , that becomes 1. So, I have an expression now which relates  $y_{C_2H_4}, y_{H_2}$  divided by  $y_{C_2H_6}$  times P.

(Refer Slide Time: 03:56)

$$K = \frac{\left(\frac{\xi}{1+\xi}\right)\left(\frac{\xi}{1+\xi}\right)}{\left(\frac{1-\xi}{1+\xi}\right)} P = \frac{\xi^2}{1-\xi^2} P$$

$$\xi = \sqrt{\frac{K}{K+P}}$$

Now, I can express this K in terms of  $\zeta$  also by replacing the composition of y in terms of  $\zeta$  if I do that I get the final expression.  $\zeta$  because this is  $\zeta$  here, so  $\zeta$  times 1 bar plus  $\zeta$  and similarly  $\zeta$  times 1 plus  $\zeta$  1 minus  $\zeta$  divided by 1 plus  $\zeta$ , so that becomes P so this is now can be written as  $\zeta$  square 1 minus  $\zeta$  square here because 1 of 1 plus  $\zeta$  multiplied by 1 minus  $\zeta$  is going to be 1 minus  $\zeta$  square times P.

$$K = \frac{\left(\frac{\zeta}{1+\zeta}\right)\left(\frac{\zeta}{1+\zeta}\right)}{\left(\frac{1-\zeta}{1+\zeta}\right)} P = \frac{\zeta^2}{1-\zeta^2} P$$

So, if you rearrange this I can get K, I can get  $\zeta$  in terms of K plus K plus P, of course P I know, what I do not know is K. So, if I want to find out the composition, equilibrium composition I need to find out K that becomes very clear evident here.

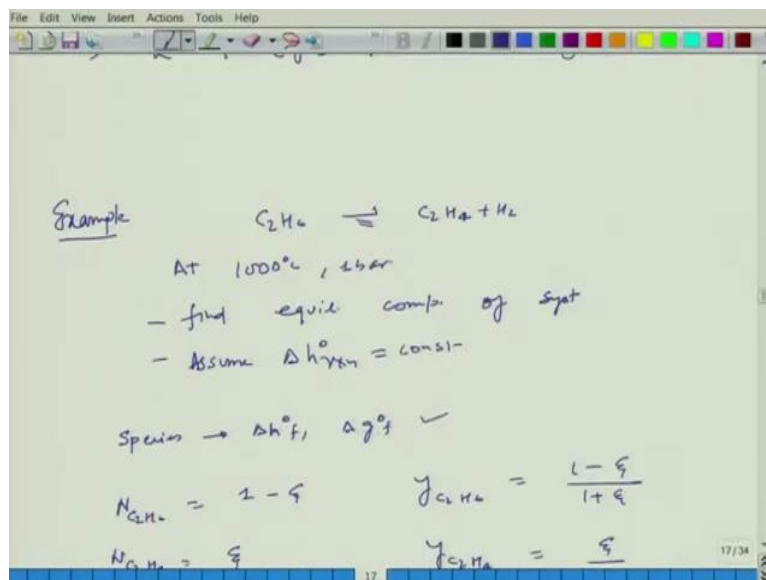
$$\zeta = \sqrt{\frac{K}{K+P}}$$

(Refer Slide Time: 04:56)

$$\xi = \sqrt{\frac{K}{K+1}}$$

$$K_{298} = \exp\left(-\frac{\Delta G_{\text{rxn}}^0}{RT}\right) \rightarrow \sum \nu_i (\Delta h_{f,i}^0)$$

$$\ln \frac{K_{1273}}{K_{298}} = \frac{-\Delta h_{\text{rxn}}^0}{R} \left( \frac{1}{1273} - \frac{1}{298} \right)$$



So, K at 298 can be written as exponential of minus delta g square reaction by RT. Now, delta g reaction here is very clear is going to be simply the summation nu i delta g formation, so this since we have we know this for each of the component, so delta g reaction is going to be simply delta g formation for C2H6 minus that of this because for this is going to be zero.

$$K_{298} = \exp\left(-\frac{\Delta G_{\text{reaction}}^0}{RT}\right)$$

So, I can calculate this easily and thus I can have this information from here and then the issue is now that given this how I find it out for 1273 Kelvin. So, that is going to be minus delta H reaction by R 1 minus T minus 298. so K 298. So, this I know, this of course is a 1273. This we can again get it from a simple summation nu i delta h formation of the species and this we know from the table, so that is why we can find it out this directly.

$$K_{1273} = \frac{-\Delta H_{\text{reaction}}}{R} \left( \frac{1}{T} - \frac{1}{298} \right)$$

(Refer Slide Time: 06:28)

Handwritten notes on a whiteboard:

$$\ln \frac{K_{1273}}{K_{298}} = \frac{-\Delta H_{\text{rxn}}}{R} \left( \frac{1}{1273} - \frac{1}{298} \right)$$

$$K_{1273} = 4.75$$

$$\xi \approx 0.91$$

Below the equation, the following terms are written:

$$y_i$$

$$z_i$$

Handwritten notes on a whiteboard:

$$= \left( \frac{\xi}{1+\xi} \right) \left( \frac{\xi}{1+\xi} \right) P = \frac{\xi^2}{(1-\xi^2)} P$$

$$\xi = \sqrt{\frac{K}{K+P}}$$

$$K_{298} = \exp \left( \frac{-\Delta G_{\text{rxn}}}{RT} \right) \rightarrow \sum \nu_i (\Delta h_f^\circ)$$

$$\ln \frac{K_{1273}}{K_{298}} = \frac{-\Delta H_{\text{rxn}}}{R} \left( \frac{1}{1273} - \frac{1}{298} \right)$$

Species  $\rightarrow \Delta h^{\circ}_f, \Delta g^{\circ}_f$  ✓

$$N_{\text{CH}_4} = 1 - \xi \quad y_{\text{CH}_4} = \frac{1 - \xi}{1 + \xi}$$

$$N_{\text{CO}_2} = \xi \quad y_{\text{CO}_2} = \frac{\xi}{1 + \xi}$$

$$N_{\text{H}_2} = \xi \quad y_{\text{H}_2} = \frac{\xi}{1 + \xi}$$


---


$$K \rightarrow \Delta g^{\circ}_{\text{rxn}}$$

Eq.  $\Pi (y_i)^{\nu} P^{\nu} = \frac{y_{\text{CO}_2} y_{\text{H}_2}}{y_{\text{CH}_4}} P$   $\nu \rightarrow 2-1=1$

$$\frac{C_{p,i}}{R} = A_i + B_i T + C_i T^2 + D_i T^{-1} + E_i T^3$$

$$\Delta h_1 = - \int_T^{298} \sum_{\text{reactant } i} R C_{p,i} dT = \int_T^{298} R \sum_{\text{reactant } i} \nu_i C_{p,i} dT$$

$$\Delta h_3 = \int_T^{298} R \sum_{\text{prod}} \nu_i C_{p,i} dT$$

$$\Delta h_{\text{rxn}, T} = \Delta h_{\text{rxn}, 298} + \int_{298}^T R \sum \nu_i C_{p,i} dT$$

→ reacting species

$$K \rightarrow \Delta g^{\circ}_{\text{rxn}}$$

Eq.  $K = \Pi (y_i)^{\nu} P^{\nu} = \frac{y_{\text{CO}_2} y_{\text{H}_2}}{y_{\text{CH}_4}} P$   $\nu \rightarrow 2-1=1$

$$K = \frac{y_{\text{CO}_2} y_{\text{H}_2}}{y_{\text{CH}_4}} P$$

$$= \frac{\left(\frac{\xi}{1+\xi}\right) \left(\frac{\xi}{1+\xi}\right) P}{(1-\xi)} = \frac{\xi^2}{(1-\xi)} P$$

And from here we can obtain  $K_{1273}$  and if you do that then this turns out to be  $K_{1273}$  is 4.95. So, once we obtain the equilibrium constant at 4.95 then becomes very straight forward exercise because I just have to plug in this and put the pressure in the one bar pressure the units of bar to obtain  $\zeta$ .

$\zeta$  turns out to be 0.91 and once I have zeta then I can plug in back this compositions in the expression of the compositions to obtain the composition. So, from here I can obtain the compositions very clearly. So, once you know this you can easily find out the compositions  $y$ 's of individual species, you can also find out  $N$ s the number of moles available at the equilibrium, so  $N$  of  $i$ 's so you can also find it out

So, that is a very simple exercise which we did, of course I did not elaborate it more and all this details of the calculation but I think you can get the gist of this exercise which would be good enough for understanding how we should proceed in this in such calculations.

Now, one of the thing which we can extend in this problem is what if we consider  $\Delta H$  reaction not to be constant, that means you need to use let us say  $\Delta H$  reaction at the temperature  $T$ , in such a case we have to use this expression. So, we can make this problem more complicated by considering this also not to be constant that means you have to use this expression and also bring this  $C_p$ s values from the system.

The other thing which you can also make it more complicated by not considering this to be ideal gas that means you have to consider the  $\phi$ 's for each individual component. So, essentially the principle of solving this problem will not differ much, it is going to be a similar in nature the more you add this the real conditions which means the reducing the number of approximation the more it will become complicated

So, I will not do more exercise to illustrate all of it but it should be very clearly evident that how you should go in that because for the case of let us say  $\phi$  if you have to bring in  $\phi$ , you have to use the equation of state and for that you have to take one of those the equation of state say such as Van der Waal equation of state and you can solve those 5 values for individual species also based on the critical properties. So, something which is available in the test book you can look at those problems to understand it.

(Refer Slide Time: 09:13)



Liquid phase or solid phase Rm

$$K = \prod \left( \frac{x_i \gamma_i f_i^0}{f_i^0} \right)^{\nu_i} = \prod \left( \frac{f_i}{f_i^0} \right)^{\nu_i}$$

If Ideal soln

$$K = \prod (x_i)^{\nu_i}$$

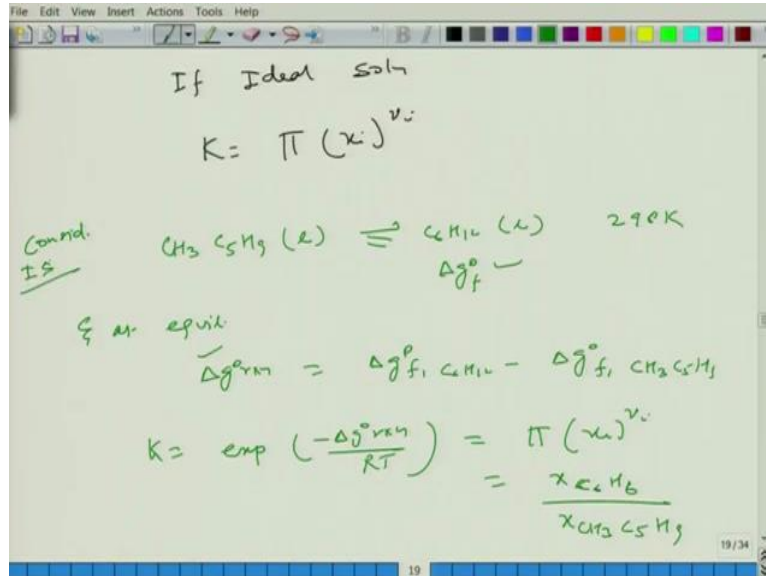
So, let me move on to a very small comment I am going to make it now is that, so we just looked at K in terms of for the case of gas phase but you can extend this K for liquid phase or solid phase, you can also extend the same thing same exercises. Now, in such a case the K can be written as this. Now, here because  $f_i$  here is for pure, so because this is a  $f_i$  which is related to  $x_i \gamma_i f_i^0$  pure I am considering the Lewis-Randall reference here.

$$K = \prod \left( \frac{x_i \gamma_i f_i^0}{f_i^0} \right)^{\nu_i}$$

Now, here also you can come up with a different approximation for example if it is ideal gas sorry if it is ideal solution then of course I can consider  $\gamma_i$  to be  $f_i$  to be simply  $x_i$  and so if ideal solution I can consider K to be simply  $\pi$  times  $x_i^{\nu_i}$  if it is not ideal solution then you have to worry about the activity models and so forth and then again you can make it more complicated. So this is for liquid phase.

$$K = \prod (x_i)^{\nu_i}$$

(Refer Slide Time: 10:39)



And let me just do an example to work on this concept. So, let us consider  $CH_3C_5H_9$  so this is a isomerization of methyl cyclopentane to cyclohexane at 298 Kelvin and we have then delta g formation for both the (com) both the species available to us, so that is a simple question which is given to us.

So, what is being asked is the equilibrium conversion that means what is zeta at equilibrium and this is a liquid phase. So, delta g reaction is going to be simply delta g formation of  $C_6H_{12}$  minus delta g formation of  $CH_3C_5H_9$ , so once we know this information we can get K which is exponential of minus delta g reaction by RT and K is also pi if we consider to be ideal solution then  $x_i^{\nu_i}$  which is nothing but x of  $C_6H_{12}$  divided by x of  $CH_3C_5H_9$ . So, considering ideal solution.

$$K_{298} = \exp\left(-\frac{\Delta G_{reaction}^\circ}{RT}\right) = K = \prod (x_i)^{\nu_i} = \frac{x_{C_6H_{12}}}{x_{CH_3C_5H_9}}$$

(Refer Slide Time: 12:23)

$$K = \exp\left(\frac{-\Delta G^{\circ}_{\text{rxn}}}{RT}\right) = \prod (x_i)^{\nu_i} = \frac{x_{\text{C}_2\text{H}_6}}{x_{\text{C}_2\text{H}_4} x_{\text{C}_2\text{H}_2}}$$
$$K = \frac{\zeta}{1 - \zeta}$$
$$\zeta = 0.875$$

So, from here of course I can write this expression X in terms of extent of reaction this would be  $\frac{\zeta}{1-\zeta}$ , so you have K. So, once you know delta g of reaction you obtain K and from there you can obtain zeta and in this case zeta would be something 0.875. So, as I said it is a straightforward exercise once you have this information such as your delta g of f and you have appropriate thermodynamic conditions available to you so that you can take appropriate approximation.

You can of course do not take approximation but then again you will be requiring other information for example in this case for the liquid phase you need activity models in order to do that which you can use one of those activity models which we have considered such as 2 suffix you know Margules equations and so forth. You can also apply it here in order to find it if the information is available to you. But, the exercise remains the same and that is something which is not going to change as far as the series of steps to be considered but you can make things little complicated as well.

Now, many systems are not just a gas phase or liquid phase reaction it is a solid phase but it also has a remaining gas phase or the liquid phase that means it is a heterogeneous reaction. So, it means both the phases need to be considered. So, in such a case of course you have to work separately and this is something which you can extend this exercise for heterogeneous reaction also but I am not going to cover this expect in this particular course if you are interested, there are couple of examples in the text book which will be very valuable illustrate in order to understand these heterogeneous reactions.

So, I would suggest or recommend you to go through those examples and for your own understanding but I think you know the whole concept of this particular chapter was or particular topic was to understand how to find the necessary conditions particularly at equilibrium or which relates to which

relates to the equilibrium conversion or in other words how to find equilibrium conversions and that is what we did.

We relate our basic stoichiometric equations and extent of reaction was introduced and subsequently the equilibrium constant was defined which relates to the  $\Delta G$  of reaction and that of course you know you can use or calculate based on the information given to you from the  $\Delta G$  of at the standard conditions. You can do this exercise in a gas phase, liquid phase and the heterogeneous phases also

And something which makes this particular chemical reaction equilibrium more rich because you can use a lot of concepts which we have done in the last so many lectures which relates the gas phase the representation in terms of fugacity for this to the equation of state and similarly the non-ideality in the liquid phase was represented in terms of activity and then to the many different models. So, all those learning all those models which we have learned can be used here to find out more realistic information as far as the reaction at equilibrium is concerned.

So, I would like to summarize what we have done in this course and this would be our last lecture. So, we started with a very simple understanding again of the first law and second law and we used our background of engineering thermodynamics where we have built up some of the understanding on those subjects on those kind of concepts particularly.

And then that after going through the revisions of the first law and second law, the focus was more on the development of thermodynamic functions which essentially depends on different different conditions for which we introduced natural variables for a given thermodynamic functions and subsequently we understand the importance of those thermodynamic functions and the conditions of the maximum and minimum for those functions in order to represent equilibrium.

Once we have understood that then we went to the also understanding of what is a molecule nature in general and what are the typical forces molecules face or experience depending on the nature so we introduced something called dispersion, interactions and you know induced dipole moment and so forth and so that provided a little bit of understanding of the molecular nature which governs a bit of all this equation of state or deviation from the ideality.

And then we talked about equation of state, then we moved into representing the non-ideality in the gas phase by something called fugacity or fugacity coefficients and subsequently, we represent equation of state, use the equation of state to obtain the fugacity and similarly if there is a thermodynamic information or data information available from the experiment we also introduced how to do that.

And subsequently we also talked about a representation of non-ideality in terms of activity models and introduced many models for such different kind of cases where we can represent gamma which we call it activity coefficients. Then our focus was more on finding out the equilibrium phases or phase equilibria. So, we spent a tremendous amount of time to find out vapour liquid equilibria followed by liquid-liquid equilibria and we also mentioned about the solubility of the gas phase, we also talked about osmotic pressure and membrane conditions.

So, enormous information we discuss about it. So, overall we covered a breadth of the information relevant for chemical engineers of particularly at equilibrium which gives you the limiting informations which can take the which can make you, you know sound enough to take a suitable decisions particularly related to the processes and at the end in the last two-three lectures we are talking about chemical reaction equilibrium.

So, I think you know we have covered a vast info thing and vast over all topics related to chemical engineering thermodynamics and I hope that this course has given you ample ammunition for you to appreciate the reaction, appreciate the natural behaviour of the phase equilibria, appreciate the non-ideality and so that you can use it in your real examples and many other processes.

So, with that I will thank you for attending this course it was a wonderful giving these lectures and I hope that you have, you can make use of the information or the lectures which we have delivered, so thank you very much and I hope you would enjoy thermodynamics more in the future as well, thank you.