Chemical Engineering Thermodynamics
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Lecture 60
Chemical reaction Equilibria

Welcome back, so today we will start a new topic, chemical reaction equilibria which is central to the chemical engineering as such.

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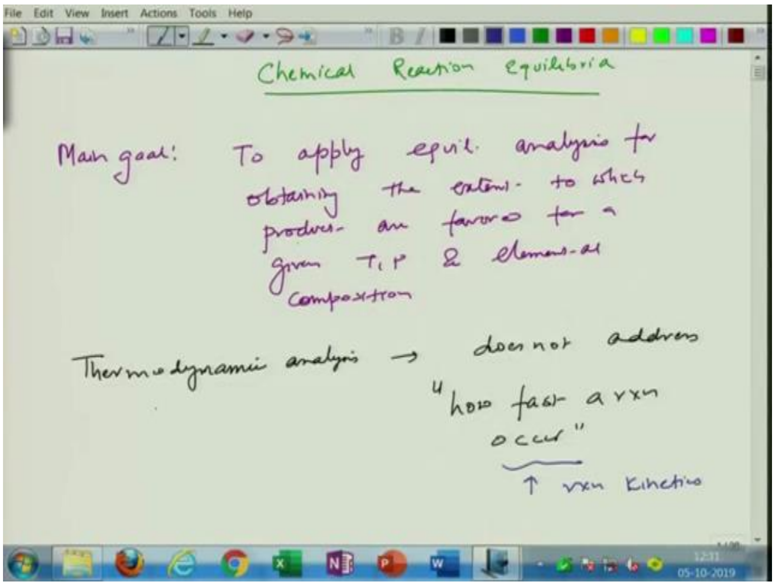
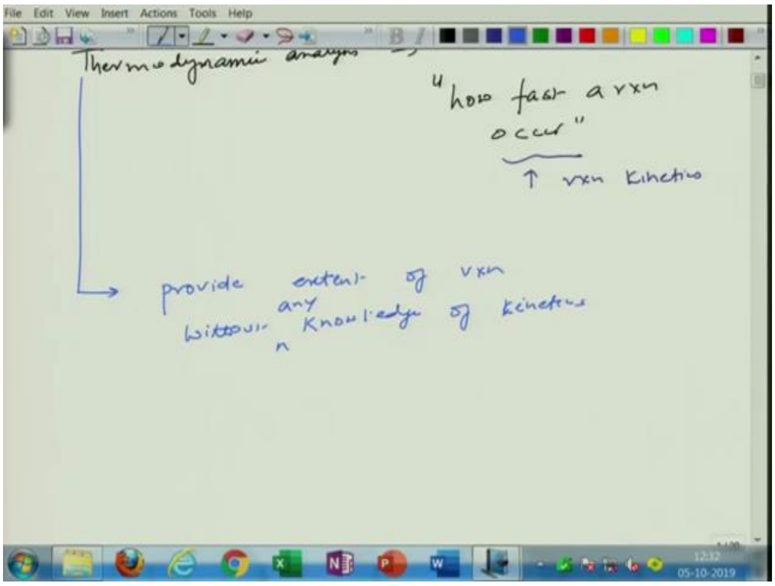


Chemical Reaction equilibria

Main goal: To apply equil. analysis for obtaining the extent to which products are favored for a given T, P & elemental composition

Thermodynamic analysis → does not address "how fast a rxn occur"

↑ rxn kinetics



Thermodynamic analysis

"how fast a rxn occur"

↑ rxn kinetics

→ provide extent of rxn without any knowledge of kinetics

So well if you know that note this, that we are writing reaction okay but also, we are saying is equilibria. So essentially what we are interested is what is the composition of a reaction at the end of the reaction when it ends that means when it is at equilibrium, okay.

So the main goal of this particular topic or this analysis is to obtain or to apply equilibrium analysis for obtaining the extent to which products are formed for a given temperature pressure and elemental composition. So, the chemical reaction equilibria does not address that how fast a reaction occurs. Okay it has nothing to do with the time, the only thing we addresses is that what is the extent of a product, extent of the product which is being formed or extent of the reaction which has occurred.

Which means basically though the product may be more favorable energetically there is a feasibility or there is a possibility that the some of the reactants are still remain un-reacted. And that is something which is governed by Gibbs free energy and this is something which we are going to spend some time to understand it. So thermodynamic analysis does not address how fast a reaction occur okay, now this particular question is addressed by reaction kinetics.

So thermodynamics and kinetics of course are critical or central part of chemical reaction or chemical engineering as such, okay. So thermodynamic analysis here this provide extent of reaction okay without knowing or knowledge of without any knowledge of kinetics, okay. So it does not talk about or uses any of this rate information in order to understand or in order to evaluate the extent of the reaction.

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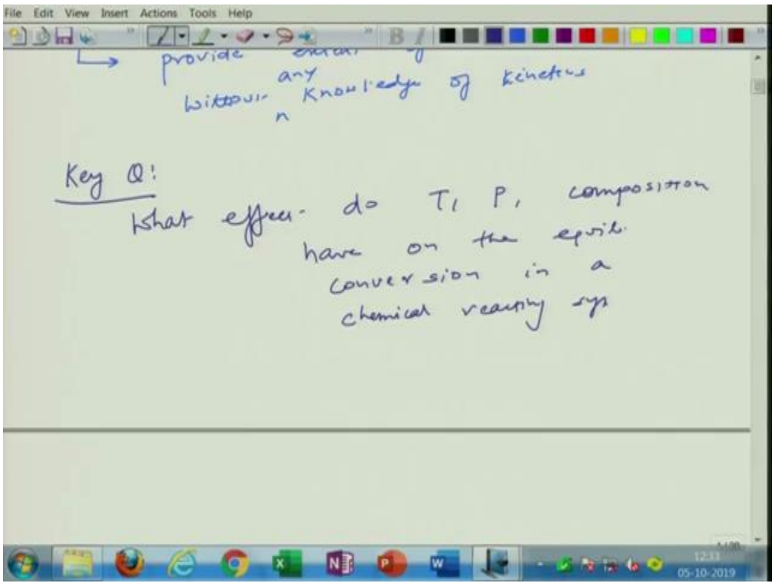

→ provide

without any knowledge of kinetics

Key Q:

What effect do T, P, composition have on the equilib. conversion in a chemical reacting sys

Now, of course it is valid if it is the thermodynamic controlled this kind of analysis. But the key question which we are going to work on is what effect do temperature, pressure and composition of the let us say reactant have on the equilibrium conversion in a chemically reactive system, okay. So again, this will not tell anything about the rates, okay. It just talks about final conversion. Now as I said that at the end of the day if you are talking about equilibrium, then you are also at a given temperature and pressure.

Then essentially it relates to you Gibbs free energy. That is a thermodynamic function, which would be minimum in order to obtain the equilibria. And if you look at thermo dynamical expression of a Gibbs free energy, it has enthalpy and entropy both, right?

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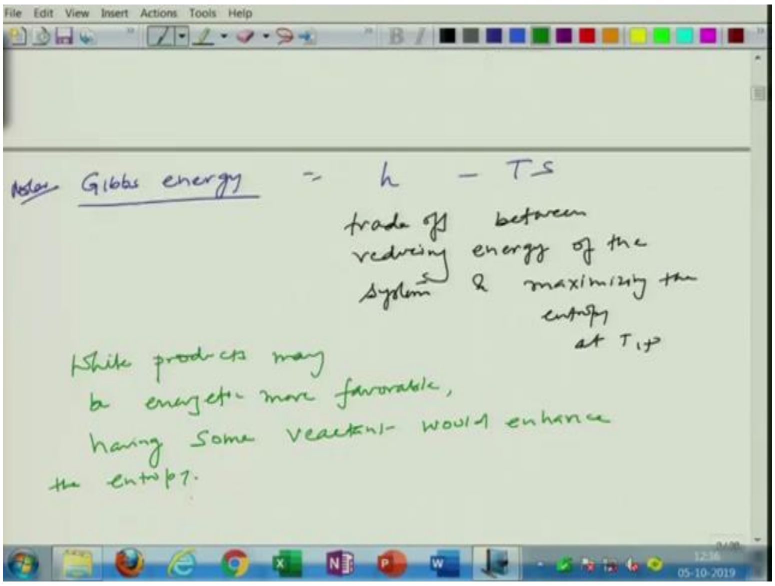
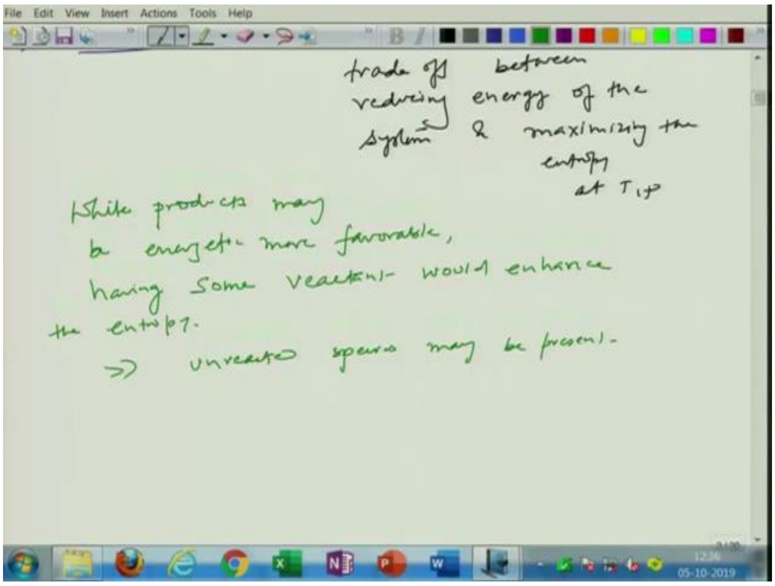


Notes Gibbs energy = h − Ts

trade offs between reducing energy of the system & maximizing the entropy at T, P

While products may be energetic more favorable, having some reactant would enhance the entropy.



trade offs between reducing energy of the system & maximizing the entropy at T, P

While products may be energetic more favorable, having some reactant would enhance the entropy.

⇒ unreacted species may be present.

$$Gibbs\ Energy = h - Ts$$

So it has enthalpy and S here T S, so this is of course a molar Gibbs free energy. Now, clearly there is a trade-off okay, the product as such will be having a lower, let us say enthalpy which essentially means it may be preferred over the reactant but then entropy, if it will be high if there species, some of the species reactants are still remain unreacted. So does there is a tradeoff, okay. So trade-off between reducing energy which is because of this, of the system and maximizing entropy at temperature and pressure.

So clearly the maximizing the entropy means that you need to have more of the species, which essentially means that some reactant would remain, you know, if the reactants are not completely converted then this will of course would mean that entropy will be higher. So a while products maybe energetically favorable, more favorable, having some reactant could enhance the entropy okay which essentially means that this implies that unreacted species may be present.

Now this happens of course at a certain temperature and pressure. Now if you want to convert this amount of the remains of the reactant or remaining amount of the reactant if you want to further reduce, you have to play with the thermodynamic condition. That means the compositions, the temperature and pressure, okay. Which essentially means you are going to change that Gibbs free energy of the systems, okay. So it is very clear there is a two competing behavior, one which tries to reduce the energy, other try to, you know, suppress this conversion because that will also increase the entropy.

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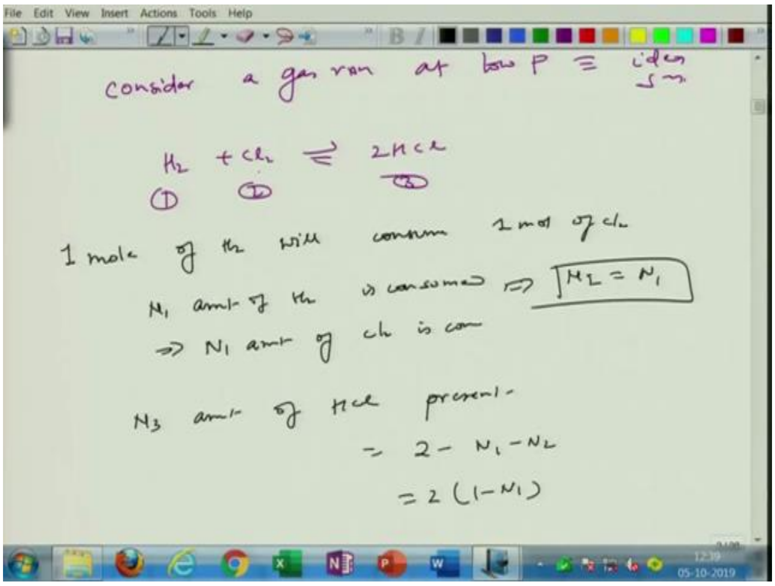

consider a gas rxn at low P ≡ ideal sol

$H_2 + Cl_2 \rightleftharpoons 2HCl$

① ② ③

1 mole of H_2 will consume 1 mol of Cl_2

N_1 amt of H_2 is consumed ⇒ $\boxed{N_2 = N_1}$

⇒ N_1 amt of Cl_2 is con

N_3 amt of HCl present

$= 2 - N_1 - N_2$

$= 2(1 - N_1)$

$$H_2 + Cl_2 \rightarrow 2HCl$$

$$N_3\ amnt.of\ H_1 is\ consumed, \qquad N_2 = N_1$$

$$N_3\ amnt\ of\ HCl\ present = 2 - N_1 - N_2 = 2(1 - N_1)$$

So let us consider an ideal gas reaction. That is assuming that it is a low pressure. So consider a reaction or gas reaction at low pressure. And we are saying this is corresponding to let us say ideal guess system, okay. So we are considering as stoichiometric equation here where H2 plus Cl 2 goes 2HCl. So essentially all the atoms are balanced here. And we are referring this to be, let us say a species1, 2 and this is 3 species, okay.

Now one mole of H2 will consume 1 mole of Cl 2, okay. So let us say if you want to say that you know N1 mole or N1 amount or is consumed of H2 is consumed which implies N1 amount of Cl 2 is consumed, okay. So N1 amount of H 2 if you want to put it there, the corresponding number of moles, if you use the reference N2 should be equal to N1. That is a number of mole of component 2 or species 2 it should be equal to N1 okay.

So then what would be the case N3? So N3 is the amount of HCl present would be 2 minus N1 minus N2 okay. Which essentially means it is a 2, 1 minus N1. So essentially it is because you considering the number of moles we have used here for N 1. And this is the number of moles because stoichiometric tells you that 1 moles of H2, when it reacts with the one moles of this, the two moles are present. So we using the reference one.

And then we are talking about simple the amount of H 2, which is consumed. If it is let us say N1 then the amount of HCl can be simply written in this balance in the simple stoichiometric balance.

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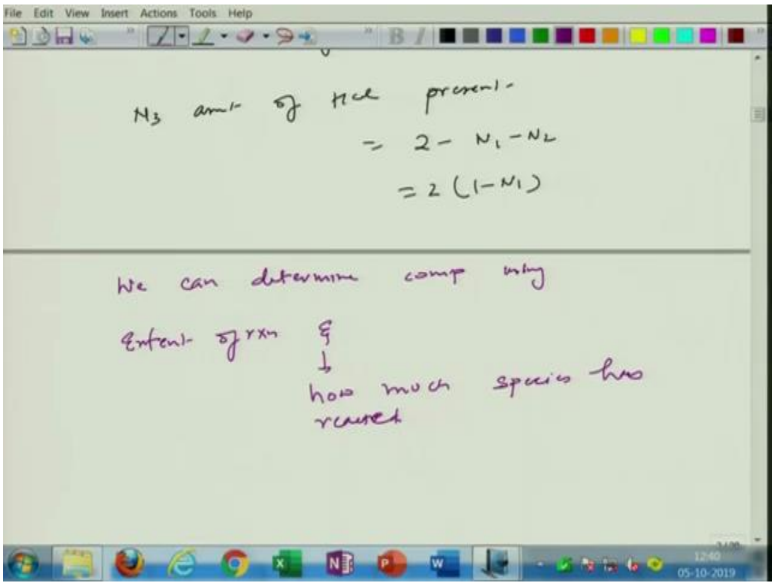

N_3 amt of HCl present

$= 2 - N_1 - N_2$

$= 2(1 - N_1)$

We can determine comp using

Extent of rxn ξ

$\downarrow$

how much species has reacted

So we can determine the composition, so we can determine composition if we use something called using something called extent of reaction. So this is something which we are going to spend a little more time on this. So, but it tells you that how much a species has reacted. So we normally use the limiting species which has other species which limits the reaction as a base, okay.

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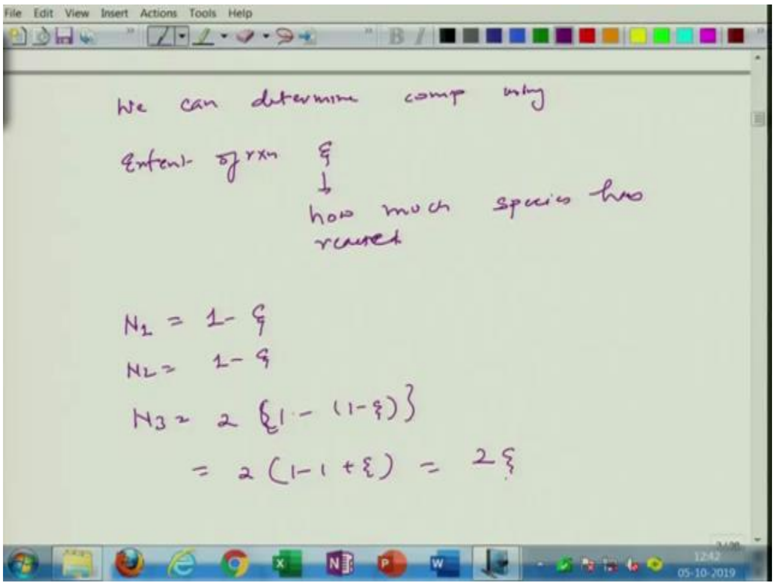

We can determine comp only

Extent of rxn ξ
↓
how much species has reacted

$N_1 = 1 - \xi$
$N_2 = 1 - \xi$
$N_3 = 2\{1 - (1-\xi)\}$
$= 2(1-1+\xi) = 2\xi$

$$N_1 = 1 - \zeta$$

$$N_2 = 1 - \zeta$$

$$N_3 = 2\{1 - (1 - \zeta)\} = 2(1 - 1 + \zeta) = 2\zeta$$

So, let us consider the, you know the X here or this zeta here in terms of N or other define N in terms of zeta. So if N1 is considered the amount which is being, you know which remains for example, then, okay initially we have used one mole. So this is the amount let us say which is consumed okay. So if this is amount which is consumed, initially we had 1 mole of a as 2 and one mole of Ca CL 2. And that is what we use the total two moles minus N1 (plus) minus N2, which means that that is amount of HCl which should be present at this moment when this amount is consumed.

Now if you are considering the extent of reaction then N1 should be 1 minus the zeta here and N2 should also be 1 minus zeta, okay. Which essentially means N3 should be 2 times 1 using the same expression here, 1 minus N 1. So it is 1 minus this okay, this is going to be 2, 1 minus 1 plus this that is going to be 2 of zeta okay.

So again, let me get back again on this reaction. so this is a basic reaction which we have considered here, 1 mole of H2 reacted with 1 mode of Cl 2, to give 2 moles of this. Let us assume that if N1 is amount of H2 which is consumed, then the same amount of Cl 2 should be consumed okay and then we can write that the amount of HCl should be the initial 2 minus whatever is consumed should be that of the Cl. That should be the amount of (CO) HCl present.

Now if we use this thing more from the perspective of extent of reaction, then essentially, I can write the amount of a H2 consumed is 1 mole minus the amount of extent of reaction. So in this case, we can take any of these bases with we can take H2 also, Cl 2 also. And if you do that, then N3 can be written this in this form. Now so the question now is that, what will be the appropriate or rather the optimal extent of reaction for a given reaction? And this is something which you can only solve it by minimizing the Gibbs free energy.

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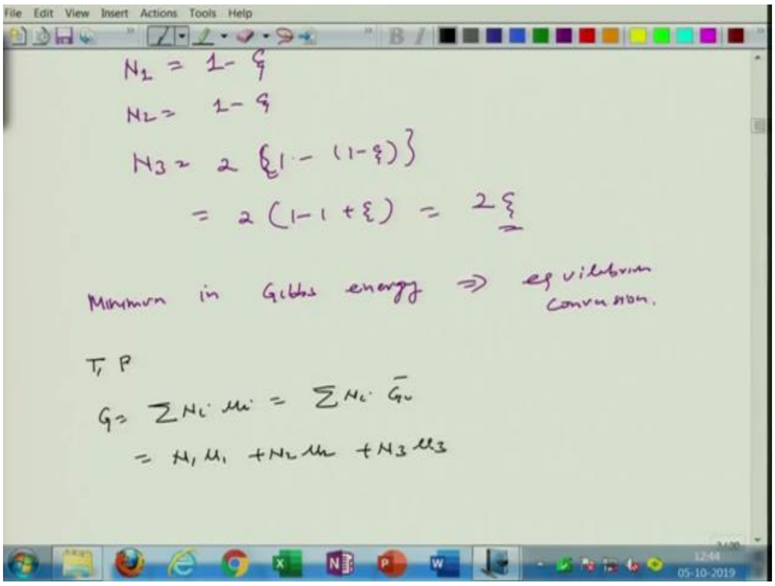


$N_1 = 1 - \xi$

$N_2 = 1 - \xi$

$N_3 = 2\{1 - (1-\xi)\}$

$= 2(1 - 1 + \xi) = \underline{2\xi}$

Minimum in Gibbs energy ⇒ equilibrium conversion.

T, P

$G = \sum N_i \mu_i = \sum N_i \bar{G}_i$

$= N_1 \mu_1 + N_2 \mu_2 + N_3 \mu_3$

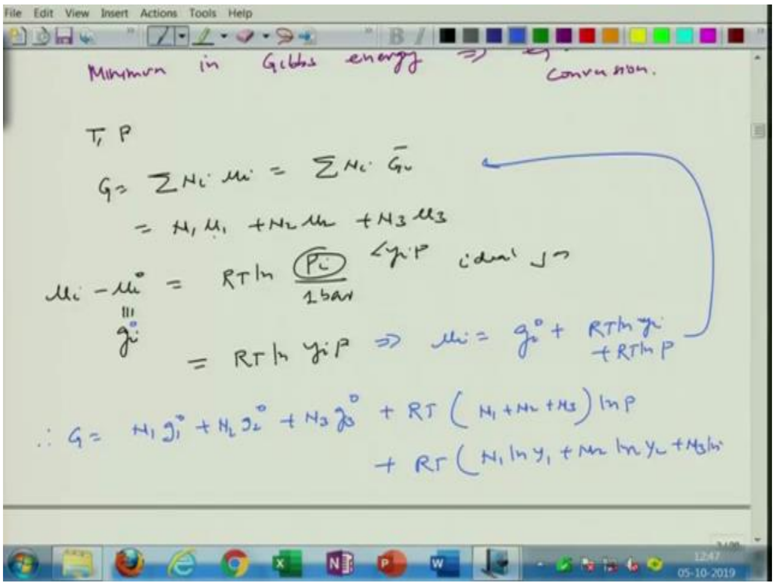
$$T, P$$

$$G = \sum N_i \mu_i = \sum N_i \overline{G_i} = N_1 \mu_1 + N_2 \mu_2 + N_3 \mu_3$$

$$\mu_i - \mu_i^0 = RTln\, P_i = RTln\, y_i P => \mu_i = g_i^0 + RTln\, y_i + RTlnP$$

$$G = N_1 g_1^0 + N_2 g_2^0 + RT(N_1 + N_2 + N_3) \ln P + RT(N_1 \ln y_1 + N_2 \ln y_2 + N_3 \ln y_3)$$

$$G = (1 - \zeta)(g_1^0 + g_2^0) + \zeta g_3^0 + 2RTlnP + RT[(1 - \zeta) y_1 + (1 - \zeta) \ln y_2 + 2 \ln y_3]$$



Minimum in Gibbs energy ⇒ eq. conversion.

T, P

$G = \sum N_i \mu_i = \sum N_i \bar{G}_i$

$= N_1 \mu_1 + N_2 \mu_2 + N_3 \mu_3$

$\mu_i - \mu_i^0 = RT \ln \frac{\boxed{P_i}}{1 \text{ bar}}$ $\leftarrow y_i P$ ideal gas

$\mu_i^0 \equiv g_i^0$

$= RT \ln y_i P \Rightarrow \mu_i = g_i^0 + RT \ln y_i + RT \ln P$

$\therefore G = N_1 g_1^0 + N_2 g_2^0 + N_3 g_3^0 + RT(N_1 + N_2 + N_3) \ln P$

$+ RT(N_1 \ln y_1 + N_2 \ln y_2 + N_3 \ln$

So minimum of, minimum in Gibbs free energy would give you the equilibrium conversion okay which means the amount which has been converted and something which we can now work on. So we can do that in the same you know, we can find it through the conversion. That means the amount of N1 or the optimum value of N1 for example okay. So let us consider the case where we write at a constant T and P then I can write this G as summation N i and Mu i.

Okay I can also write this as Ni partial Gi okay and this for the 3 species is N1, Mu 1 plus N2 Mu 2 plus N3 Mu 3. Now I represent Mu as we have done in the past. Mu i is Mu i0 reference value which is nothing we can consider Gi 0 also, which is same as this coolant.

And this is going to be RT ln Pi divided by the reference we are considering bar okay. So that is a considering an ideal gas. Okay this is something which we can consider an ideal gas that is what we have done that and this I can write this as a Yi p okay. The reference state is again 1 bar that is a something which we have written and this is a RT ln Yi p, okay. So, now I can plug this expression back in here. So if I do that for all the 3 components, I am going to get the first term N1 G1 0. Okay so because Mu i 0 is nothing but gi 0 and N2 g2 0 okay.

So this is the first term because Mu i is nothing but gi 0 plus RT ln yi plus RT ln P, so that is 3 terms we have. And if you plug in back here, we are going to get first term this plus RT N1 plus N2 plus N3 ln P plus this term which is again RT but N1 ln Y1 plus N2 ln Y2 plus N3 ln Y3 okay.

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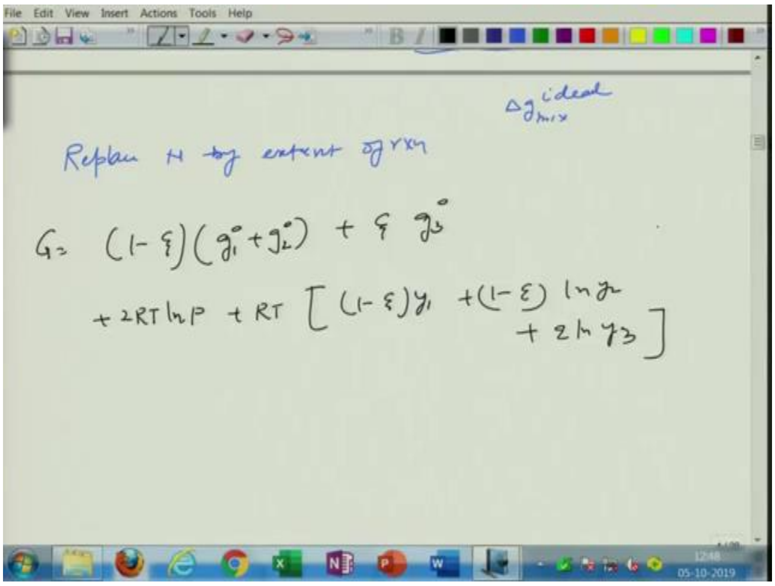
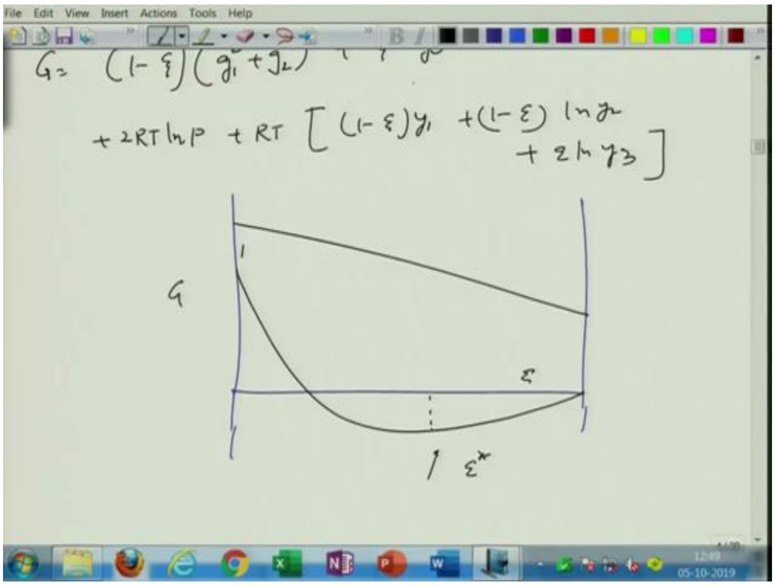


Δg_{mix}^{ideal}

Replace N by extent of rxn

$$G = (1-\xi)(g_1^0 + g_2^0) + \xi g_3^0$$
$$+ 2RT \ln P + RT\left[(1-\xi) y_1 + (1-\xi)\ln y_2 + \xi \ln y_3\right]$$



$$G = (1-\xi)(g_1^0 + g_2^0)$$
$$+ 2RT \ln P + RT\left[(1-\xi) y_1 + (1-\xi)\ln y_2 + \xi \ln y_3\right]$$

Now clearly this last term is nothing but is decrease in the free energy due to the mixing. So this represent your Delta g makes ideal okay. Now you can replace N1 by extent of reaction. So if you replace N by extent of reaction as we have done for this specific case which is this, right. Okay so we can write this in this way and if we do that, I get an expression which is G as 1 minus zeta G1 0 plus G2 0 plus zeta G3 0. That is a first part which comes from the this expression, okay and then you have other term plus RT 1 minus zeta Y1 plus 1 minus zeta ln Y2 plus zeta ln Y3, okay.

So we have now this expression. Now if you want to minimize this, you have to minimize with respect to a zeta here to get that, that means the derivative of G with this respect to zeta, obtain the optimum value of it. But let us look at what if you are just considering the G as a function of a zeta here. So the first term which was nothing but this term okay would be as seen as simply a linear combination, which will be something like this. The Delta G idle mixture is a one which we will bring it here, this whole shift here to something like this okay.

And somewhere here you will get a minimum G. okay so this could be your G optimum. So it is clearly that a mixing term reduces the G for a certain zeta and there is a tradeoff between the energy and entropy is something which we can clearly see by a simple equation as example, which we have considered for the ideal gas system. Now the next thing is, which we have to worry about is that, you know, can we come up with a generic, you know, mechanism to analyze the reaction equilibrium? And that something which we will focus now.

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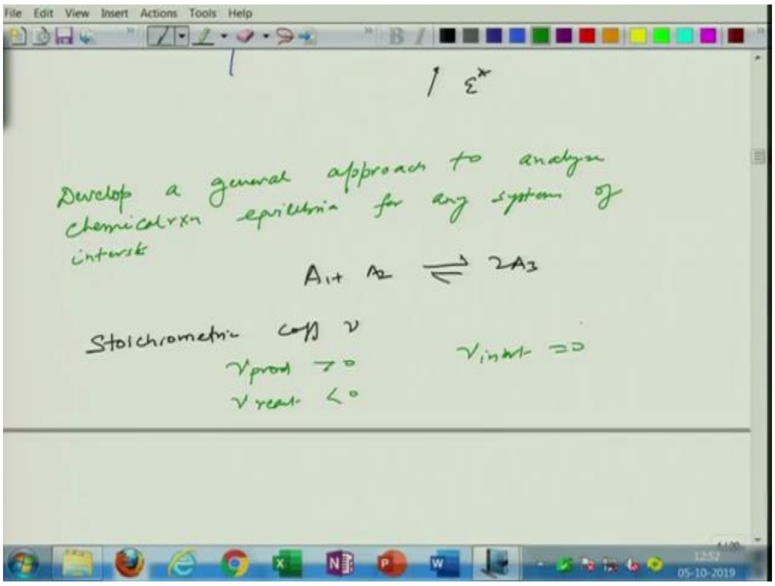


$\uparrow \varepsilon^*$

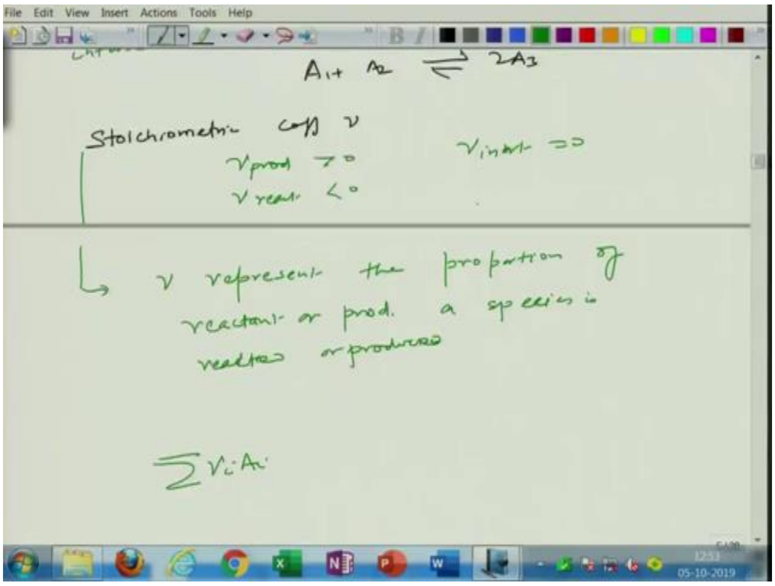
Develop a general approach to analyze chemical rxn equilibria for any system of interest

$A_1 + A_2 \rightleftharpoons 2A_3$

Stoichrometric coff ν

$\nu_{prod} > 0$ $\nu_{inert} = 0$

$\nu_{react} < 0$



$A_1 + A_2 \rightleftharpoons 2A_3$

Stoichrometric coff ν

$\nu_{prod} > 0$ $\nu_{inert} = 0$

$\nu_{react} < 0$

↳ ν represent the proportion of reactant or prod. a species is reacted or produced

$\sum \nu_i A_i$

So, next objective is to develop general approach to analyze chemical reaction for any system of interest okay. So let us consider a simple example okay which could be your A1 plus A2 goes to 2A 3 which is nothing, but the same example of H2 plus Cl 2 goes to 2 HCl. Now here what we are going to do is, we are going to define something called stoichiometric coefficient which is quite useful for analyzing such a system.

So but conventionally we considered a Nu product to be greater than 0 that means the, let us say in this case 2 is (positive) the Nu of this would be 2 and Nu of a1 would be minus 1 Nu of A2 would be minus 1 and reactant as I said, is going to be negative. But if they are inert species then we are going to consider the Nu is 0. So the meaning of Nu, now it is obviously evident is that Nu represent the proportion of reactant or product a species is reacted or produced, okay.

So of course, it is uses a, the basic stoichiometric equations to obtain that. Now for given reaction here, we can represent this reaction using a simple Nu i Ai okay. So this is your basically reaction. If you think about it, this is what the representation of this 1 plus A2 goes to A3.

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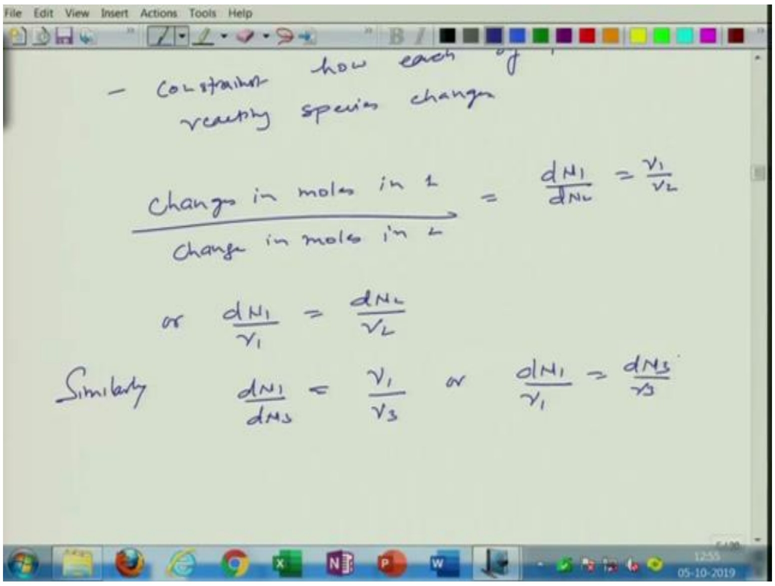


- constraint how each of reacting species change

$$\frac{\text{Change in moles in 1}}{\text{Change in moles in 2}} = \frac{dN_1}{dN_2} = \frac{\nu_1}{\nu_2}$$

$$\text{or} \quad \frac{dN_1}{\nu_1} = \frac{dN_2}{\nu_2}$$

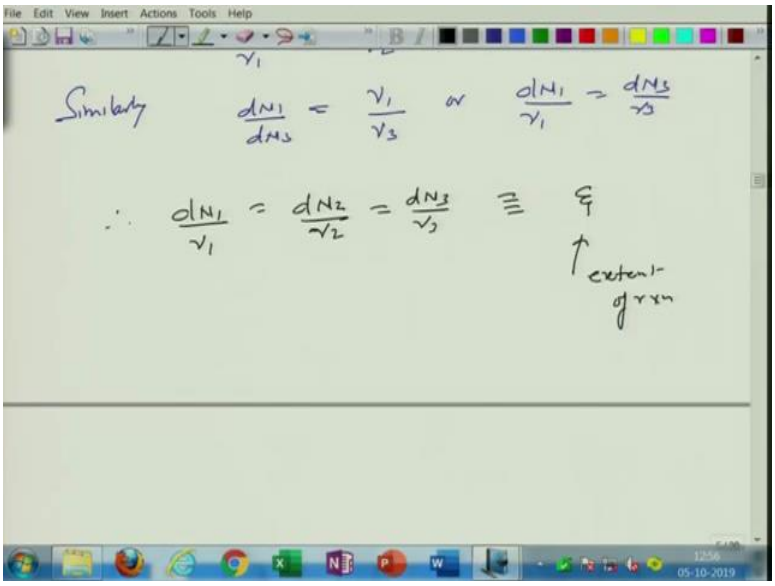
$$\text{Similarly} \quad \frac{dN_1}{dN_3} = \frac{\nu_1}{\nu_3} \quad \text{or} \quad \frac{dN_1}{\nu_1} = \frac{dN_3}{\nu_3}$$

$$\frac{changes\ in\ moles\ in\ 1}{changes\ in\ moles\ in\ 2} = \frac{dN_1}{dN_2} = \frac{\gamma_1}{\gamma_2}$$

$$or, \frac{dN_1}{\gamma_1} = \frac{dN_2}{\gamma_2}$$

$$Similarly, \frac{dN_1}{dN_2} = \frac{\gamma_1}{\gamma_3} \quad or, \frac{dN_1}{\gamma_1} = \frac{dN_3}{\gamma_3}$$

$$\frac{dN_1}{\gamma_1} = \frac{dN_2}{\gamma_2} = \frac{dN_3}{\gamma_3} = \zeta$$



ν_1

Similarly $\frac{dN_1}{dN_3} = \frac{\nu_1}{\nu_3}$ or $\frac{dN_1}{\nu_1} = \frac{dN_3}{\nu_3}$

$\therefore \frac{dN_1}{\nu_1} = \frac{dN_2}{\nu_2} = \frac{dN_3}{\nu_3} \equiv \xi$

$\uparrow$ extent of rxn

Now this particular understanding or this particular, you know introduction of this stoichiometric coefficient also brings some kind of constraint, right? How H of the species or reacting species change. So though the constraint is there as a part of the reaction you are basically are is nothing but constraint. But using this we can understand it much easier so let us try to put that mathematically.

So for example, okay, if we, if I am saying that well, what is the ratio of change in moles in species 1 divided by change in moles in species 2. So this would be your dN 1 by dN 2 okay and this would be if there is a change in dN 1 by dN 2 okay these are now related to the stoichiometric coefficient, okay in the following way. Okay this will be nothing but the ratio of the stoichiometric coefficient or in other word dN 1 by Nu 1, Nu 1 is going to be dN 2 by Nu 2.

Similarly, dN 1 by dN 3 is also going to be simple, simply the ratio of Nu 1 and Nu 3 or we can write here as dN 1 by Nu 1 is nothing but dN 3 by Nu 3. So this brings to us obvious brings a very generic expression that the change in the moles of a species and its ratio with the stoichiometric coefficient is basically a constant for all the species okay, why? Because you can clearly see here if you look at these 3 equations therefore dN 1 by Nu 1 which was here, that is equal to dN 2 but this is also equal to dN 3.

So which means this ratio of the change in the moles and its corresponding stoichiometric coefficient is basically a constant okay and this we represent as the extent of reaction. We can show it also that earlier definition, the way I have written is nothing but consistent with this, okay. So let us also think about this unit. So though, since this is going to be coefficient, the unit of extent of reaction is going to be units of moles okay.

It can be negative because if it is negative it simply means that the change you know or the kind of reaction which you have written, the progress or the direction of the reaction is basically opposite to what we have anticipated.

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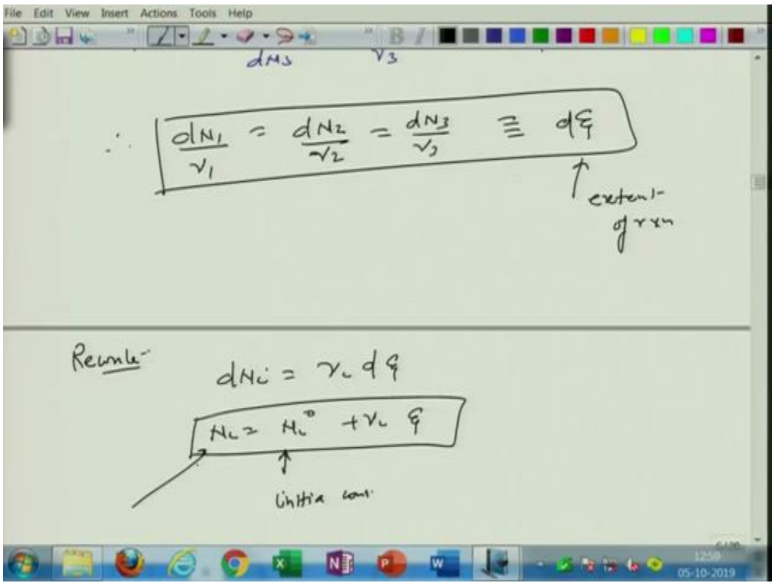

$$\therefore \boxed{\frac{dN_1}{\nu_1} = \frac{dN_2}{-\nu_2} = \frac{dN_3}{\nu_3} \equiv d\xi}$$

$$dN_i = \nu_i \, d\xi$$

$$\boxed{N_i = N_i^0 + \nu_i \xi}$$

$$Rewrite, dN_i = \gamma_i d\zeta$$

$$N_i = N_i^0 + \gamma_i \zeta$$

So let us rewrite, now we now can write in general dNi is Nu i, so let me go back here. So this is the differential amount and hence this should be also differential amount. Okay so that we can write in this way, so this is a differential change in extent of reaction okay, right? So these are, this is constant and now if you can consider this in the generic form, we can write dNi is equal to gamma I d zeta.

And if you integrate this, this is going to be Ni, is it going to Ni 0 that means something at an initial concentration and Nu i is anyway constant. So this is what would be a generic expression. This is nothing about the same thing which we have written earlier, so let us go back and check what we have done earlier.

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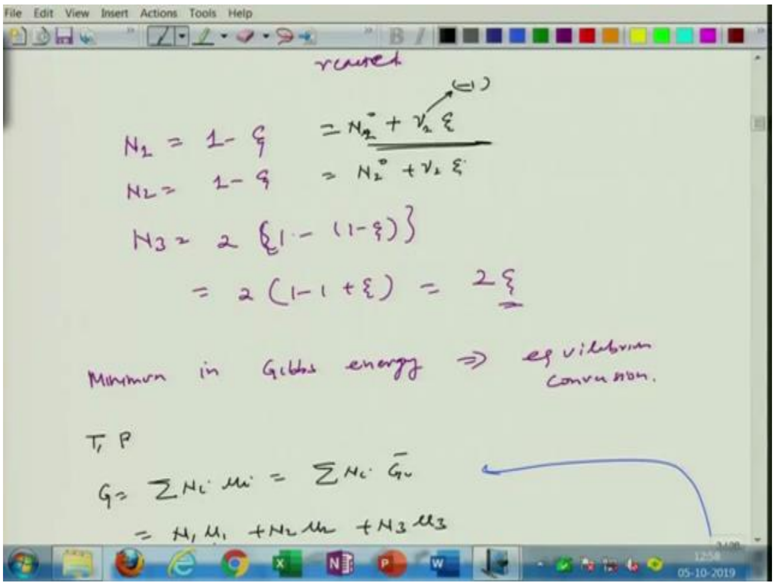

reused

$N_1 = 1 - \xi \quad = N_1^0 + \overset{(-1)}{\nu_1} \xi$

$N_2 = 1 - \xi \quad = N_2^0 + \nu_2 \xi$

$N_3 = 2\{1 - (1-\xi)\}$

$= 2(1 - 1 + \xi) = 2\xi$

Minimum in Gibbs energy ⇒ equilibrium conversion.

T, P

$G = \sum N_i \mu_i = \sum N_i \bar{G}_i$

$= N_1 \mu_1 + N_2 \mu_2 + N_3 \mu_3$

Okay, we have considered this, so if you look at again here this is 1 which was initially Ni 0 and if you look at it Mu of 1 zeta Mu of 1 is Mu of 1 or Mu of 1 is nothing but being a reactant by definition Mu of 1 is negative. So this is very equivalent, so to what we have written earlier. So this is again N2 0 plus Nu 2 zeta. So this is the same expression but now more formal the extent of reaction which you have reused okay.

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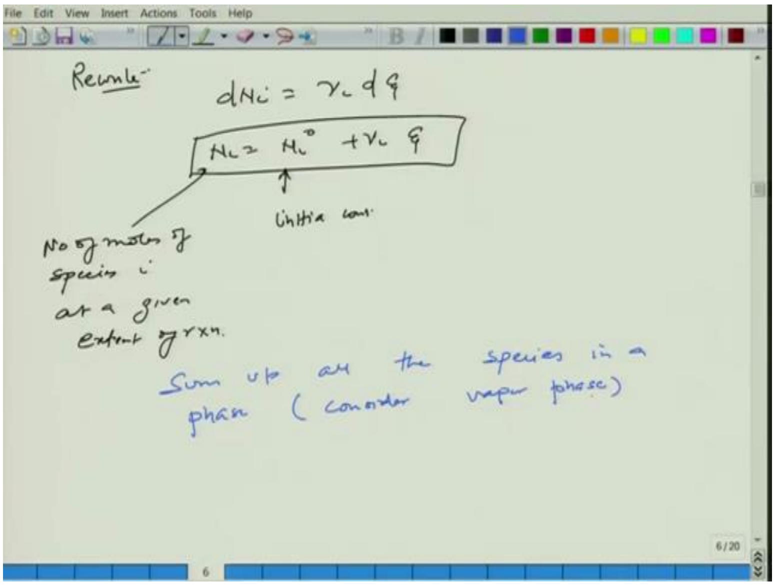


Recall

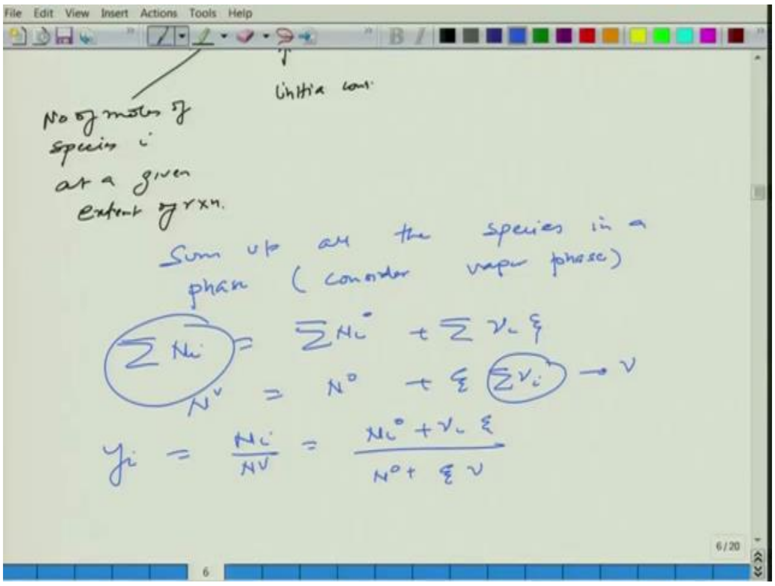
$dN_i = \nu_i d\xi$

$\boxed{N_i = N_i^0 + \nu_i \xi}$

initial cond.

No of moles of species i at a given extent of rxn.

Sum up all the species in a phase (consider vapor phase)



initial cond.

No of moles of species i at a given extent of rxn.

Sum up all the species in a phase (consider vapor phase)

$\Sigma N_i = \Sigma N_i^0 + \Sigma \nu_i \xi$

$N^v = N^0 + \xi \Sigma \nu_i \rightarrow \nu$

$y_i = \frac{N_i}{N^v} = \frac{N_i^0 + \nu_i \xi}{N^0 + \xi \nu}$

So remember that the differential change in the ratio of differential change with the stoichiometric coefficient is constant in and it is basically is also related to something we call it a differential change in extent of reaction. So with that we have a generic expression and if you integrate we got this. So this is nothing but the number of moles of species i at a given extent of reaction okay, all right.

So, now let us try to sum it up okay, so let us try to sum this completely let us consider because what we want is a composition using this extent of reaction. So if we sum up okay all the species present in a phase and okay and let us consider a vapor phase, so I can do a simple Ni this would be your simple summation Ni 0 plus summation Nu i zeta okay and this is nothing but of course than the total number of moles in the vapor phase. And this is the initial number of moles present right.

But the zeta is constant, so this is going to be some Nu I okay so this is let us say total number of moles in the vapor phase. So what would be Yi in the vapor phase? That is a composition of a species i it will be simply Ni divided by NV and this is going to be Ni 0 plus Nu i zeta divided by N0 plus Nu i and this I can say generic Nu, okay. So this allows us this kind of an analysis allows us to calculate the composition in the vapor phase for reactive systems. Okay what we have done is, we have simply introduced extent of reactions and we have made use of the stoichiometric you know reaction equation.

$$\sum N_i = \sum N_i^0 + \sum \nu_i \zeta$$

$$N^V = N^0 + \zeta \sum \nu_i$$

$$y_i = \frac{N_i}{N^\nu} = (N_i^0 + \nu_i \zeta)/(N^0 + \zeta\nu)$$

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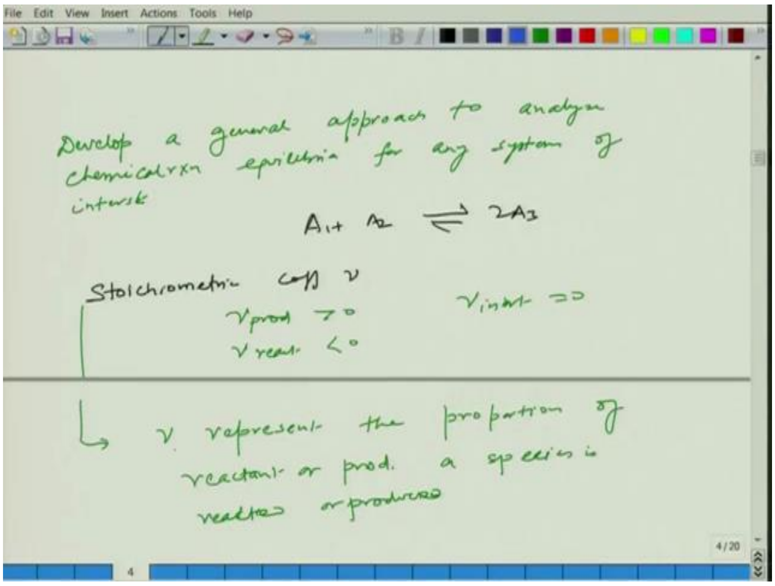


Develop a general approach to analyze chemical rxn equilibria for any system of interest

$A_1 + A_2 \rightleftharpoons 2A_3$

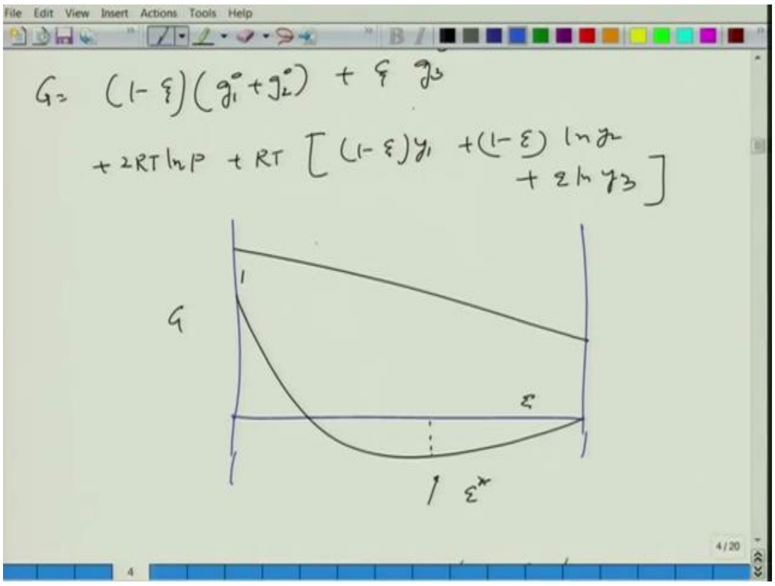
Stoichrometric coff ν

$\nu_{prod} > 0$

$\nu_{react} < 0$

$\nu_{inert} = 0$

ν represent the proportion of reactant or prod. a species is reacted or produced



$$G = (1-\xi)(g_1^0 + g_2^0) + \xi g_3$$

$$+ 2RT\ln P + RT\left[(1-\xi)y_1 + (1-\xi)\ln y_2 + 2\ln y_3\right]$$

And subsequently we have used basic understanding of basically the way we have tried to made you make use of the expressions in this case but at this point we have not tried to come up with a generic term say this but we did understand that that there is a possibility of un-reacted reactants. And this is feasible or this is possible because the Gibbs free energy can be reduced by increasing the entropy as well.

And thus, it is you know very important to understand that the you know both the components enthalpy and entropy plays a competing role. Okay so given this introduction what we are going to do is next is we are going to do a little bit of examples and connect this a free energy to something called equilibrium constant of reaction and that is something we shall take it up in the next class. So I will stop here and we will continue this exercise in the next lecture, see you.