Engineering Thermodynamics

Prof. S. R. Kale
Department of Mechanical Engineering
Indian Institute of Technology, Delhi

Lecture - 53
Phase and Chemical Equilibrium: Introduction. Chemical equilibrium. Gibbs function.

This is the 4th module of Thermodynamics 2 and in this module, we will look at Phase and Chemical Equilibrium. So, the keyword here is equilibrium and this has to do with everything we learnt in the beginning courses where we said that a system is in equilibrium or rather thermodynamic equilibrium.

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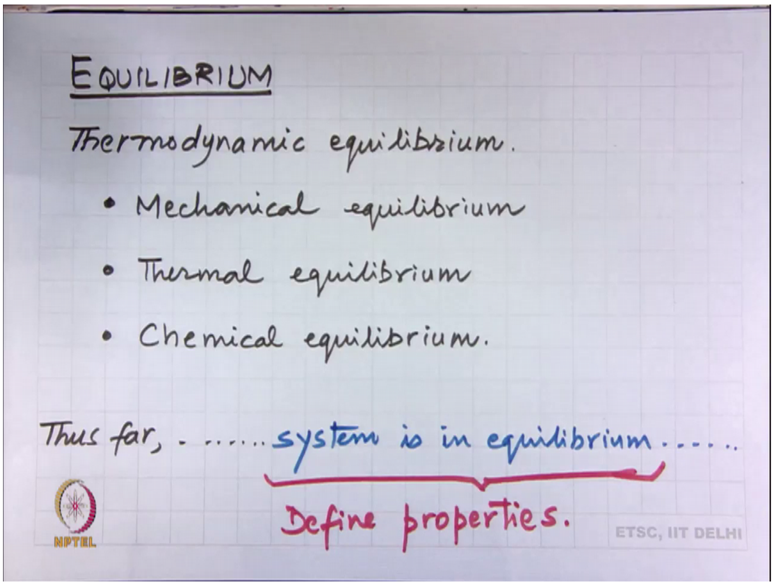

EQUILIBRIUM

Thermodynamic equilibrium.

- Mechanical equilibrium
- Thermal equilibrium
- Chemical equilibrium.

Thus far, ...system is in equilibrium.....

Define properties.

If it is in mechanical equilibrium, thermal equilibrium, chemical equilibrium and any other forms of equilibrium and we invoked this idea of equilibrium for a very fundamental reason that unless a system is in equilibrium, we cannot define its properties

So, everything that we have learnt so far in thermodynamics anytime we have assigned properties to the substance, we have implicitly or explicitly said that the system is in equilibrium. So, let us see what type of situations we have already come across. We begin with the simplest one from properties of a pure substance.

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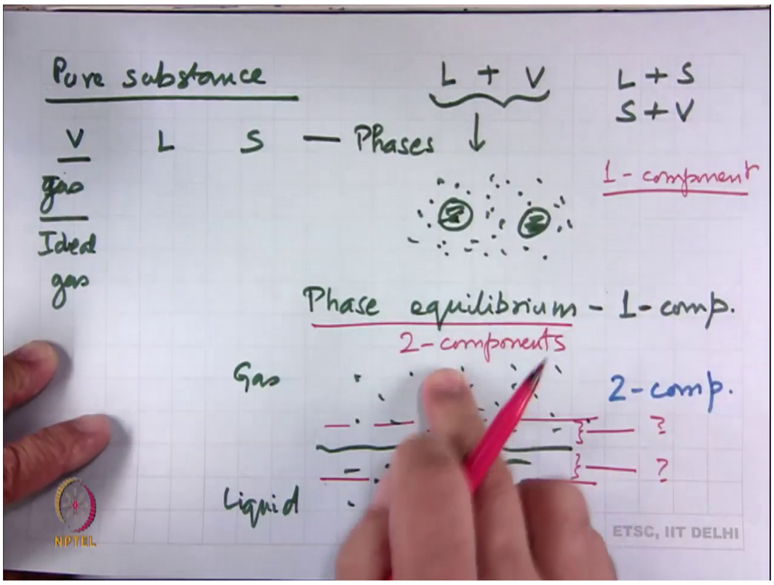

So, if I said that we were looking at vapour, liquid and solid and in each case some sub class of vapour was a gas subclass of that when ideal gas. And, we said that if in a system we have any of these, any one of these, then if the pressure is same everywhere, the temperature is same everywhere and the system has no, it does not change its state spontaneously, then the system is in equilibrium, but we also look at another case where we had a liquid and a vapour existing in equilibrium.

So, these were the phases and now we are looking at a mixture of 2 L plus V or it could be liquid plus solid or solid plus vapour that there is a equilibrium between phases and the criteria we put there was exactly the same that the pressure is same everywhere and the temperature is same everywhere. So, what we are saying is that two phases say this is a liquid drop existing in the vapour of the substance, then the pressure everywhere in the gas phase and the liquid phase is the same, then this system is in equilibrium.

So, this is what we will study now as to what is the condition under which we will have this type of equilibrium which we will call phase equilibrium with one component we will extend this idea to a second case where you have a liquid surface and about that is a gas and we are saying is that these two need not be the same.

So, you are looking at now a two component system. So, this is different from the earlier system you are looking at and we are asking what is the condition under which there is equilibrium and in particular what we will ask for is in a vicinity of this surface in the gas phase in this region what is happening and similarly in the vicinity of the surface in the liquid we ask what is happening and under equilibrium what can we say about liquid in the gas in this region and gas in the liquid in this region.

So, this is looking at phase equilibrium, but for two components. So, that is the second category that we will look at, but now what we have done in this case we are looking at one component, then we look at two components and thirdly we will look at a gas mixture of two or more components.

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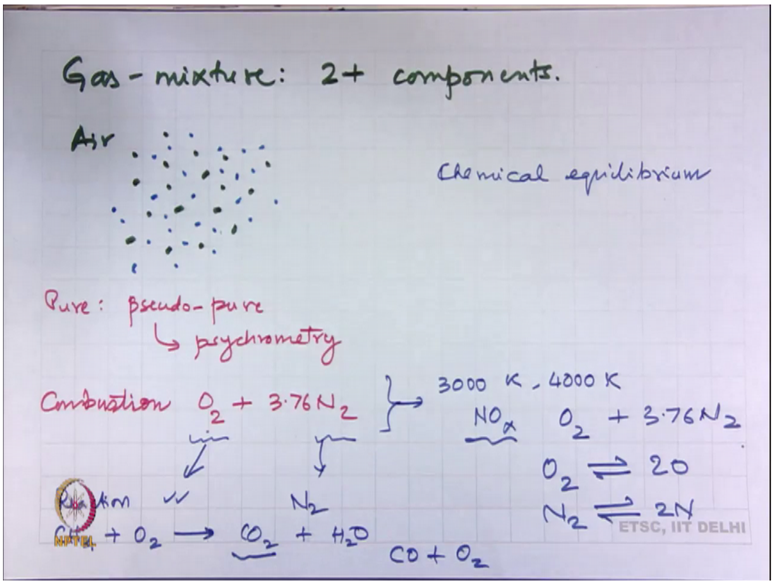

Gas - mixture: 2+ components.

Air

Chemical equilibrium

Pure: pseudo-pure

↳ psychrometry

Combustion $O_2 + 3.76 N_2$ } → 3000 K - 4000 K

$\underset{\sim}{NO_x}$ $O_2 + 3.76 N_2$

$O_2 \rightleftharpoons 2O$

$N_2 \rightleftharpoons 2N$

N_2

$+ O_2 \longrightarrow \underset{\sim}{CO_2} + H_2O$

$CO + O_2$

The simplest two component mixture comes to mind is air and if you say that these are nitrogen molecules and within that we have oxygen molecules, then this type of a system we have come across at every stage in thermodynamics. In the simplest case when we were looking at properties of a pure substance be model air as a pseudo pure substance we also use this idea to study psychometric, but then we did not make it in pseudo pure substance. When you were looking at combustion, there we said that air is two types of molecules O2 plus 3.76 N 2. And we implicitly assume that as it is air or even in the case of a reaction that is happening at their elevated temperatures what we are saying is that O2 remains O2, N 2 remains N 2 and they are not reacting with one another.

So, in the chemical reaction O2 could get consumed. So, this will get used up, but N2 stays as N2. What we will now look at is that if we do have this mixture and we then subject it to say at very high temperature 3000-4000 Kelvin. Then these two will start reacting and you will start getting formation of various oxides of nitrogen which in any combustion process is very undesirable because it is classified as a pollutant. So, what happened here was that O 2 and N 2 instead of being inert and not reacting with one another under some conditions, they began to react.

And so, what you will have air at this type of a temperature is O 2 largely plus 3.76 N2 very large, but two things can happen. O 2 can dissociate and form 2O. Nitrogen can dissociate and form atomic nitrogen and partly both of them can react and form a whole bunch of oxides of nitrogen. The question we ask now is how can we predict that for a given temperature and pressure what species we have, what will be the species concentrations not this the major species, but these ones which occur in very small quantities, what about them. And then we will also extent that idea that instead of just looking at oxygen plus 3.6 nitrogen.

We even ask the question that if we have CH4 plus O2, then we wrote a stiochiometric reaction, but well what there could be many other possibilities that the atom balance is very much there, but it is not giving going fully to CO 2 plus H 2 O. It could be possible that instead of forming all CO 2, it could form CO and some of the oxygen could remain unutilised as O2. It satisfies conservation of mass, the conservation of energy which can also be checked and satisfied. The question is which reaction will take place and to what extent. So, this is what we will look at is now chemical equilibrium where reactions take place and the system comes to new situation new state. So, this is what the scope of this module is. So, before we get into the physics of this let us this is recapping again.

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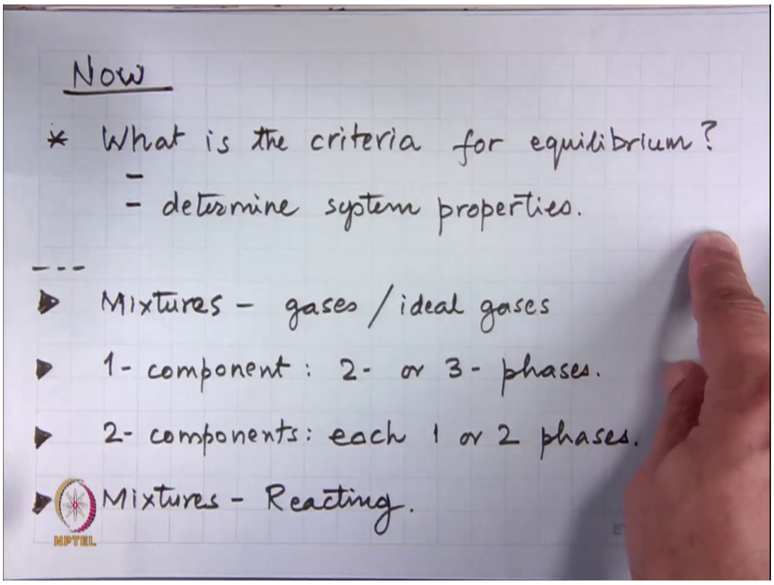

Now

- What is the criteria for equilibrium?
  - determine system properties.

- ▶ Mixtures – gases / ideal gases
- ▶ 1- component : 2- or 3- phases.
- ▶ 2- components: each 1 or 2 phases.
- ▶ Mixtures – Reacting.

We will understand what is the criteria for equilibrium and how can we determine system properties at equilibrium. This could be one component, it could be 1 component with 2 phases, it could be two component with 2 phases or multi components which react with one another. So, these are all those possibilities that we will look at.

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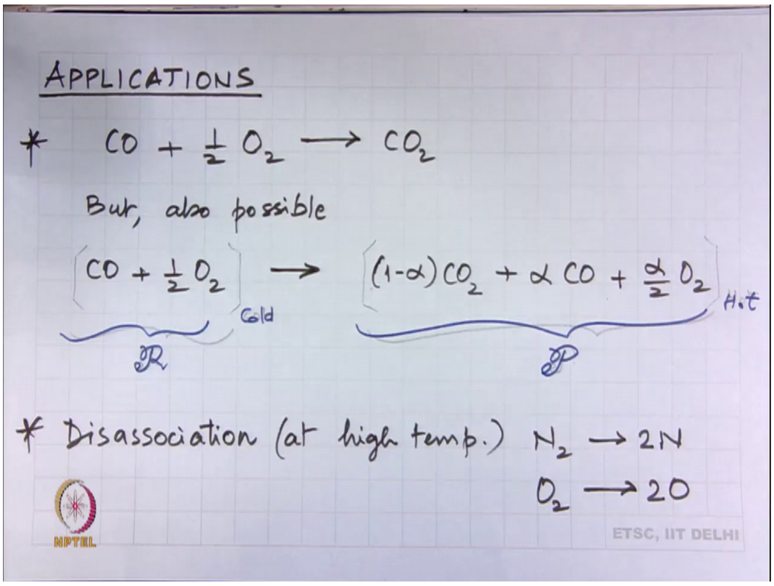

APPLICATIONS

- $CO + \frac{1}{2}O_2 \longrightarrow CO_2$

But, also possible

$$\underbrace{\left\{CO + \frac{1}{2}O_2\right\}_{\text{Cold}}}_{\mathcal{R}} \longrightarrow \underbrace{\left\{(1-\alpha)CO_2 + \alpha CO + \frac{\alpha}{2}O_2\right\}_{\text{Hot}}}_{\mathcal{P}}$$

- Disassociation (at high temp.) $N_2 \longrightarrow 2N$
  $O_2 \longrightarrow 2O$

So, let us see that some applications a reaction like CO plus half O 2 going to CO 2 looks perfectly fine, but it is also possible that this thing which is the reactants could form many combinations of CO 2 plus CO plus O 2. So, in general if we make this as 1 minus alpha, this becomes alpha by 2, then there can be a very large number of values of alpha for which this reaction is completely satisfied.

So, what you are saying is that on this side we have cold reactants and this side we have hot products and many combinations of products are possible which one will be the most likely situation. This is what we want to know, then there is dissociation at high temperature that you take diatomic nitrogen or oxygen or any other gas and you raise it to a sufficiently high temperature. It breaks up into its respective atoms to what extent does this reaction happen, how much energy it takes on or gives out this is what we are going to ask.

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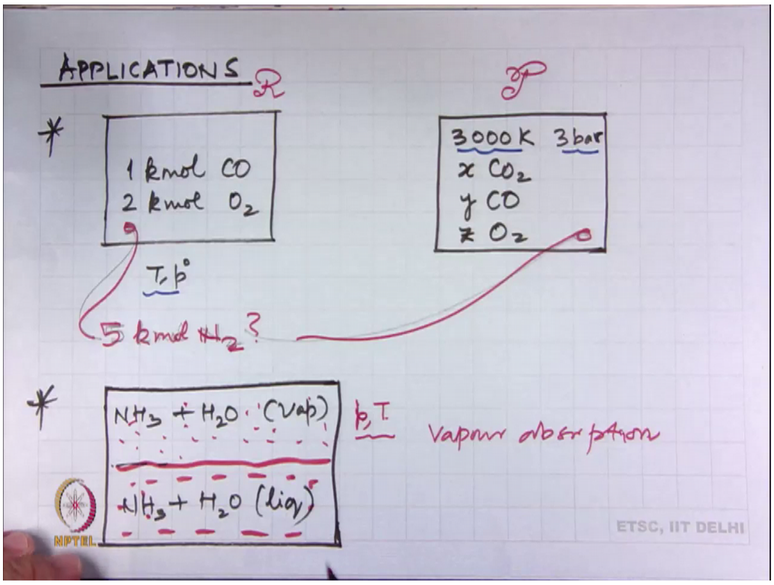

Now, then we have same CO and O 2 mixture going to CO 2, CO and O 2, but it could be from standard pressure and temperature it could be going to any pressure any pressure and temperature and we can add yet another factor into this. Whole thing we say that along with the CO and O 2 what if you also had say 5 kilo moles of nitrogen and from what we have learnt so far we say that this 5 kilo moles of nitrogen we will also find their way into the products. So, this is the products, this is the reactants. So, will you get the same composition of CO 2 CO and O 2 if there were no nitrogen or if there were some nitrogen or the concentration of nitrogen could be different for different situations.

So, that is another question we are asking. All these are relevant to combustion applications whether it is a gas turbine combustor, there is a power plant or whether you are burning LPG at home or a wood burning cook stove. Everywhere these are the type of questions we would like to ask ok. Application that comes from two substances in two phases is your vapour absorption system. A typical one is ammonia plus water and throughout the system we have different concentrations of ammonia in water. In one case we like to dissolve ammonia in water; in another case we would like to drive out ammonia. So, the system in those situations can be looked at this way that you have a liquid in which there is some ammonia and some water in liquid phase and then in the vapour phase we have ammonia and water.

So, here the ratio of these two could vary the system pressure and temperature could be different or what we want to know is at what condition will the system come into equilibrium and if we know that one system and we say that we want to go to another state of equilibrium that will also be told to us by what we will learn here, but what we will not be learning in all these cases is the kinetics or the path by which the system got from here to there or it got to this is equilibrium in the first place. So, we are not going to be looking at processes. We are only be going to be looking at the state.

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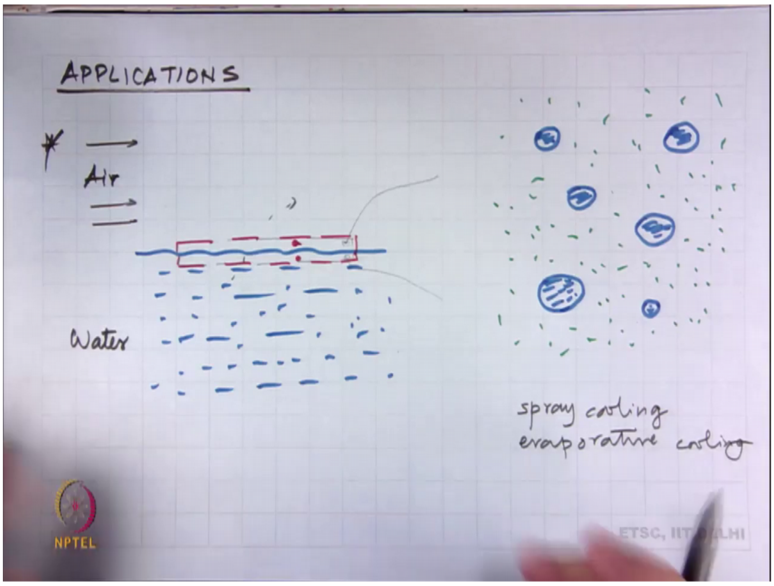

Another application is air and water. For example, this is a surface of water like a sea or an ocean or a lake or a river and on top of that we have air flowing. So, this is air going here and then we ask how much is the moisture going out from here, how does the air properties change a very common of application of this is in climate change models or monsoon models where you like to predict how much moisture does the air pickup and then, we ask how does that moisture get transported and finally, how does it precipitate. And in this case we are looking at a small region that encloses the surface and we want to ask what is the what is happening here and what is happening over here. Another application of the same thing is that water instead of being a bulk liquid is in form of a small drop like a mist or a spray and this air around it.

And then we ask well what is this water, how does it evaporate into the air and what happens to the pressure and temperature and how much it can it go to extent to which this process can happen. So, applications of this like in spray cooling and in some type of evaporative coolers also. So, a modified form of this is also is what you are looking at in evaporative cooling. This could be cooling towers of power stations or industries or even the desert coolers that one uses in their homes.

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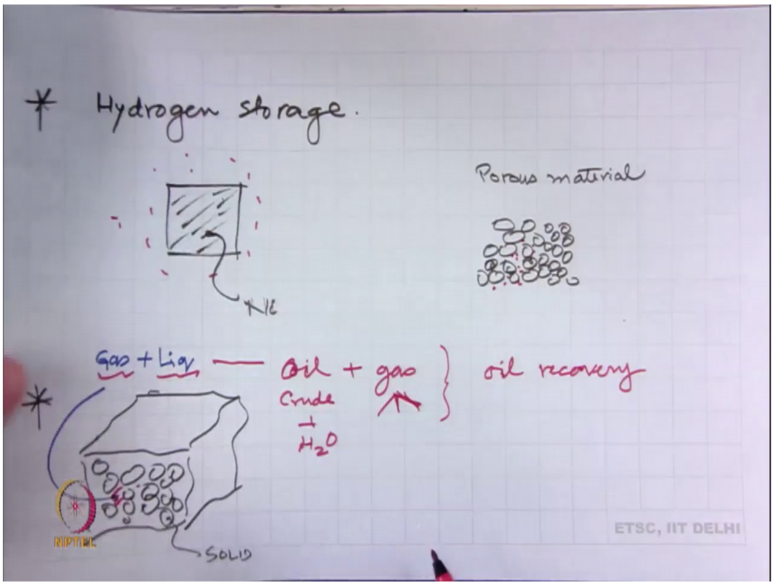

Another application of this is in hydrogen storage where we have a matrix, a particular form of nickel and we ask you know this is the got lot of pores in it and then we ask that if I subject it expose this to hydrogen how much of the hydrogen will go in and settle down inside this.

So, what is the criteria that determines how much hydrogen a certain amount of material. In this case say nickel can absorb this is one of the techniques being looked at for hydrogen storage. Then we can also look at a gas liquid system where you have a porous solid and in the spaces in that we have a mixture of a gas and the liquid and this is what you have in oil exploration and oil recovery where you have oil plus gas and this could be more than one gas species. Oil is of course not a pure oil this is a crude oil with no fixed formula as such and there could even be some water in it and we are asking is how what happens to this mixture in this sort of a thing when you try to take it out or when you try to inject more hydrogen into more steam into it things questions like that.

So, this is a very complex multi-component system in two phases, but this is very crucial in all type of oil recovery and gas recovery processes. So, with that brief background about the applications we will now go into the first part of the module where we look at the criteria for chemical equilibrium. So, what we have done in some sense is started with the most complex of the various systems like we had this listed and said that in chemical equilibrium with two phases there, how can we understand its equilibrium properties. And then if we say that well if there is no chemical equilibrium, then what happens and that brings us to the simple case of non reacting gas mixtures. So, that becomes sort of a subset of a reacting chemical equilibrium.

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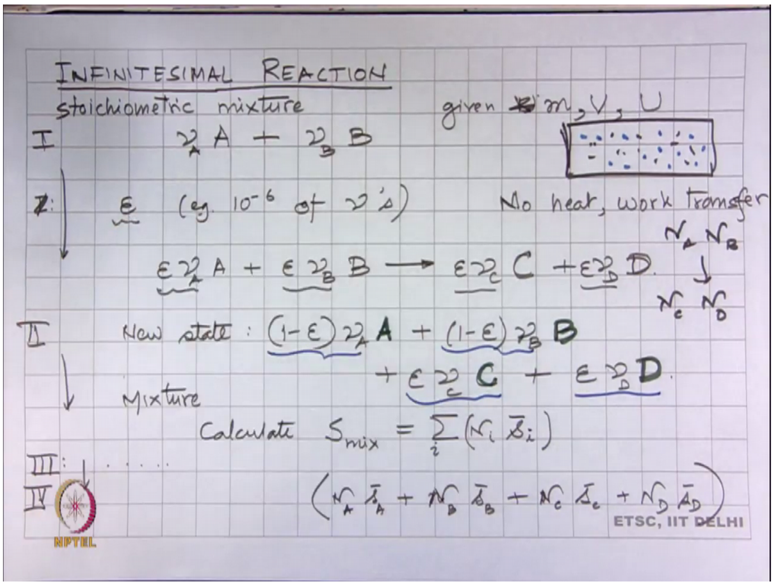

INFINITESIMAL REACTION

stoichiometric mixture

given ~~B~~ m, V, U

I $\nu_A A + \nu_B B$

II: $\underbrace{\epsilon}$ (eg. 10^{-6} of ν's)

No heat, work transfer

$\underbrace{\epsilon \nu_A} A + \underbrace{\epsilon \nu_B} B \longrightarrow \underline{\epsilon \nu_C} C + \underline{\epsilon \nu_D} D.$

$N_A \; N_B \downarrow N_C \; N_D$

II New state : $\underbrace{(1-\epsilon)\nu_A} A + \underbrace{(1-\epsilon)\nu_B} B + \underbrace{\epsilon \nu_C} C + \underline{\epsilon \nu_D} D.$

Mixture

Calculate $S_{mix} = \sum_i (N_i \bar{s}_i)$

III: . . . . .

IV

$(N_A \bar{s}_A + N_B \bar{s}_B + N_C \bar{s}_C + N_D \bar{s}_D)$

So, we begin while writing a typical reaction and say well we will look at a point when the reaction proceeds in a every infinitesimal way. So, let us take a mixture. So, we have say a container in which we have some amount of one substance and some amount of another substance. One we call A, one we call B and the mixture is nu A plus nu B.

Where nu A and nu B are the stiochiometric coefficients of whatever reaction will take place, it is not necessary that we will always will have this, but there could be differential. But the point to note is that in any chemical reaction that takes place no matter what the initial nu A and nu B, the number of moles of A and B are say N A and N B.

When they react, the reaction will always be in a stiochiometric ratio. So, if you do a very small element or a very small step and say look from this state, there is a very small reaction where some of the A and B went to becoming N C which is the N D which are the reactants products. Then few of the molecules went from the reactants to products, but the others did not and that is what we are calling here that this is written as epsilon which is a very infinitesimal progress in the reaction and we say that this reaction will always take place in a stiochiometric ratio. So, we will multiply everything by epsilon epsilon nu A times A plus epsilon nu B times of B molecule becomes epsilon nu C of product which is C and epsilon nu D of product species D;

So, after this reaction has happened the system reaches a new state and let us for the time being assume that the reaction has stopped. So, what we have in the container now is this mixture. We have this much of left, this much of B. Some of it is reduced 1 minus epsilon, this much of C and this much of D. So, you now have a mixture which has got certain amounts of each of the four species A B C and D and now we can do one thing having learnt the thermodynamics of mixtures that we know that if I want to calculate the entropy of this mixture where S mix is I for every species which is the product of the number of moles of each species multiplied by its molar specific entropy.

So, if you have to break this up, we can write this as N A s bar A plus N B S bar B plus N C s bar C plus N D s bar D. So, that is how we calculate the entropy of the mixtures. So, we have reached a new state and then we can say that same the sort of a infinitesimal reaction happens. After this now what happens and we can write that also and call it a state. This this is we can call it as a new state II, this was state I where no reaction took place and then, we can come up state III, then a state IV, each one of which were infinitesimal changes from the earlier state. In reality this may not be happening. What we are doing is we are just saying that if this were to happen and we come to new equilibrium, we will now ask the question now what happens to say entropy, this is what we are done.

So, like this we led this in reaction happened in many steps and each step produces a new composition and finally, all of A and B disappears and you are only left with C.

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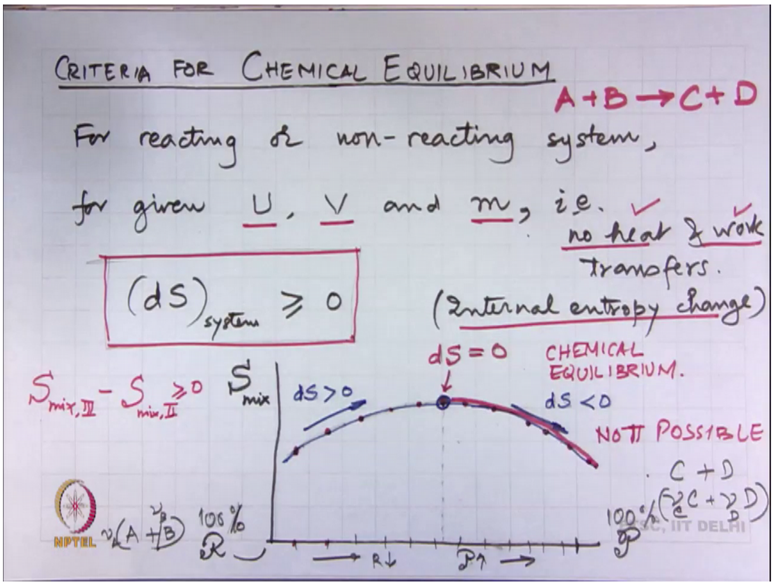

CRITERIA FOR CHEMICAL EQUILIBRIUM

$A + B \rightarrow C + D$

For reacting or non-reacting system,

for given U, V and m, i.e. no heat & work transfers.

$$\boxed{(dS)_{system} \geq 0}$$

(Internal entropy change)

$S_{mix,III} - S_{mix,II} \geq 0$

So, here is what we can do. Now we can plot on an axis where this is 100 percent reactants which means this was only A plus B in whatever the stiochiometric coefficients were there. So, you can if you want, you can write there nu A, this side is nu B and this side is only products which is 100 percent products which is only C plus D. So, you have nu C times C plus nu D times D. That is all. There is no A and B in this, there is no C and D or this point and these are states where R keeps decreasing and P keeps increasing. So, R decreasing in this direction and products increasing in this direction. And on the Y axis, we will plot the entropy of the mixture and we will say that in this system we have been given a fixed volume, fixed mass and its internal energy.

So, what we are saying is that you have in this system the process that we have looked at there is no heat transfer and no work transfer, but internal entropy change this could happen. The 2nd law tells us that under these conditions this is the condition that the system must satisfy that delta S of the system must be greater than equal to 0. That means, S mix in our case say in state II state III minus mix in state two this should be greater than 0 or equal to 0. So, one step to the step what this law is telling is that the entropy of the system must keep increasing and what is the system? System is the mixture of all those four species. So, if we do all of this and do a calculation and calculate the mixture entropy at each one of these points, then at this point we will get some value there.

Here we will get some value, here like that we can get a whole bunch of points and we see that this curve passes through a maximum. So, if we draw a curve there, so what we will have is this and this is a point where there is a maximum and what this plot tells us is that when you are going from this state to this state, the entropy of the mixture increased this state to this state entropy increased. So, in this direction whatever steps we took until we reach this point, this was a satisfied d S greater than 0 that means this process is possible.

What is happening on this side is that when you go from this state to this state, entropy has decreased, here to here entropy has decreased. So, what is happening is that in this direction this tells us that delta S is less than 0 and this is called the 2nd law of thermodynamics requires delta S of the system to be greater than 0. So, what we are saying is that this curve is not possible. The system will not violate going from one point in the process, does not violate conservation of mass, it does not violate conservation of energy, but this sequence of events violates the 2nd law of thermodynamics and so this is not possible. So, what we are left with is that the entropy of the system will keep increasing until we reach a point where d S is equal to 0 which is this point and once it has reached that point, it will it cannot go to this point because then the entropy decreases.

The 2nd law does not let that happen. So, system will stick here and this is what we say that the system has now reached the point where by itself it does not have any tendency to change and this is the criteria for chemical equilibrium. And what we have just done with this thought experiment is to look at a system which has got a fixed internal energy volume and mass and there is no heat and no work transfer.

So, this is a fairly restrictive family of processes for which we have seen that the 2nd law tells us that you will reach a point where d S is equal to 0, This is the criteria for equilibrium. Now, what happens if the system thus have heat and work transfer, then we have to do a slightly different approach and we say that now there is heat and work transfer.

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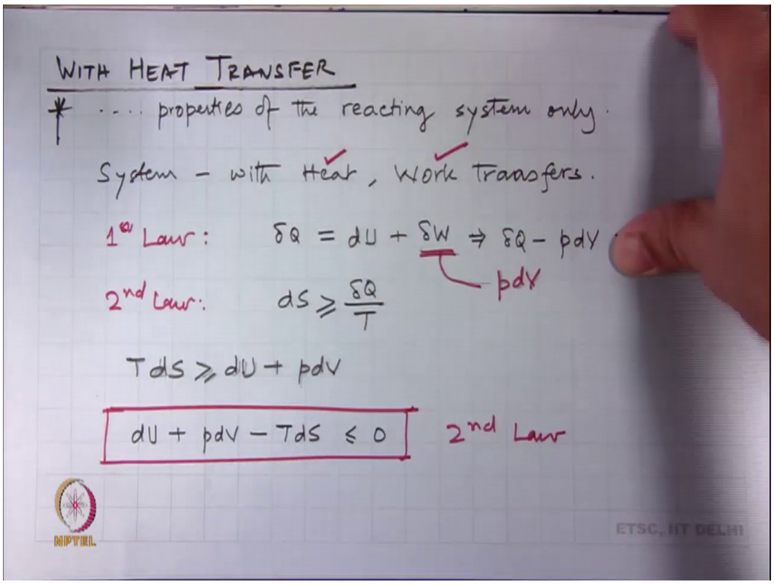

WITH HEAT TRANSFER

* ... properties of the reacting system only.

System – with Heat ✓, Work ✓ Transfers.

1st Law: $\delta Q = dU + \underbrace{\delta W}_{pdV} \Rightarrow \delta Q - pdV$

2nd Law: $dS \geq \frac{\delta Q}{T}$

$TdS \geq dU + pdV$

$\boxed{dU + pdV - TdS \leq 0}$ 2nd Law

The 1st law statement tells us delta Q equal to d u plus delta W, but delta Q minus pdV is equal to d u because this work we said is only at the work done at the system boundary and the substance is simple compressible substance.

And the 2nd law tells us the d S will be greater than or equal to delta Q by T. Now delta Q is finite. So, we combine these two, we get a new equation which say that T d S is greater than or equal to d u plus p d V or if you rearrange it we get this expression the d u plus p d V minus T d S is less than 0. So, this is a 2nd law statement. Now, we will start working with some more items on this one because this equation is little bit elongation does not tell us too much in a very elegant simple way and so we invoke what is called the Gibbs function.

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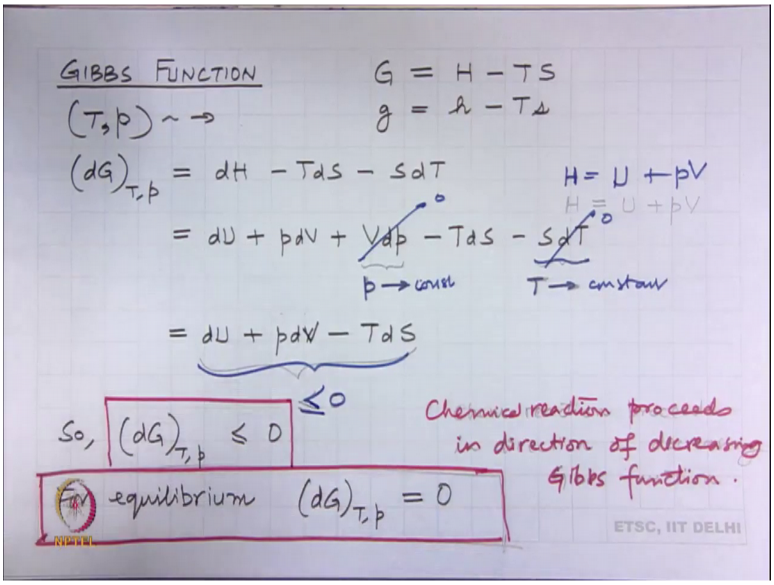

GIBBS FUNCTION

$G = H - TS$

$g = h - Ts$

$(T, p) \rightsquigarrow$

$(dG)_{T,p} = dH - TdS - SdT$

$H = U + pV$

$= dU + pdV + \cancel{Vdp}^{\,0} - TdS - \cancel{SdT}^{\,0}$

$p \rightarrow$ const $T \rightarrow$ constant

$= \underbrace{dU + pdV - TdS}_{\leq 0}$

So, $\boxed{(dG)_{T,p} \leq 0}$

Chemical reaction proceeds in direction of decreasing Gibbs function.

$\boxed{\text{equilibrium} \quad (dG)_{T,p} = 0}$

G defined as a H minus TS a specific Gibbs function as H minus T capital T into small s. So, these are the specific properties extensive properties. So, we say that the change in the Gibbs function which will we now differentiate this for a given temperature and pressure. So, now we only restriction we have putting on the system is that its temperature and pressure are practically invariant. Heat and work transfer is allowed and internal energy you can change, but we say that in a small change where T and p are same.

So, this we differentiate this equation is d H minus T d S minus S d T, then we further put d H as u plus p V. This is what we had from earlier and this gives us this whole expression this part is p V differential minus T d S plus d T because pressure is constant. This term will go to 0 and because temperature constant this term goes to 0 and we are left with d U plus p d V minus T d S and this we are just seen a minute ago that according to the 2nd law requirement d U plus p d V minus T d S, this entire thing must be less than or equal to 0.

And so, we get a condition that delta d G T p is less than or equal to 0 and this is the second more important result that we just get that for equilibrium d G at T and p that Gibbs function change has to be 0 and the 2nd laws requirement is that processes can only take place in direction with change of Gibbs function is decreasing. So, what you are saying is that a chemical reaction proceed in a direction of decreasing Gibbs function.

So, while earlier we had the entropy increasing what we have now is a little more general expression that for equilibrium d G at T and p is equal to 0 and that reactions and processes can proceed with the direction where d G is less than 0. So, if we did a same thing that we did earlier where we plotted entropy.

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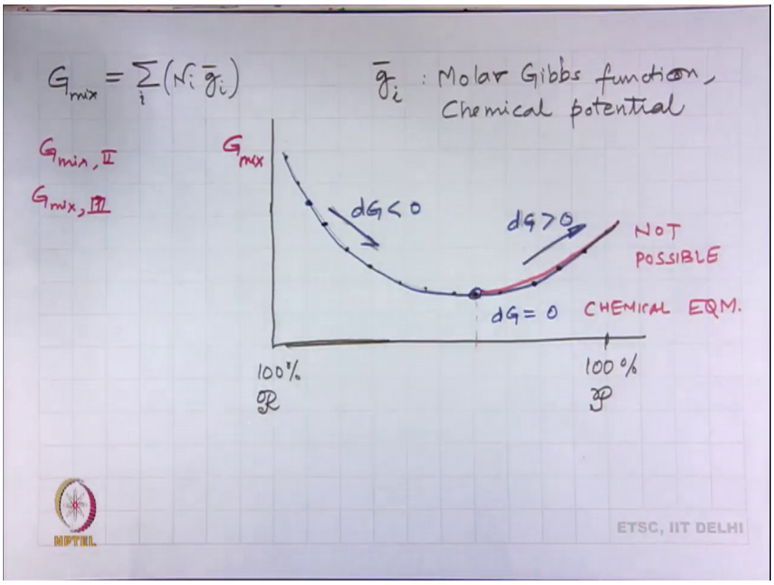

Now we do mixture, Gibbs function plotting this side is 100 percent reactant, this side is 100 percent products and this side we are plotting G mix and again the mixture Gibbs energy is number of moles of each product multiplied by its molar Gibbs function and then we do the same thing and you say that G mix what is it at state two, then what is G mixture at state three and plug that then we get these set of points.

As the ratio of reactions to products reactants decreases and products increases, these are the points we will get and then after while until we come to the products, it will again go up. So, this curve as exactly the opposite shape of the entropy curve in that it goes into a minimum. And minimum is the point where d G is equal to 0 and it tells us that when you are going from this state to this state, Gibbs function is decreasing. So, d G is less than 0 which is by 2nd law.

When you go from here to here or here in this direction, d G is greater than 0 and these processes are not possible. So, again we have this set of processes over here this is not possible. So, a chemical reaction proceeds in the direction of decreasing Gibbs function and at when the Gibbs function is minimized, this is when we have chemical equilibrium.

So, that is a nice thing to hear know now that we are not restricting ourselves to entropy maximization, but much more broader definition comes when you say that the Gibbs function is get in to a minimum. And so, we can say that an important conclusion that has come out is that for chemical equilibrium.

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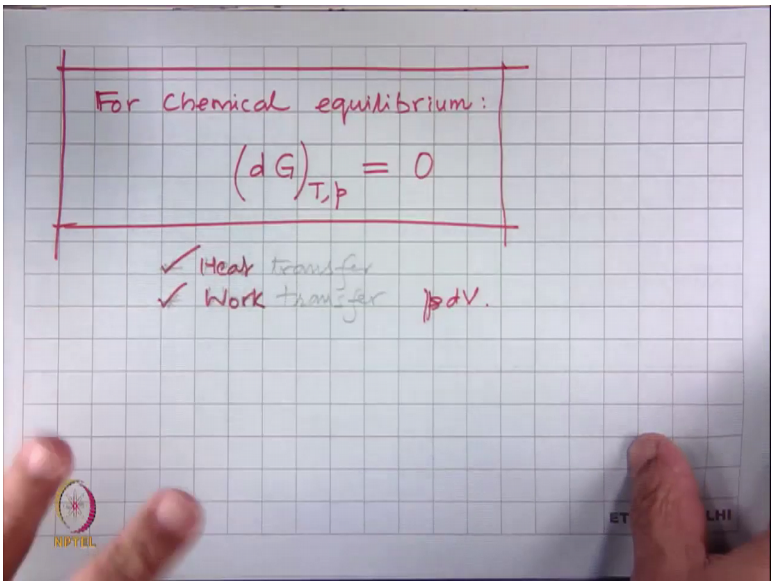

For chemical equilibrium:

$$(dG)_{T,p} = 0$$

✓ Heat transfer

✓ Work transfer pdV.

d G at a given T and p is 0 and here there is heat transfer and there is work transfer at the boundary of the p d V type. So, this is an important thing that we are now learnt and what is the condition for equilibrium. And so, if you know the individual properties, Gibbs function properties of this species that comprise the mixture from that we can calculate the value of G, look at the changes in different directions and say if there is equilibrium or if there is a reaction that is going to happen in which direction which we will proceed.

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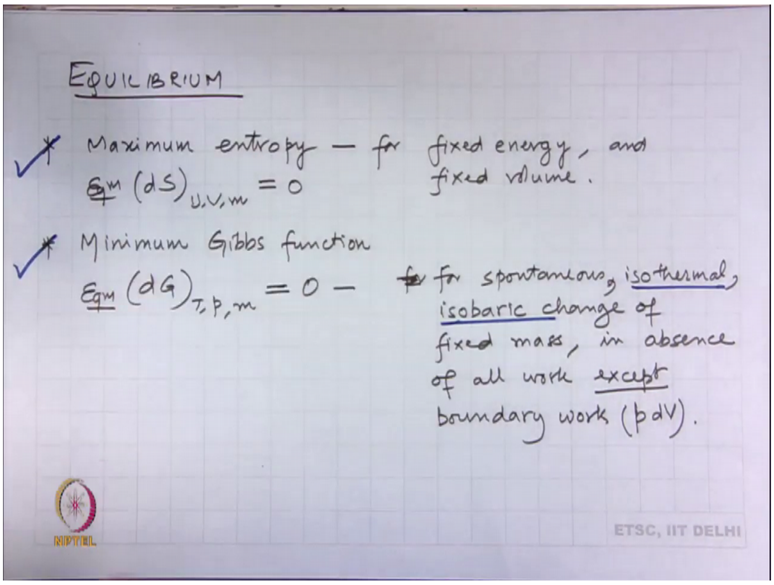

EQUILIBRIUM

✓ Maximum entropy — for fixed energy, and fixed volume.

Eqm $(dS)_{U,V,m} = 0$

✓ Minimum Gibbs function

Eqm $(dG)_{T,p,m} = 0$ — ~~fo~~ for spontaneous, isothermal, isobaric change of fixed mass, in absence of all work except boundary work $(p dV)$.

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So, we can summarize this thing in two ways that you will have for fixed energy and fixed volume and mass dS UVm equal to 0 is the condition for equilibrium and for spontaneous isothermal isobaric change of fixed mass. So, this is what we are saying that T and p are constant in the absence of all work except boundary work p d V. We have equilibrium d G T p m is equal to 0. So, p d v work is there, everything else in the form of work is not there. So, we got the criteria that we were looking for what is the criteria for the system to be in equilibrium.

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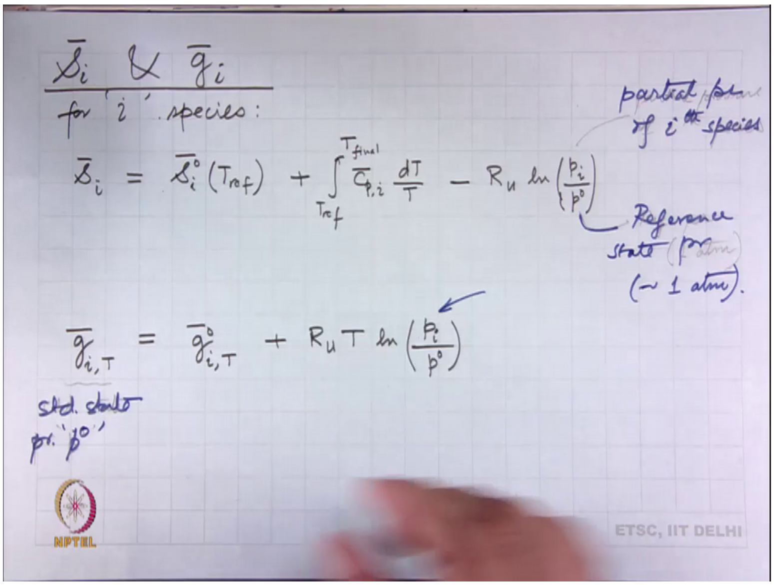

$\bar{s}_i$ & $\bar{g}_i$

for 'i' species:

$$\bar{s}_i = \bar{s}_i^0(T_{ref}) + \int_{T_{ref}}^{T_{final}} \bar{c}_{p,i} \frac{dT}{T} - R_u \ln\left(\frac{p_i}{p^0}\right)$$

partial pr. of i^{th} species

Reference state (pr. ~~atm~~) (~ 1 atm).

$$\bar{g}_{i,T} = \bar{g}^0_{i,T} + R_u T \ln\left(\frac{p_i}{p^0}\right)$$

Std. state pr. 'p^0'

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Now we quickly revise how to get in both the cases. The properties s i bar and g i bar i being the species that we are looking at s i bar was the entropy at standard state at, but p 0 pressure at T ref integral c p bar T ref to T final d T by T minus R u T ln p i by p 0, p i is the partial pressure of the i th species. This is important to note and p 0 is the reference pressure, the reference state pressure, usually one atmosphere and we can do a little bit of derivations.

We will not going to the details of it and to get the molar specific entropy of each species at temperature T again this is at standard state pressure p 0. This is the standard state specific molar energy at temperature T plus R u T times l n p i by p 0. Again this is the partial pressure of the species. So, with this we can as we calculate explicitly using these relations, the values of this and this or we can use the tables where you can take these properties from the tables and the change of the property is listed in the separate column which you can take from the tables. So, this is exactly what we have done in looking at reacting systems.

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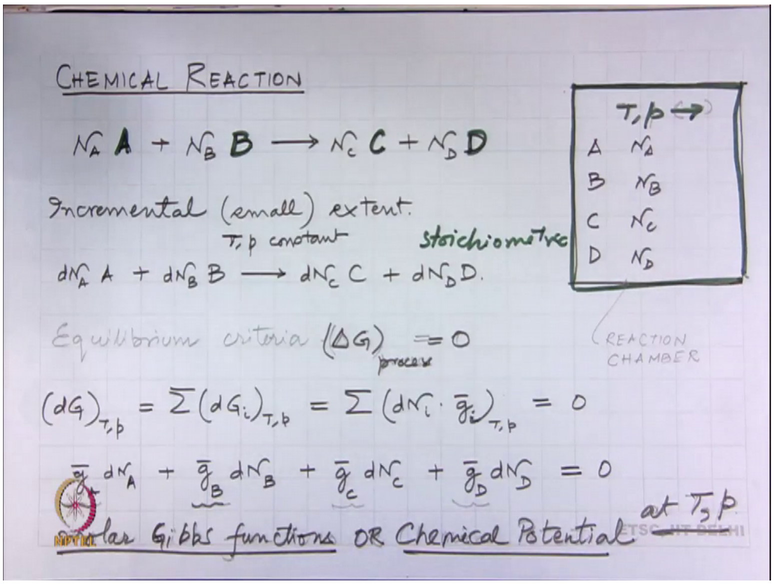

CHEMICAL REACTION

$N_A\,\mathbf{A} + N_B\,\mathbf{B} \longrightarrow N_C\,\mathbf{C} + N_D\,\mathbf{D}$

Incremental (small) extent.

T, p constant   stoichiometric

$dN_A\,A + dN_B\,B \longrightarrow dN_C\,C + dN_D\,D.$

Equilibrium criteria $(\Delta G)_{\text{process}} = 0$

$(dG)_{T,p} = \sum (dG_i)_{T,p} = \sum (dN_i \cdot \bar{g}_i)_{T,p} = 0$

$\bar{g}_A\,dN_A + \underbrace{\bar{g}_B}\,dN_B + \underbrace{\bar{g}_C}\,dN_C + \underbrace{\bar{g}_D}\,dN_D = 0$

molar Gibbs functions OR Chemical Potential at T, p

T, p

A N_A

B N_B

C N_C

D N_D

REACTION CHAMBER

Now, let us go back and see a chemical reaction which says that initially we have N A moles of A plus N B moles of B going to N C moles of C plus N C moles of D. So, what do you do is exactly what we are talking of a few minutes back what if there is an increment will change in this reaction goes to a very small extent. That means, a very small number of moles of a reacted with a small number of moles of B in a stoichiometric ratio and became C and D. So, this is what we were looking at. We have system in which we have put at any instant. We will find some A B C and D and we are asking what will happen when temperature and pressure are constant.

Now, we have already seen that the equilibrium criteria for this condition is that delta G for the process should be equal to 0. So, delta G d g here if you look at this incremental reaction, this will be d G i at T and p which is the number of moles of each species at that temperature and pressure and this specific Gibbs energy molar Gibbs energy. So, this has to be equal to 0 and then we can further rewrite this as g a bar d N A plus GB bar d N B plus C and D equal to 0. So, these are molar specifics Gibbs functions or they or also known as chemical potential at a particular temperature and pressure. This is molar Gibbs functions and chemical potentials at T p.

So, this is an important property that is there and we will have to come back and keep using it in solving problems. Now let us see an important definition that we have now come across what is G bar; A G bar B G bar C. Now we go back to the point that when the reaction it proceeds in an incremental way it will always do.

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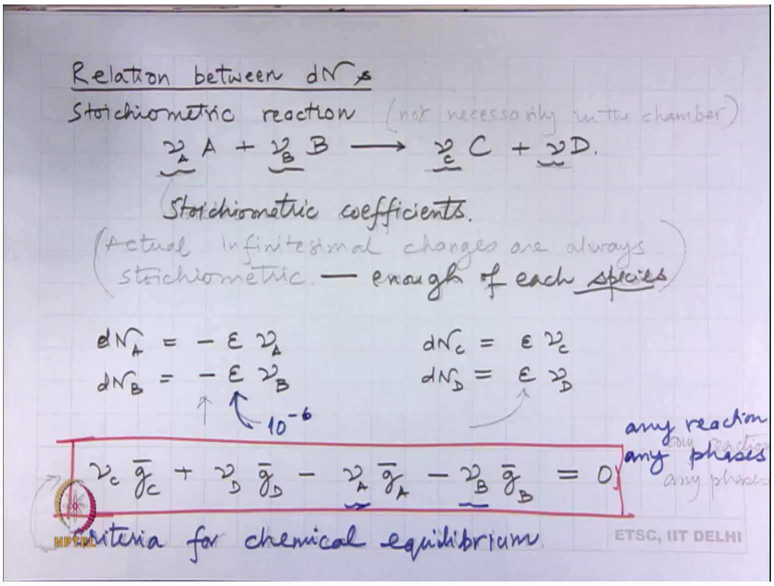

Relation between dNs

Stoichiometric reaction (not necessarily in the chamber)

$$\underset{\sim}{\nu_A} A + \underset{\sim}{\nu_B} B \longrightarrow \underset{\sim}{\nu_C} C + \underset{\sim}{\nu} D.$$

Stoichiometric coefficients.

(Actual infinitesimal changes are always stoichiometric. — enough of each species)

$dN_A = -\varepsilon \nu_A$ $\qquad$ $dN_C = \varepsilon \nu_C$

$dN_B = -\varepsilon \nu_B$ $\qquad$ $dN_D = \varepsilon \nu_D$

10^{-6}

$$\boxed{\nu_C \bar{g}_C + \nu_D \bar{g}_D - \underset{\sim}{\nu_A} \bar{g}_A - \underset{\sim}{\nu_B} \bar{g}_B = 0}$$

any reaction

any phases

criteria for chemical equilibrium.

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So, in a stoichiometric ratio so this is what was happening and the chamber need not necessarily have NA NB NC ND in the stoichiometric ratio. So, these are here the stoichiometric coefficients, we are saying that actual of infinitesimal changes are always stoichiometric under the assumption that there is always enough of each species present.

What do we mean by that, is that it is not happened that in a very small change B gets completely consumed and does not exist anymore, then of course the reaction will not proceed any further, but then we have what we are asking for is also being violated. So, we are saying that actual infinitesimal changes are always stoichiometric and we are showing there will always be enough for each species. So, d NA can be written as an incremental value of epsilon A minus epsilon nu A d NB is minus epsilon nu B and similarly C and D where epsilon is the extent to which the reaction takes place and we say this is very very small nearly like 10 to the power minus 6, 10 to the power minus 8 something like that.

So, having done that we write now nu C g C plus nu D g D minus these two is equal to 0. The minus sign because these are decreasing in quantity. So, this is our criteria for chemical equilibrium and this could be for any reaction any number of phases. So, this is a very broad definition we have now come across that for equilibrium this is what we should have. If it is not satisfied and if Gibbs function decreases, the reaction will proceed. If Gibbs function is increasing, its reach it is not possible. So, nu C g C bar plus nu D g D bar minus nu A g A bar minus nu B g B bar equal to 0. This we can write as a summation. This also can be written as a summation and that is more compact form of this expression.

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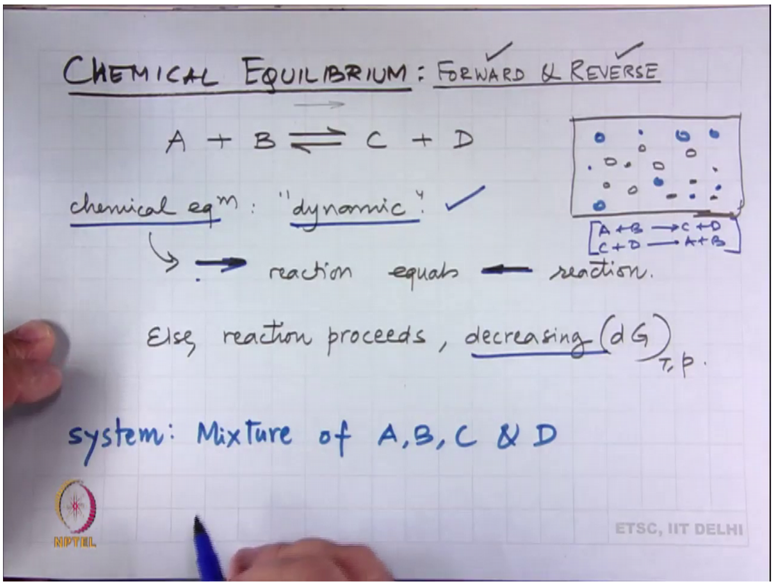

CHEMICAL EQUILIBRIUM : FORWARD & REVERSE

$A + B \rightleftharpoons C + D$

chemical eq^m : "dynamic" ✓

→ reaction equals ← reaction.

Else reaction proceeds, decreasing $(dG)_{T,p}$.

system: Mixture of A, B, C & D

Then next thing about chemical equilibrium is that it isn't always that A plus B always goes to C plus D. At any instant the reverse is also happening that some amount of C plus D is reacting to become A and B. So, A plus B going to C plus D, this is what we call the forward reaction and C plus D becoming A plus B, this is the reverse reaction. So, even when we have equilibrium, that means that no more reaction taking place at that state also you would have A B C and D in the system. So, these are say A and B and then we have C and D and at the macroscopic level this is the equilibrium, but at the microscopic level something else is going on in the sense that some A and B are reacting to become C plus D. At the same time some C plus D are reacting to become A plus B.

And in equilibrium the rates of the forward and the reverse reactions are the same. So, at the overall level we see the same concentration of A B C and D. So, in that sense chemical equilibrium is not a static equilibrium, but sort of a dynamic equilibrium. It is always reactions going on, but at the overall level then amounts are constant. So, if the forward reaction which is this direction equals the rate at which the reverse reaction takes place, we have equilibrium otherwise the reaction will proceed in the direction of decreasing d g at the temperature and pressure, ok. So, this is the next thing we realize that chemical equilibrium is a dynamic situation.

So, we have now got one level of criteria for what is chemical equilibrium and how a reaction will proceed until it gets to chemical equilibrium. Now we will spend some time looking at the Gibbs function because then this will help us to further refine or equilibrium condition and come up with the little more elegant solution.

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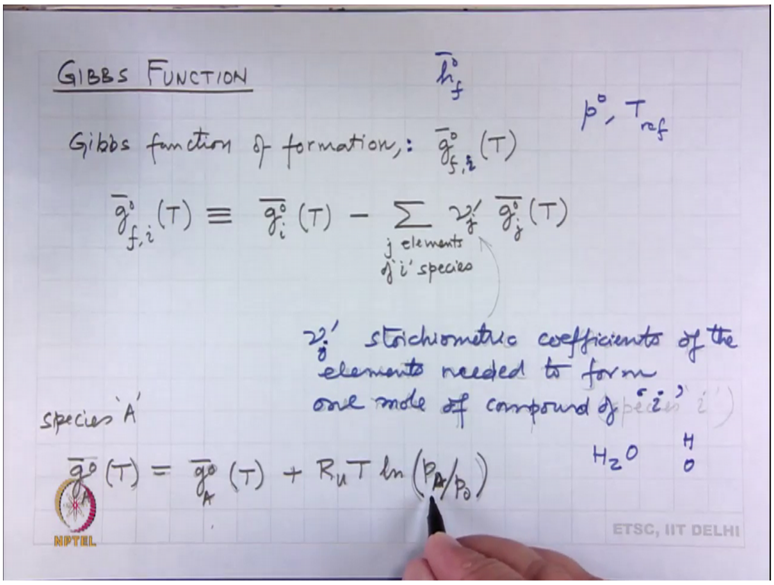

GIBBS FUNCTION

$\bar{h}^0_f$

p^0, T_{ref}

Gibbs function of formation: $\bar{g}^0_{f,i}(T)$

$$\bar{g}^0_{f,i}(T) \equiv \bar{g}^0_i(T) - \sum_{\substack{j \text{ elements} \\ \text{of 'i' species}}} \nu_j' \bar{g}^0_j(T)$$

ν_j' stoichiometric coefficients of the elements needed to form one mole of compound of 'i'

species 'A'

$$\bar{g}^0(T) = \bar{g}^0_A(T) + R_u T \ln(p_A/p_0)$$

H_2O

H

O

So, Gibbs function you can define it as in two parts like we did for entropy which was the or enthalpy of formation. So, we now look at Gibbs function of formation. So, this is g 0 which is standard pressure p 0, T is the temperature and this was the reference temperature. So, g 0 of f, f is the formation Gibbs function which is like we had earlier h 0 bar f what is the Gibbs function in that for the same situation for the ith species at that temperature. So, we write that g f the formation Gibbs function is defined as g i 0 of T minus summation of nu j hash g 0 j t. There nu j hash this is the stoichiometric coefficients of the elements that are required to form one mole of the compound of species 'i'.

So, what we are saying here is that if I want a Gibbs formation function formation Gibbs function for say water, then you are expressing this equation in terms of this which is H and O. So, by getting the Gibbs function for H and O at that temperature and pressure in the right stoichiometric ratio separating it from what we have at T, we get the formation Gibbs function.

So, this can be further modified and we can express it for a gas state the g 0 of a at T equal to g 0 of A at T plus R u T l n p i by p 0 which are the expression that we had earlier, but now what we have done is written it for species 'A' where p i this becomes p A p o being a partial pressure of species A in the mixture p 0 remember is the standard state pressure. So, this should be p 0 here.

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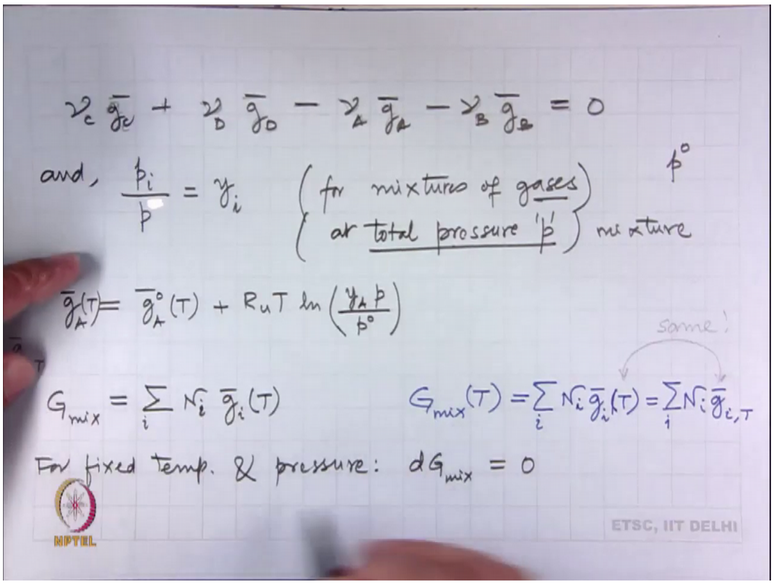

$$\nu_C \bar{g}_C + \nu_D \bar{g}_D - \nu_A \bar{g}_A - \nu_B \bar{g}_B = 0$$

and, $\frac{p_i}{p} = y_i$ (for mixtures of gases at total pressure 'p') mixture p°

$$\bar{g}_A(T) = \bar{g}_A^\circ(T) + R_u T \ln\left(\frac{y_A p}{p^\circ}\right)$$

$$G_{mix} = \sum_i N_i \bar{g}_i(T)$$

same!

$$G_{mix}(T) = \sum_i N_i \bar{g}_i(T) = \sum_i N_i \bar{g}_{i,T}$$

For fixed temp. & pressure: $dG_{mix} = 0$

Now we go back to that equation that we had did in earlier which was nu C g C bar plus nu D g D bar minus same things for the products is equal to 0 and you know that p i by p, this is now p is the total pressure of the mixture not to be confused with p 0 which was the standard state pressure and p i which is the partial pressure of the ith species. So, you have mixture of gases only at total pressure p then g A becomes we can write the earlier equation in terms of the numerator where we write y A times p which is the total pressure and then using this expression we can calculate the Gibbs function for the mixture.

So, what we do now is to combine two things that this is now our definition of the Gibbs function for the mixture two entities are there. The number of moles of each species and the product with the Gibbs function of the species and for fixed temperature and pressure we require that d G mix should be equal to 0. So, what we will do next is differentiate this term. So, we will have in one case this is constant, this is changing plus this is changing, this is constant. So, we will get two terms and the sum of those has to be 0.

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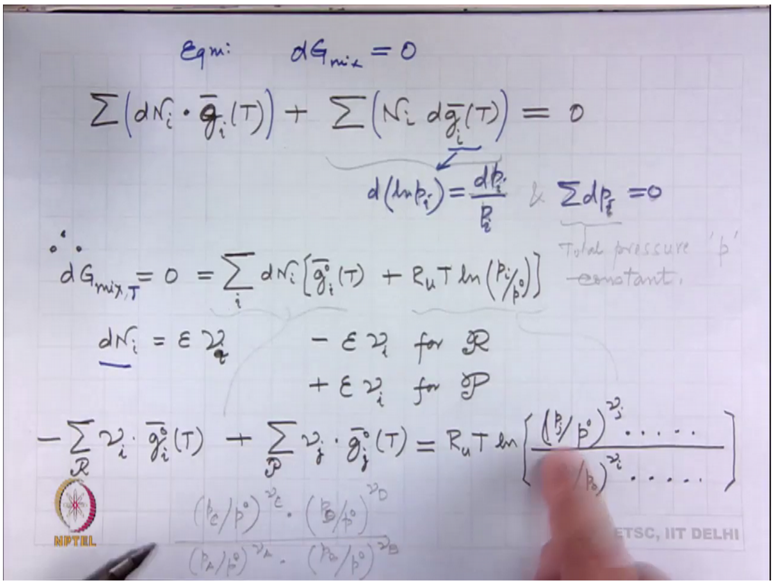

Eqm: $dG_{mix} = 0$

$$\sum\left(dN_i \cdot \bar{g}_i(T)\right) + \sum\left(N_i\, d\bar{g}_i(T)\right) = 0$$

$$d(\ln p_i) = \frac{dp_i}{p_i} \quad \& \quad \sum dp_i = 0$$

Total pressure 'p' constant.

$$\therefore dG_{mix,T} = 0 = \sum_i dN_i\left[\bar{g}^0_i(T) + R_uT\ln\left(p_i/p^0\right)\right]$$

$dN_i = \varepsilon \nu_i$

$-\varepsilon\nu_i$ for $\mathcal{R}$

$+\varepsilon\nu_i$ for $\mathcal{P}$

$$-\sum_{\mathcal{R}} \nu_i \cdot \bar{g}^0_i(T) + \sum_{\mathcal{P}} \nu_j \cdot \bar{g}^0_j(T) = R_uT\ln\left[\frac{(p_j/p^0)^{\nu_j}\cdots\cdots}{(p_i/p^0)^{\nu_i}\cdots\cdots}\right]$$

$$\frac{(p_C/p^0)^{\nu_C}\cdot(p_D/p^0)^{\nu_D}}{(p_A/p^0)^{\nu_A}\cdot(p_B/p^0)^{\nu_B}}$$

This is what we have done here summation of d N i times g i T plus summation of N i times d g T. This is equal to 0. So, here we are saying that both these are in the summation bracket and this came about from the fact that d G of the mixture for equilibrium is equal to 0. So, we can see that this term we will get l n p i we coming up there the change in that from this part this will be equal to d p i by p i and since we know the d p i is equal to 0, total pressure is 0. So, this term will disappear now this term rewrite in this way.

So, we have d G mix at a temperature T be equal to 0 which is d N i g i T i bar plus R u T l n p i by p 0 and with number of moles of each species being infinitesimal change from its stoichiometric ratio, we can further write this d N i in terms of nu and put up A to summation there that this is nu i g i 0 bar T for reactant which was the minus sign plus products equal to R u T into A product.

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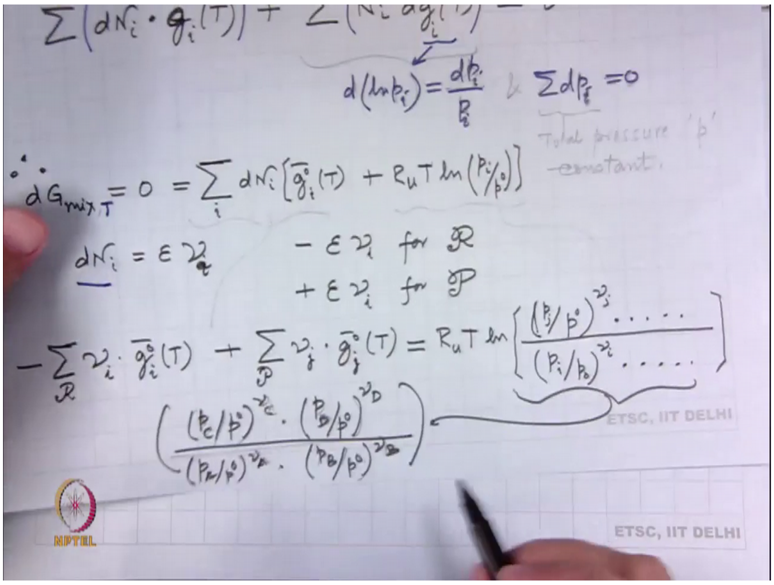

$$\Sigma\left(dN_i \cdot g_i(T)\right) + \Sigma\left(N_i\, dg_i(T)\right)$$

$$d(\ln p_i) = \frac{dp_i}{p_i} \quad \& \quad \underbrace{\Sigma dp_i = 0}$$

Total pressure 'p' constant.

$$\therefore dG_{mix,T} = 0 = \sum_i dN_i \left[\bar{g}_i^0(T) + R_u T \ln(p_i/p^0)\right]$$

$$dN_i = \varepsilon \nu_i \qquad -\varepsilon \nu_i \text{ for } \mathcal{R}$$

$$+\varepsilon \nu_i \text{ for } \mathcal{P}$$

$$-\sum_{\mathcal{R}} \nu_i \cdot \bar{g}_i^0(T) + \sum_{\mathcal{P}} \nu_j \cdot \bar{g}_j^0(T) = R_u T \ln\left[\underbrace{\frac{(p_j/p^0)^{\nu_j}\cdots\cdots}{(p_i/p_0)^{\nu_i}\cdots\cdots}}\right]$$

$$\left(\frac{(p_C/p^0)^{\nu_C} \cdot (p_D/p^0)^{\nu_D}}{(p_A/p^0)^{\nu_A} \cdot (p_B/p^0)^{\nu_B}}\right)$$

Because all these things will now get added up and the logarithm is becomes the products, so this become p C upon p 0 to the power nu C times p D upon p 0 to the power nu D divided by p A by p 0 to the power nu A into p B by p 0 to the power nu B. So, this is what this term in the brackets is going to become.

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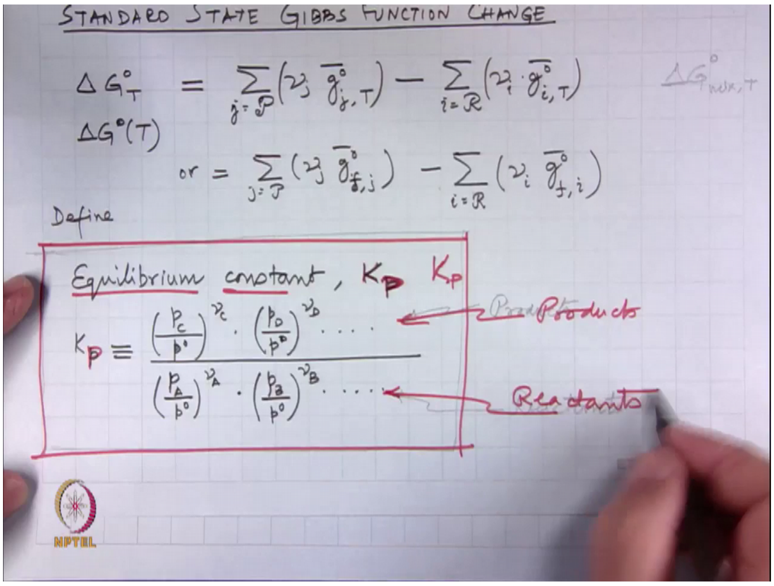

STANDARD STATE GIBBS FUNCTION CHANGE

$$\Delta G_T^0 = \sum_{j=\mathcal{P}} \left(\nu_j\, \bar{g}_{j,T}^0\right) - \sum_{i=\mathcal{R}} \left(\nu_i \cdot \bar{g}_{i,T}^0\right) \qquad \Delta G^0_{rxn,T}$$

$$\Delta G^0(T)$$

$$\text{or} = \sum_{j=\mathcal{P}} \left(\nu_j\, \bar{g}_{f,j}^0\right) - \sum_{i=\mathcal{R}} \left(\nu_i\, \bar{g}_{f,i}^0\right)$$

Define

Equilibrium constant, K_p K_p

$$K_p \equiv \frac{\left(\frac{p_C}{p^0}\right)^{\nu_C} \cdot \left(\frac{p_D}{p^0}\right)^{\nu_D} \cdots\cdots}{\left(\frac{p_A}{p^0}\right)^{\nu_A} \cdot \left(\frac{p_B}{p^0}\right)^{\nu_B} \cdots\cdots}$$

Products

Reactants

And now when we simplify this we can say that delta G T at 0 is summation of nu i into this minus for the reactants the same thing and then since we got this product coming up there, we now define this as a new entity which will be a great help and as lot of other significance in chemical reactions that this is the equilibrium constant k P defined as this ratio that we wrote a few minutes back. In the numerator we have the products and the denominator reactants. So, we have now come to a point where we got much information about chemical equilibrium.

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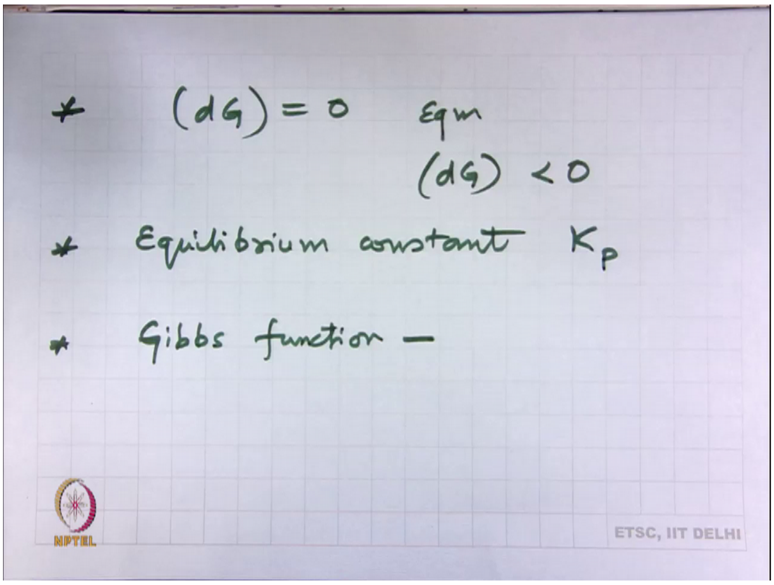

* $(dG) = 0$ Eqm

$(dG) < 0$

* Equilibrium constant K_p

* Gibbs function —

We said that d G equal to 0 is a reaction definition for equilibrium and reactions can only proceed in the direction of d G decreasing. This is one important thing we have learnt. The next thing is we came across now what is called the equilibrium constant and before that we came across lot more treatment and the importance of the Gibbs function as something that is relevant for chemical reactions. So, we have reached an important point in our discussion of having defined what is the criteria for equilibrium and why the criteria from entropy was not adequate. We invoke the Gibbs function and came up with the idea of a equilibrium constant.

So, we will conclude this lecture here and we will pick it up in the next lecture and start looking at the equilibrium constant and its implications in more detail.

Thank you.