# Fundamentals Of Combustion (Part 1)
Dr. D. P. Mishra
Indian Institute Of Technology, Kanpur
Department of Aerospace Engineering

## Lecture – 16
## Chemical equilibrium and Gibbs free energy

Let us start this lecture with the thought process from Abraham Lincoln.

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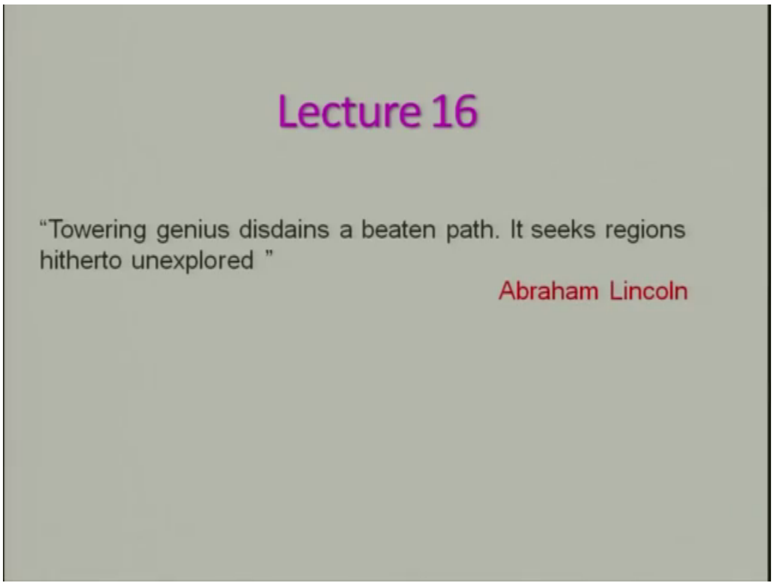

Lecture 16

"Towering genius disdains a beaten path. It seeks regions hitherto unexplored "

Abraham Lincoln

Towering genius disdains a beaten path it seeks regions hitherto unexplored, but unfortunately we always take a path which is easier; that means, taken by others and let us recall what we learned in the last lecture. We basically looked at about the equilibrium constants right and equilibrium constant from the reaction rate point of by invoking the law mass action. But now we will have to look at from the thermodynamics point of view how to determine the equilibrium constants and what is its meaning right.

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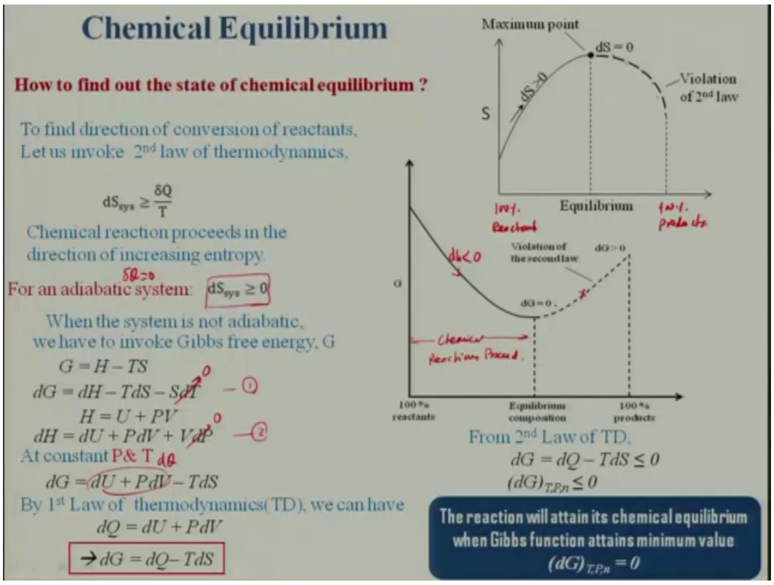

## Chemical Equilibrium

**How to find out the state of chemical equilibrium ?**

To find direction of conversion of reactants,
Let us invoke 2nd law of thermodynamics,

$$dS_{sys} \geq \frac{\delta Q}{T}$$

Chemical reaction proceeds in the direction of increasing entropy.

For an adiabatic system: $\overset{\delta Q = 0}{}$ $\boxed{dS_{sys} \geq 0}$

When the system is not adiabatic, we have to invoke Gibbs free energy, G

$$G = H - TS$$

$$dG = dH - TdS - S\cancel{dT}^{\,0} \quad - ①$$

$$H = U + PV$$

$$dH = dU + PdV + V\cancel{dP}^{\,0} \quad - ②$$

At constant P& T $dQ$

$$dG = dU + PdV - TdS$$

By 1st Law of thermodynamics(TD), we can have

$$dQ = dU + PdV$$

$$\boxed{\rightarrow dG = dQ - TdS}$$

From 2nd Law of TD,

$$dG = dQ - TdS \leq 0$$

$$(dG)_{T,P,n} \leq 0$$

**The reaction will attain its chemical equilibrium when Gibbs function attains minimum value**
$(dG)_{T,P,n} = 0$

Because we need to determine the state of chemical equilibrium right; for that we will have to find out what is the direction in which the chemical reaction is positive right or what is the percentage of extent of reaction is taking place right. And for that we will have to invoke the second law of thermodynamics because the second law of thermodynamics indicates the direction which the process will be proceeding right. And we know the second law of thermodynamics for a system that is change in entropy will be greater than equal to dQ by T right and of course, it is a reversible process that will be change in entropy is equal to dQ by T.

If it is irreversible process it will be greater right and that is the principle what is known as the increase in entropy principle; that means, the chemical reaction will be proceeding in the direction of increasing entropy. If it is decreasing then it will not proceed right. So, if you want to look at you know for an adiabatic system right because in the chemical reactions which will be taking place right will it be adiabatic system or non adiabatic system? For a chemical reactions will you consider adiabatic right.

You will not there will be some heat will be going out, but; however, for adiabatic system dQ will be 0. So, therefore, the change in entropy will be greater than or equal to 0 right because dQ is 0 no; see if it is for adiabatic process for adiabatic process delta Q will be 0 right.

So, therefore, change in entropy will be greater than or equal to 0. Now if you look at that in a pictorially see change in entropy is increasing; that means, you know equilibrium will be achieved wherever there is a no change in entropy is equal to 0 for an adiabatic process are you getting? But if it is less than that; that means, it is violating the second law of thermodynamics in this region right..

So, therefore, it cannot really be change in this thing. So, if you look at this side what will be this will be 100 percent what? Reactant right this will be 100 percent product , but in between there will be reactant and product right in equilibrium. But keep in mind that if it is a non adiabatic system right then how you will handle? We cannot really apply this one right. So, then how we will handle? We will have to basically look at free energy Gibbs energy and Helmholtz free energy right.

And Gibbs free energy if you look at that is G is Equal to H minus TS by definition you might be aware this Gibbs free energy basically thermodynamic potential; one of them is Gibbs free energy Helmholtz free energy is another thermodynamic potential right. If I differentiate these thing; what I will get? DG is equal to dH minus TdS Sdt right and what is H? H is your enthalpy is nothing, but U plus PV right.

So, if I differentiate that thing I will get dH is equal to dU plus PdV plus VdP right. If at a constant temperature and a constant pressure right what will happen because when you are talking about equilibrium, we will be keeping the pressure constant temperature constant; otherwise it will be changing we have seen. So, at constant pressure and temperature at the constant pressure what will happen? This term will be 0 at constant temperature these term will be 0. So, if I combine these things; that means, in a if I say this is equation 1 and this is equation 2 and combine this thing; what I will get? I will get dG is equal to dU plus PdV right minus TdS.

Now this is from the basically Gibbs free energy; now and also you can say second law of thermodynamics ok. Now we will have to connect into the heat right because here dQ is there. So, from the first law of thermodynamics we know that dQ is equal to dU plus PdV; that means, these will be nothing, but your dQ right. So, therefore, this change in Gibbs free energy is equal to dQ minus TdS right and according to the second law of thermodynamics basically dG will be less than or equal to 0, right.

Keep in mind that change in Gibbs free energy at a constant temperature and pressure right of course, the number of moles are not changing right; if you are adding some more concentration as I told then it will be also changing less than or equal to 0. So, this is the condition under which the equilibrium will be a possible and that; that means, some chemical reaction will be going on and when it is equal to 0 right.

So, that will be the point of equilibrium right that; that means, the reaction will attain its chemical equilibrium when Gibbs free energy or sometimes we call Gibbs function attains minimum value that is change in Gibbs free energy is equal to 0. So; that means, in this way the reaction will be proceeding right, but this is not possible like this line because the second law of thermodynamic being violated dG is greater than 0, but this is dG is less than 0 right..

So, therefore, in this region chemical reaction will be say if you look at in this region; the reaction chemical reaction proceeds right proceed. These no chemical reaction will be occurring right; so, basically what we will have to do? We want to find out the equilibrium composition then we will have to mix your that you know or use this condition change in Gibbs free energy is equal to 0 for the mixture right. Now if you look at like how we will handle this Gibbs free energy of the mixture how will do that for a mixture of ideal gases we can determine G of mixture.

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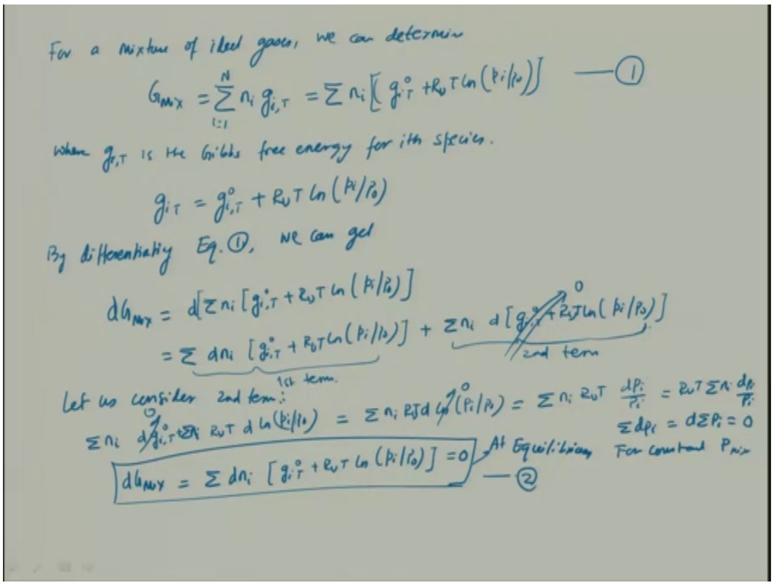

For a mixture of ideal gases, we can determine

$$G_{mix} = \sum_{i=1}^{N} n_i g_{i,T} = \sum n_i \left[ g^\circ_{i,T} + R_u T \ln(p_i/p_0) \right] \quad \text{— ①}$$

where $g_{i,T}$ is the Gibbs free energy for ith species.

$$g_{i,T} = g^\circ_{i,T} + R_u T \ln(p_i/p_0)$$

By differentiating Eq. ①, we can get

$$dG_{mix} = d\left[\sum n_i \left[g^\circ_{i,T} + R_u T \ln(p_i/p_0)\right]\right]$$

$$= \underbrace{\sum dn_i \left[g^\circ_{i,T} + R_u T \ln(p_i/p_0)\right]}_{\text{1st term}} + \underbrace{\sum n_i\, d\left[\overset{0}{\cancel{g^\circ_{i,T}}} + R_u T \ln(p_i/p_0)\right]}_{\text{2nd term}}$$

Let us consider 2nd term:

$$\sum n_i\, d\overset{0}{\cancel{g^\circ_{i,T}}} + \sum n_i R_u T\, d\ln(p_i/p_0) = \sum n_i R_u T\, d\overset{0}{\cancel{\ln(p_i/p_0)}} = \sum n_i R_u T \frac{dP_i}{P_i} = R_u T \sum n_i \frac{dP_i}{P_i}$$

$$\sum dP_i = d\sum P_i = 0$$

For constant $P_{mix}$

$$\boxed{dG_{mix} = \sum dn_i \left[g^\circ_{i,T} + R_u T \ln(p_i/p_0)\right] = 0} \quad \text{— ②}$$

At Equilibrium

What is that? Summation of ni; gi T right because there are several mixtures are there and we are saying some all those things that is the mixture; mixture can be let us say for example, you have taken hydrogen, oxygen if you are taking hydrogen or oxygen system hydrogen or oxygen OH; O H right, water all those things will be coming into pictures right.

And this i can be equal to N; you can say total number of space is whatever it is there right and what is this g i T is the Gibbs free energy or ith species. And this is basically if you look at is the total right and these we can right down this g i T is equal to g i T corresponding to standard state of the; you know pressure one atmosphere pressure plus R U T; L n p i divided by P naught and P naught is basically what?

Student: Standard atmosphere.

Standard atmospheric pressure P naught. So, there therefore, I can write down G mixture as right I can write down here itself right n i bracket g i T naught plus R U Ln p i by P naught right and another brocket I will have to put. So, let us say this is your equation 1 right and keep in mind that this T is you know whatever the temperature at which you we are finding out basically equilibrium right R U TS you are right.

This T is the and now we want to find out the change in the Gibbs free energy of the mixture; that means, we will have to differentiate the equation 1 right by differentiating equation 1, we can get dG mixture is equal to d right of this thing d of ni is equal to; if you look at that is dni right into g I T naught plus R U T; L n p i by P naught right. First term I have to get ni bracket. Then next I will do summation of ni d this term i T naught plus R U L n; p i by P naught term.

right. So, if you look at let us look at these term second term; this is second term right and this is your first term. So, can I say that these will be 0 kind of things? Let us consider second term only right that is n i, I can say d g i T naught right I can write down them I am missing here T will be there right R U T R U T I will take it out then d Ln; p i by P naught ok.

And of course, there will be also ni right is that fine? Is equal to if you look at there will not be any change in the Gibbs free energy right; there will not be any change. So, these will be 0 right what will happen to these term? These I can write down n I; R U d Ln; pi by P naught there will be T there will be T ok.

So, is equal to if you look at ni right summation of ni right R U T and I can write down this d P i by P i can I write that way? This d p Ln; Ln pi anyway P naught is basically a constant right is not changing. So, Ln p i if I differentiate what it will be? Basically it will be d P i right d P i by i.

And if I sum it right if I take R U T if I take and if I sum these thing or R U T and then ni; d p i by p i right; if I sum it up what I will get? I will get basically summation of d p i right will be d if I say p i is basically 0. Can I write this? Because what is happening you are summing the partial pressure of spaces is equal to the pressure of the mixture and that is remaining constant for constant P P; this is basically P of mixture right. So, therefore, it will be 0 is that clear? So, therefore, this term also is equal to 0 so; that means, these term is equal to 0. So, what you will get?

You will get dG mixture is equal to dni right g i T 0 plus R U T Ln p i by P naught is equal to what? It would be is equal to 0 at equilibrium at equilibrium; are you getting because what we have done? We have basically looked at that this term is at equilibrium this is 0; is that clear? Now keep in mind that we will have to basically determine this g i T right if I will get then I can also looked at it like how we can determine.

Let us say that this is your equation 2 what we will do? We will now consider a arbitrary constant the reaction whatever we have taken.

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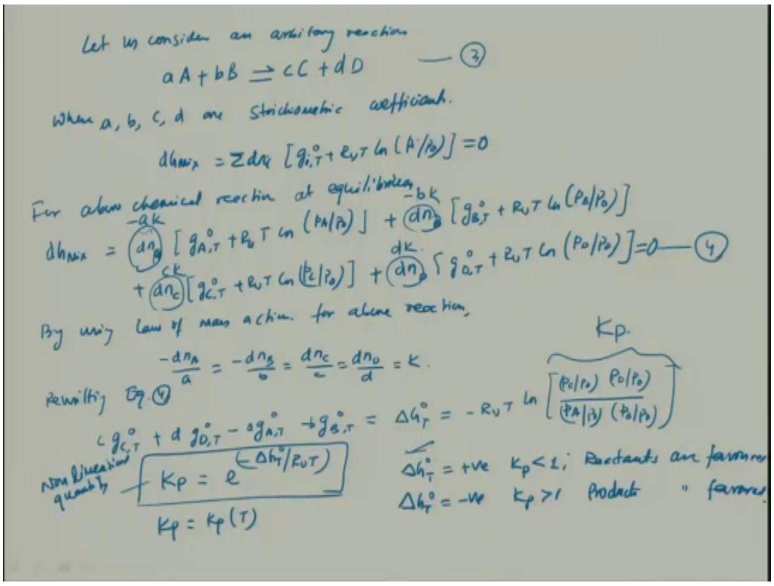

Let us consider an arbitrary reaction

$$aA + bB \rightleftharpoons cC + dD \quad — ③$$

Where a, b, c, d are Stoichiometric coefficient.

$$dG_{mix} = \sum dn_i \left[g^0_{i,T} + R_u T \ln(P_i/P_0)\right] = 0$$

For above chemical reaction at equilibrium

$$dG_{mix} = \overset{-ak}{dn_A}\left[g^0_{A,T} + R_u T \ln(P_A/P_0)\right] + \overset{-bk}{dn_B}\left[g^0_{B,T} + R_u T \ln(P_B/P_0)\right] + \overset{ck}{dn_C}\left[g^0_{C,T} + R_u T \ln(P_C/P_0)\right] + \overset{dk}{dn_D}\left[g^0_{D,T} + R_u T \ln(P_D/P_0)\right] = 0 \quad — ④$$

By using law of mass action for above reaction,

$$-\frac{dn_A}{a} = -\frac{dn_B}{b} = \frac{dn_C}{c} = \frac{dn_D}{d} = k.$$

Rewriting Eq. ④

$$c\,g^0_{C,T} + d\,g^0_{D,T} - a\,g^0_{A,T} - b\,g^0_{B,T} = \Delta G^0_T = -R_u T \ln \overbrace{\left[\frac{(P_C/P_0)(P_D/P_0)}{(P_A/P_0)(P_B/P_0)}\right]}^{K_p}$$

Non dimensional quantity

$$\boxed{K_p = e^{(-\Delta G^0_T/R_u T)}}$$

$$K_p = K_p(T)$$

$\Delta G^0_T = +ve$ $K_p < 1$; Reactants are favoured

$\Delta G^0_T = -ve$ $K_p > 1$ Product " favoured

Let us consider an arbitrary basically by molecular reaction a A plus b B going to the product of c moles of spaces C and d moles of spaces D. And a b c d basically b c d are stochiometric coefficients right. Now we will have to basically look at change in spaces right; how will do that? We are interested to find out the equilibrium compositions we know if we look at equation 2 this is d G mixture equal to d n i into g i T naught plus R U T Ln p i by P naught equal to 0; this condition; that means, we will have to find out what is this change in the moles of mixture; how I am going to do for this reaction? How I am going to find out this d n i?.

I will have to basically for this reaction what I want to write down what I will have to do for let us say this is I am saying c for above chemical reaction the dG mixture will be basically if I sum it of what will happen? This will be change in d n a right into g A T naught plus R U T Ln P A divided by P naught plus R U T Ln P B by P naught plus plus R U T Ln partial pressure of c by P naught R U T Ln by P naught right.

Keep in mind that this will be capital P; this will be p. Now how I will have to find out this? And all these things I need to know; I will get for that we will have to invoke law of mass action; by using law of mass action for above reaction what we will get? We will get d n A by a is equal to minus d n B by b is equal to d n C by c; d n D by d is equal to basically a constant let us say K.

So, now, what we will do? We will use this thing here in this expression let us say this is 4 right and what I will do? I will instead of this I will write down basically in this place what I will write down? Minus a K K is your constant let n B will be in this place minus what b constant in this place, c constant this place, d constant right. And then I will re write this expression equation 4; what I will get right and this is equal to what? This is equal to 0 is not it at equilibrium.

At equilibrium right; this is equal to 0 and what I will do? I will write down g c T naught plus is it I am missing? I am missing c right then d g D T naught minus g A right and doing the same thing you know like this minus coming this minus is coming A T naught minus g B T naught right. And this is nothing, but what? Delta G is not it? T naught of the mixture change in Gibbs energy of the mixture because all this thing this is I have done something wrong here; that is a, this will be b; yes or no and which is equal to what? If you look at I can take this right and side right; I will get minus R U T Ln.

P c by P naught I can write down here P D by P naught divided by p A by P naught p B by P naught. These term we are defining as K p right. So, therefore, I can write down this basically K p will be equal to e minus delta G T naught divided by R U T. Can I write down ? What is the meaning of this thing?

If you look at delta G e naught is positive value what I will be getting? K p will be less than 1 or not? That means, reactants are favored if delta G T naught is negative value K p greater than 1; reactance are sorry products are favored keep in mind that this K p is a dimensional quality or non dimensional?

Student: Dimensional quantity.

Is it so?

Student: (Refer Time: 27:38).

It is a non dimensional quantity; that means, it will be unit less K p is a non dimensional. And K p is a look at function of what? Temperature only it is not a function of pressures yes. So; we will stop over here and we will discuss more about this thing in the next lecture; how we can apply this right and how all this what do we call values we need to calculate. Basically we will have to learn in the next lecture, how we will calculate these values change in Gibbs free energy. Because if I know this thing right, then I can estimate very easily what is K p, right.

Thank you very much.