Chemical and Biological Thermodynamics: Principles to Applications

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Lecture - 25
Chemical Equilibrium

Today we will discuss a very important concept of chemical equilibrium and equilibrium constant which is very important academically as well as industrial. We know that the chemical reactions proceed towards a dynamic equilibrium at which both the reactants and products may be present in the mixture. At equilibrium we may have a lot of product formed or we may have a very small amount of product form or we may have an equilibrium composition where both the products and reactants are present in appreciable amounts.

Synthetic chemise would like the yield to be high when we talk about yield; that means, we are talking about the amount of the product formed and in this lecture we will connect the Gibbs free energy chemical potential with the equilibrium constant, but before that let us discuss in details that why this concept of equilibrium constant is so important. In chemical industries it is worse than even saying useless to construct a plant in which the reaction goes in the wrong direction. If we want high yield, high yield means we want the reaction to proceed towards the right direction.

So, therefore, optimizing the conditions becomes very important optimization of conditions means we need to have an appropriate temperature. So, therefore, we need to know whether more products will be formed at higher temperature or it will be formed at a lower temperature. Or in order to increase the yield or the amount of product formed should the pressure be increased should the pressure be decreased, should the product be removed immediately after it is formed or should we take lower concentration of reactants in order to get a good yield all these issues we will be discussing in the topic of equilibrium and equilibrium constant.

For example we may be interested in knowing how the food that we are taking is used up in a variety of biochemical processes because we derive energy from the food that we eat. So, how that energy is used in the nervous system, muscle contraction and various other biochemical processes, it will be very important to get question answer to this question. The equilibrium constant as we will discuss soon which tells us about the yield the amount of product formed we will derive several equations to discuss the process is quantitatively. One thing we must keep in mind that thermodynamics will tell us the direction of a spontaneous process. Let us recall when we discuss the criteria of spontaneity in terms of changes in Gibbs energy.

One of the criteria of spontaneity that we discussed was dG at constant temperature and pressure should be less than or equal to 0 that is the processes proceed towards lower value of Gibbs energy at constant temperature and pressure. And when we talk about pure components this also we have discussed that in place of molar Gibbs energy I can write chemical potential. In our earlier discussion I said that chemical potential is central to chemistry and today we will derive various equations in terms of chemical potential which eventually will let us discuss about the equilibrium constant.

But as I was saying that the thermodynamics tells us about the direction of spontaneity, but it does not tell us whether there is a kinetically viable pathway existing or not, how much time it will take that it will not tell. Let us take an example of carbon graphite and carbon diamond, the chemical potential of carbon graphite is lower than the chemical potential of carbon diamond; that means, there is a thermodynamic tendency of carbon diamond to spontaneously convert into carbon graphite because the processes will move towards lower chemical potential.

If that were to happen then it would have been disastrous because when you buy a fresh diamond and by the time you come home it converts into graphite that is what thermodynamic predicts, but it does not happen. It does not happen because if we look at the molecular structure of carbon diamond and carbon graphite these are different and there is a huge kinetic barrier between the two it is because of the huge activation energy the transition from carbon graphite to carbon diamond or vice versa in fact, the thermodynamic says that the carbon diamond should convert into carbon graphite because carbon graphite as a lower chemical potential it does not happen because of the kinetic factors.

So, we must keep in mind that thermodynamics tells us the direction, but we must also consider the kinetic factors whether there is a kinetically viable path way existing or not that we have to also consider.

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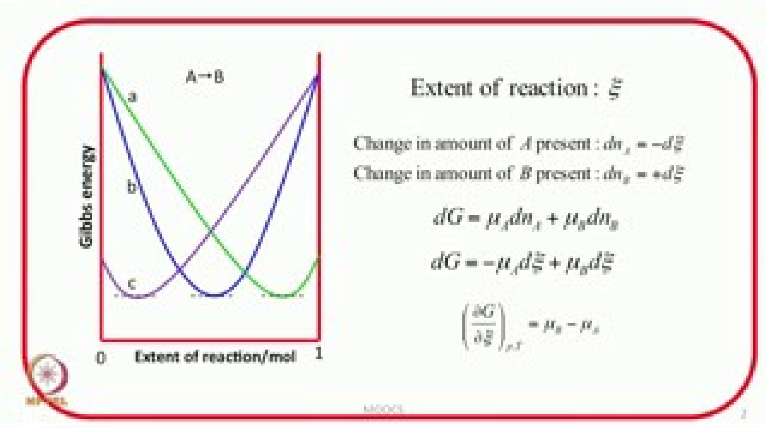

Extent of reaction : ξ

Change in amount of A present : $dn_A = -d\xi$
Change in amount of B present : $dn_B = +d\xi$

$$dG = \mu_A dn_A + \mu_B dn_B$$

$$dG = -\mu_A d\xi + \mu_B d\xi$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \mu_B - \mu_A$$

So, let us start discussing about the chemical equilibrium. In chemical equilibrium we will talk about the processes.

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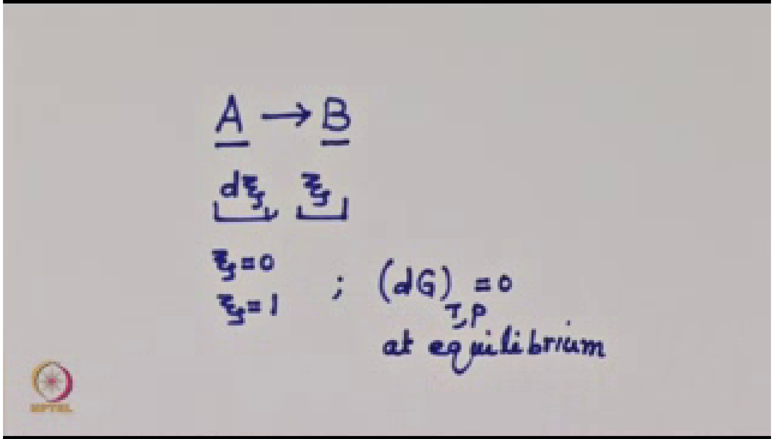

$\underline{A} \longrightarrow \underline{B}$

$d\xi$, ξ

$\xi = 0$
$\xi = 1$; $(dG)_{T,P} = 0$
at equilibrium

Let us start with a process A going towards B. There are several examples of this kind for example, isomerisation reactions pentane to methyl butane that is one example L-alanine to D-alanine that is another example. So, we can find several examples, we can quote several examples of the type A going to B.

Let me introduce, let us take a look at the slide a parameter it term the extent of reaction it is very important to understand the meaning of extent of reaction the extent of reaction I will use d psi and I will reuse psi both in my discussion this term I will use for a finite change and this for a very small change. Extent of reaction means how much the reaction has advanced, extent of reaction equal to 0 means the reaction has not proceeded you have pure A and extent of reaction equal to one means one mole of A has been converted to one mole of B. This must be very clear that when psi is equal to one it means one mole of A has been converted to one mole of B.

Now let us take a look at the slide. We again take this example of A going towards B and if we plot the overall Gibbs energy, by overall Gibbs energy and Gibbs energy of A plus Gibbs energy of B total Gibbs energy versus the extent of reaction the behaviour let us first look at B. The behaviour let us say it could be like as seen in B that there is a minima. The Gibbs total Gibbs energy decreases and finally, it reaches corresponding to pure B is psi is equals to 0 means pure psi is equal to 1 means one mole of A has been converted to B. And in fact, as you can see in all the three cases A B and C there is a minima in each case.

So, what we have is Gibbs energy plotted against extent of reaction and the Gibbs energy is changing. Our earlier discussion let us recall we wrote the dG at constant temperature and pressure is equal to 0 at equilibrium we have discussed it many times; that means, when you plot G against something the derivative should be equal to 0, so the point in the figure where the slope is 0 that is the position of equilibrium.

Let me discuss these three cases, let us first take up the case one. Here the minima is lying very close to the product because here we are considering A going to B. So, therefore, this line represents product where psi is equal to 1 the minima is lying very close to the product; that means, the reaction is essentially complete. If we take C the minima is lying very close to the reactants; that means, the reaction almost does not proceed it does not form appreciable amount of products and in B where the minima you see is quite in between 0 and 1 that means, at equilibrium you will have appreciable amount of product as well as appreciable amount of reactant.

So, in other words in terms of yield in terms of the amount of product formed in the case of green curve the reaction is almost complete and a large amount of product will be formed. In case of C the reaction almost does not take place because very small amount of product will be formed, the minima is very close to the reactant and here in case of blue curve at equilibrium you will have appreciable amount of product as well as appreciable amount of reactant because here extent of reaction is almost equal to 0.5 where the minima in this curve lies.

Let us discuss further, now let the reaction A to B start, let the reaction proceed by a very small amount then the change in amount of a dn A let us write that as dn A will be equal to minus d psi. Please note that this minus sign indicates that a is being consumed in the reaction or in other words the concentration of A is decreasing in the reaction that is why negative sign and change in amount of B. Now B is being formed therefore, we will write this as plus d psi. So, the meaning of this negative sign, meaning of this positive sign should be very very clear - negative means reactant and positive mean products.

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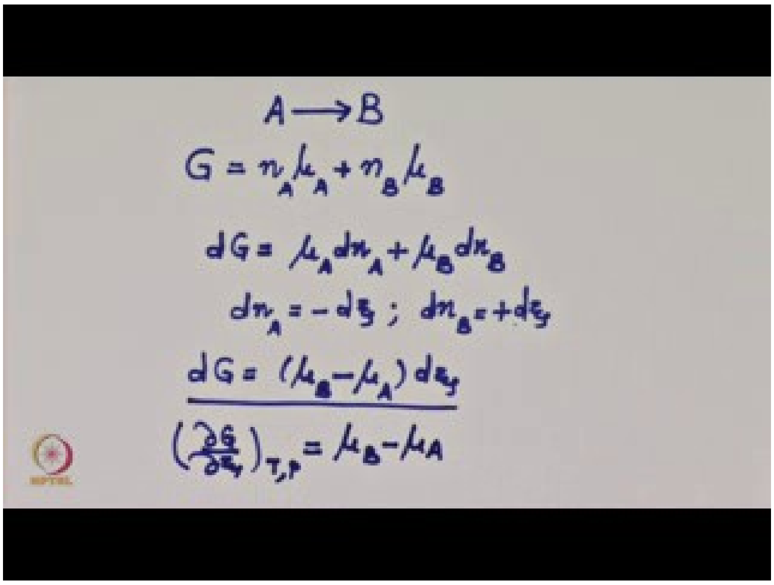

$$A \longrightarrow B$$

$$G = n_A \mu_A + n_B \mu_B$$

$$dG = \mu_A dn_A + \mu_B dn_B$$

$$dn_A = -d\xi \; ; \; dn_B = +d\xi$$

$$\underline{dG = (\mu_B - \mu_A)\, d\xi}$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \mu_B - \mu_A$$

Now for this reaction going from A to B: the total Gibbs energy is equal to n A times mu A plus n B times mu B we have discussed earlier you remember when we were discussing the partial molar quantities and dG also we discussed earlier that this is equal to mu A times dn A plus mu B times dn B at constant temperature and pressure. And we have just shown or discuss the dn A because we are talking about a going towards B, dn A is equal to minus d psi and dn B is equal to plus p psi we have just discuss let us substitute this into dG.

So, dG is equal to it will be if I substitute the in this way it will turn out to be mu B minus mu A into d psi because instead of dn B I will put plus d psi is in place of dn A I will put minus d psi and I take d psi outside the bracket I have this expression - dG is equal to mu B minus mu a into d psi.

Now, let us take a look at the slide. This is what I discuss the dG can be expressed in terms of dn A and dn B and when you substitute for dn A and dn B in terms of the small extent of reaction or advancement of reaction and then we take d psi with the dG for example, from here I can write variation of G with psi of course, we have kept temperature and pressure constant is equal to mu B minus mu A and that is what we have found over here that dG by d psi is equal to mu B minus mu A where mu B is the chemical potential of B and mu A is the chemical potential of A.

And you see what we have done here is expressed, the change of total Gibbs energy with respect to extent of reaction in terms of chemical potential of B and chemical potential of A. And whatever we have derived here whatever we have obtained here it carries a lot of meaning and let us see that in the next slide.

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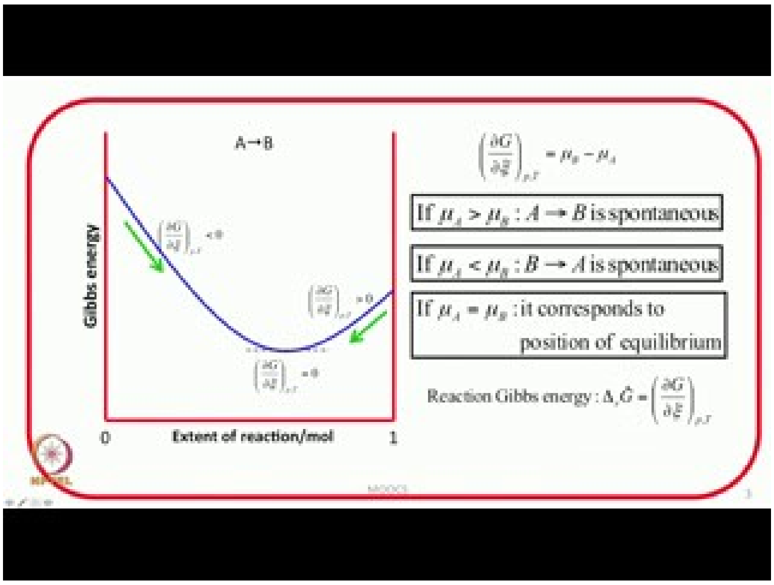

$$\left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \mu_B - \mu_A$$

If $\mu_A > \mu_B : A \rightarrow B$ is spontaneous

If $\mu_A < \mu_B : B \rightarrow A$ is spontaneous

If $\mu_A = \mu_B$: it corresponds to position of equilibrium

Reaction Gibbs energy : $\Delta_r \hat{G} = \left(\frac{\partial G}{\partial \xi}\right)_{p,T}$

So, we have come up to here that if you plot Gibbs energy against extent of reaction then the slope this is actually slope of the plot of G verses psi which is equal to difference in chemical potential of A and B. Let us look at the wider meaning of this. So, when you plot G against extent of reaction and if the variation is like the shown in blue line over here the slope is different at different points.

For example, if I consider this region the slope is negative that is dou G by dou psi at constant pressure and temperature is negative and here at is composition of the reaction the slope is positive and at this composition of the reaction the slope is equal to 0. First let us discuss the slope equal to 0 because this we have discussed many times that when slope is equal to 0, dG is equal to 0 this is the position of equilibrium.

So, how to find the position of equilibrium? You calculate the total Gibbs energy plot against extent of reaction and in the curve you look for the minima where ever you have the minima that is the position of equilibrium. On the left hand side the slope is negative; that means, reaction will proceed from A towards B if you choose a composition in this region the reaction will proceed from A to B, if we choose a composition in this region the reaction will proceed from B to A in the reverse direction and if we choose this competition then this composition corresponds to the equilibrium. You know it is like a valley if you put a ball over here in a valley it will roll in this direction, if I put a ball here in this valley it will roll in this direction and eventually you know when it the ball is rolling it will come to an equilibrium at the minima.

So, under what conditions the slope is negative. The slope will be negative if chemical potential of A is higher than the chemical potential of B means this difference is negative. So, if A is chemical potential of A is higher than the chemical potential of B then the reaction a going towards B is spontaneous; that means, we are talking about this region. On the other hand if chemical potential of B is higher than the chemical potential of a then this difference is positive, positive means the reverse direction is spontaneous; that means, we are talking about this region it will go from B towards A. So, B to A is spontaneous and the equivalence if the chemical potentials of A and B are equal then that is a position of equilibrium and this corresponds to this minima where the slope is equal to 0.

So, it is this chemical potential of the reactants and the products which will decide in which direction the reaction will go whether the reaction will be spontaneous from A towards B or the reaction will be spontaneous from B towards A or the composition corresponds to equilibrium. And this slope is called reaction Gibbs energy. Please note down here the reaction Gibbs energy is a slope here it is not the difference it is a slope, we are talking about slope and this slope turns out to be the difference in the chemical potential.

So, spontaneity is connected to the slope which in turns is equal to difference in the chemical potentials of the product and reactants.

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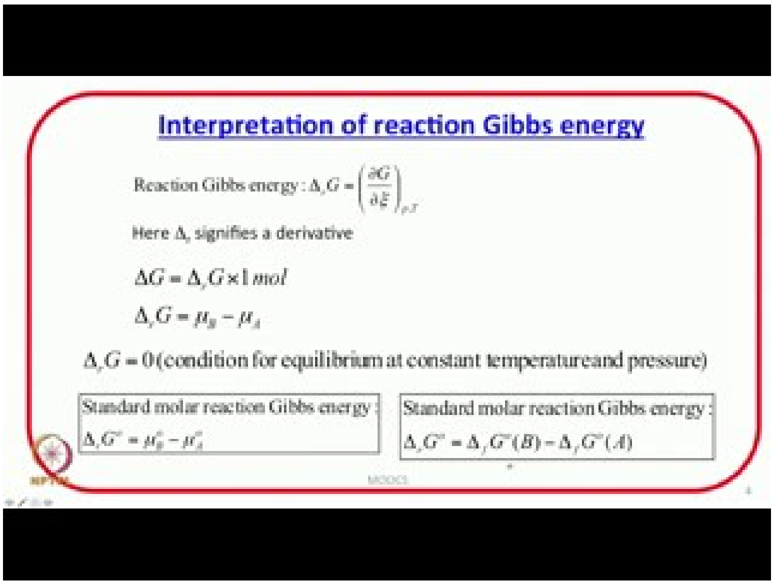

Interpretation of reaction Gibbs energy

Reaction Gibbs energy : $\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T}$

Here Δ_r signifies a derivative

$\Delta G = \Delta_r G \times 1\, mol$

$\Delta_r G = \mu_B - \mu_A$

$\Delta_r G = 0$ (condition for equilibrium at constant temperatureand pressure)

Standard molar reaction Gibbs energy : $\Delta_r G^\circ = \mu_B^\circ - \mu_A^\circ$

Standard molar reaction Gibbs energy : $\Delta_r G^\circ = \Delta_f G^\circ(B) - \Delta_f G^\circ(A)$

Let us discuss more about this interpretation of reaction Gibbs energy. We have discussed that the reaction Gibbs energy is written as delta r G which is the slope of the plot of total Gibbs energy versus the extent of reaction and delta r we have written delta r in this context delta r signifies a derivative means it is we are talking about the slope.

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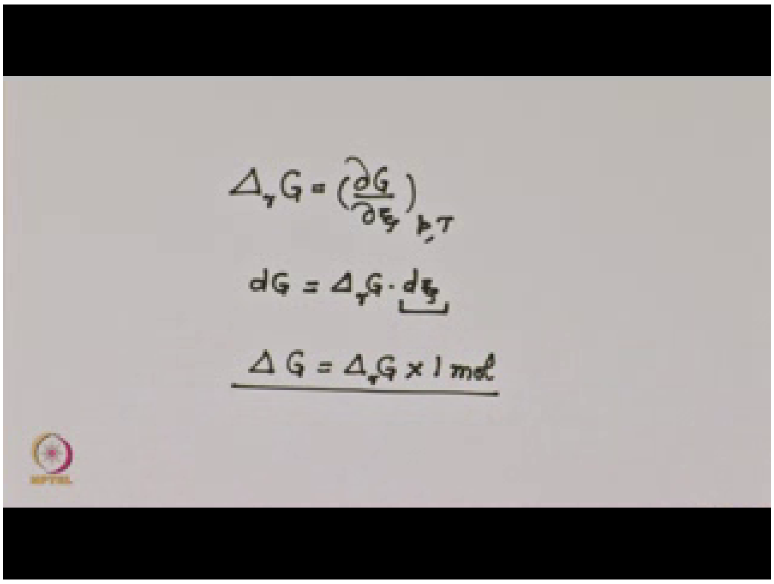

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T}$$

$$dG = \Delta_r G \cdot \underbrace{d\xi}$$

$$\underline{\Delta G = \Delta_r G \times 1\,\text{mol}}$$

And if we want to calculate delta G from delta r then we are writing delta r G is equal to two G by dou psi at constant pressure and temperature therefore, I can write dG is equal to delta r G into d psi.

So obviously, when d psi is equal to 1 if I integrate from 0 to 1 then I can write delta G is equal to delta r G into one mol. The difference is connected to the slope when we are talking about d psi equal to 1 mol when 1 mol of the reactant has been converted to 1 mol of the product that is what is mentioned on this slide. And we have also discussed that the reaction Gibbs energy which is this is slope over here is equal to difference in the chemical potential of B and A and when delta r is equal to 0 when the chemical potentials are equivalent then this is a condition for equilibrium constant, this is a condition for equilibrium at constant temperature and pressure.

If I apply this equation under standard state conditions then the standard reaction Gibbs energy will be equal to difference in the chemical potentials of B and A in their standard states, this equation also holds. We also know that we can get the standard molar reaction Gibbs energy from the Gibbs energy of formation of the product and Gibbs energy of formation of the reactants. So, if we have to calculate delta G naught or delta r G naught we need information on chemical potential of the product and reactant in their standard state or alternatively if we have the information on free energy is Gibbs free energy of formation of the product and reactant still we can get the value of delta G naught.

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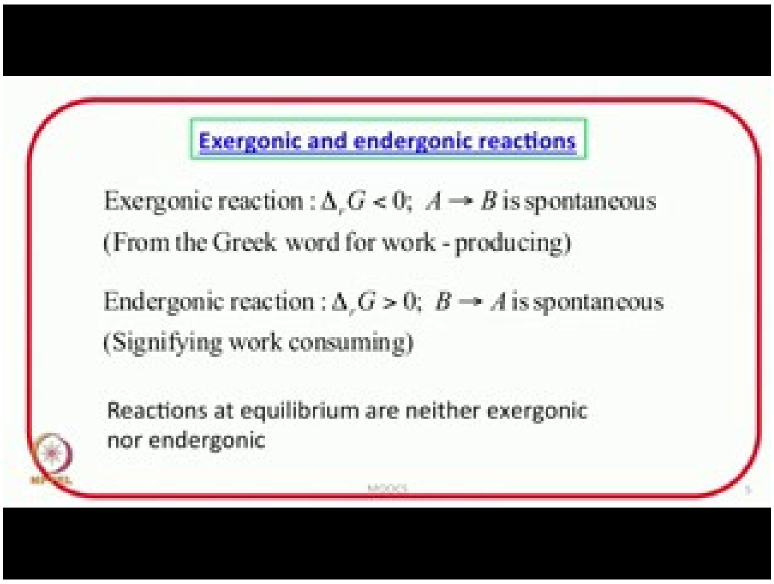

Exergonic and endergonic reactions

Exergonic reaction : $\Delta_r G < 0$; $A \rightarrow B$ is spontaneous
(From the Greek word for work - producing)

Endergonic reaction : $\Delta_r G > 0$; $B \rightarrow A$ is spontaneous
(Signifying work consuming)

Reactions at equilibrium are neither exergonic nor endergonic

Now, suppose delta d or r G this slope is negative we have discussed that a going to B is spontaneous and such reactions where delta r G or the slope is negative are called Exergonic reaction, this exergonic reactions is derived this name is derived from the Greek word for work producing; that means, you can extract the work from the system here- delta G is negative. If delta G is negative we can use this for driving the non spontaneous process. For example, the combustion of carbohydrates is a spontaneous process and the biosynthesis of proteins is a non spontaneous process.

So, here this is an example of spontaneous process; that means, if I extend this example to combustion of carbohydrates this spontaneity of this reaction can be used to drive in non spontaneous biosynthesis of proteins and if delta r G is negative the Greek word for exergonic is work producing. And similarly for endergonic reaction this slope delta r G is positive; that means, in that case B going to A is spontaneous and positive means it is work consuming it signifies that it is work consuming and the reactions which are at equilibrium or neither exergonic nor endergonic in any direction.

So, what we have discussed in this lecture is that why the concept of equilibrium is important we have still not discussed about equilibrium constant that we will be discussing in the next lecture, but the meaning of the extent of reaction should be very clear because it is the extent of reaction and the dependence of the Gibbs free energy on the extent of reaction which will decide that at what composition the reaction will be spontaneous in what direction.

We will discuss more about this in our next lecture, but let us remember that the chemical potentials of the product and reactants will eventually decide in which direction the reaction will go towards equilibrium.

Thank you very much.