# Aspects of Biochemical Engineering Prof. Debabrata Das Department of Biotechnology Indian Institute of Technology, Kharagpur

# Lecture – 10 Reaction Thermodynamics II

Welcome back to my course that is the aspects of biochemical engineering. Now in the last lecture, I try to concentrate on the thermodynamics and we thermodynamics as a whole; how thermodynamics, what is the definition of thermodynamics and then also, we also discussed the spontaneous reaction, non spontaneous reaction with respect to the change of entropy; with respect to the free energy change and we have given how to calculate the entropy of the process that we can easily do that now and this particular lecture will give you more stress on the chemical thermodynamics.

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Thermodynamics of the Biomethanation process	
In the biomethanation process, 1 mole of glucose produce	s 3 moles of acetic acid. The change of
free energy is - 74.3 KCals according to the equation	
$C_6H_{12}O_6 + 4H_2O \rightarrow 2CH_3COO^{-} + HCO_3^{-} + 4H_2 + 4H^{+},$	$\Delta G^{O} = -49.2 \text{ Kcal}$
$2\mathrm{HCO}_3 + 4\mathrm{H}_2 + \mathrm{H}^+ \rightarrow \mathrm{CH}_3\mathrm{COO}^* + 4\mathrm{H}_{2,3}$	$\Delta G^{O}$ = -25.1 Kcal
$C_6H_{12}O_6 \rightarrow 3CH_3COO^*$	$\Delta G^0 = -74.3 \text{ Kcal}$
	Das D, Ph.D. thesis, IIT Delhi, 1985
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Now first thing that I want to show you that is the thermodynamics of Biomethanation process; as you know that that Biomethanation process is kind of anaerobic digestion process, where the organic material is converted to methane and carbon dioxide. Now when it produces methane and carbon dioxide, this usually takes place in two different stages, one is called acid formation, another we call gas generation. Now in case of acid formation, mostly it produces the volatile fatty acid like acetic acid, propionic acid, butyric acid and this acid subsequently that will be converted to methane and carbon

dioxide. Now this year, we have given some examples that the kind of free energy change that we have in this.

So, when you when you consider the glucose in presence of water it produce acetic acid and hydrogen like this and this is the carbonic acid and the free energy change is minus 49.2 kilo cals. Now this again this hydro; this carbonic acid in presence of hydrogen, it produce acetic acid the one mole of glucose usually produce 3 moles of acetic acid now we have total free energy change of this system is 74.3 kilo cals. So, these free energy changes clearly indicate that the reaction is favorable. Now if you look at the anaerobic digestion process when you carry out the anaerobic fermentation process the acid formation processes are quite fast and the. So, we do not have much a problem with the acid formation process.

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Thermodynamics of the	Biomethenation proce	ss (continued)	
In this process, the formation	of acetic acid from carbon	- dioxide is favourable as	the standard
free energy change is found to	be negative.		
$2\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_3 \text{COOH} +$	- 2H <sub>2</sub> O,	$\Delta G^{\circ} = -18.7 \text{ Kcal}$	
This reaction is not favourable	e in a process involving met	hanogens due to the lower	standard free
energy change in following re	action compared to the abov	re reaction:	
$\mathrm{CO}_2 + 4\mathrm{H}_2 \rightarrow \mathrm{CH}_4 + 2\mathrm{H}_2\mathrm{O},$		$\Delta G^{\circ} = -33.2 \text{ Kcal}$	
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Now, let us say this acid also can be formed from the carbon dioxide, you see the carbon dioxide and hydrogen that form as it that acetic acid, but if you look at the free energy change is minus 18.7 kilo cals. Now this free energy change and what we have previously free energy change this is much less as compared to that. So, that indicate the previous reaction is more favorable as compared to this reaction now when this carbon dioxide and hydrogen forms the methane and water the free energy change is minus 33.2 kilo cals; that means, this carbon dioxide and hydrogen is most favorable for the production of methane rather than for the production of acetic acid.

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Thermodynamics of the Biomethenation process (continued)
The degradation of volatile fatty acids to methane, as occurred in this process, has different change of standard free energy.
$\begin{array}{ll} CH_{3}COO^{*} + H_{2}O \rightarrow CH_{4} + HCO_{3}^{*}, & \Delta G^{\circ} = -7.4 \text{ Kcal} \\ CH_{3}CH_{2}COO^{*} + 2H_{2}O \rightarrow CH_{3}COO^{*} + 3H_{2} + CO_{2}, & \Delta G^{\circ} = +19.5 \text{ Kcal} \\ CH_{3}CH_{2}CH_{2}COO^{*} + 2H_{2}O \rightarrow 2CH_{3}COO^{*} + 2H_{2} + H^{+} & \Delta G^{\circ} = +9.95 \text{ Kcal} \end{array}$
Degradation of butyric and propionic acids are not favoured in a thermodynamic sense. Free energy change involved in the reduction of carbondioxide by NAD(P)H is shown below.
$4 \text{ NAD}(P)H + 4H^+ \rightarrow 4 \text{ NAD}(P)^+ + 4H_2, \qquad \Delta G^\circ = + 18.4 \text{ Kcal}$
$4H_2 + CO_2 \rightarrow CH_4 + H_2O$ , $\Delta G^\circ = -33.2$ Kcal
SUM: $4H^+ + 4NAD(P)H + CO_2 \rightarrow 4NAD(P) + +CH_4 + 2H_2O$ , $\Delta G^\circ = -14.8$ Kcal
Das D, Ph.D. thesis, IIT Delhi, 1985

Now, here as I pointed out that intermediate the volatile fatty acid that forms in this reaction is the acetic acid this is propionic acid and this is the butyric acid. Now when this acid is converted to acetic acid or this converted to methane and this. So, you find that if you look at the free energy change this conversion, propionic acid to acetic acid is not favorable; the plus the free energy change is plus 19.5 kilo cals, but butyric acid to acetic acid is 9.95 kilo cals. Now those who has the experiences with the anaerobic digestion process, they know when you operate the anaerobic digestion process for longer period of time we find the accumulation of propionic acid that takes place in the system.

Because that is in this that you can find out is a thermodynamically this degradation is the unfavorable that is why we get in the long time operation we get in the fermentation broth we get more accumulation of propionic acid rather than butyric acid or acetic acid. Now another is that the how NAD; NAD P H that converted to hydrogen and then to then this hydrogen how is converted to methane. So, overall that conversion process is like this minus 14.8 kilo cals. So, if you now you if you compare this with the previous result, you will find previous reaction, if you look at this one and if you look at this one you will find this reaction is favorable as compared to this reaction this is how we can thermodynamically how we can determine which reaction is favorable which reaction is unfavorable.

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Enthalpy of formation $(\overline{\Delta H}_f)$	
□ The enthalpy change when one mole of a pure compound is fo elements in their most stable states is called the enthalpy of fo	rmed from its rmation and is
$C_{(Graphite)} + O_2(g) \rightarrow CO_2(g) \qquad \Delta H_j$	<sub>f</sub> = -393.5 kJ/mol
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Now, heat of formation that the enthalpy of formation that how is the enthalpy change when one mole pure compound is formed from its element most stable state is called the enthalpy of formation is denoted as del H f. Now graphite; graphite when you heat with water heat with the oxygen, it produce in presence of oxygen and graphite burn, it produce carbon dioxide and this is the; this is carbon dioxides quite stable form and the heat of formation is minus 393.5 kilo joules per mole.

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Now, the enthalpy of combustion; now that is the enthalpy of formation, I shall give you; I shall solve one problem, then there the enthalpy of formation will be much clear. Now here the enthalpy of combustion means you burnt ethanol in presence of oxygen and what is the final product that we have final product we have carbon dioxide and water and this is heat of combustion is minus 1365.5 kilo joules per mole the enthalpy of combustion. So, we can express as this.

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Now, there is a important law what is called Hess's law. The Hess's law is says that the standard enthalpy of a reaction is the sum of standard enthalpies of the reaction in which the overall reaction may be divided. So, this I shall show you that how this analysis can be done. So, let me tell you.

Again the Hess's law says the standard enthalpy of a reaction is the sum of the standard enthalpy of the reaction in which the overall reaction may be divided if I solve one problem; I hope the conception will be clear.

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Problem (using Hess's law)
In biological cells that have a plentiful supply of O <sub>2</sub> , glucose is oxidized completely to
$CO_2$ and $H_2O$ . Muscle cells may be deprived of $O_2$ during vigorous exercise and in that
case, one molecule of glucose is converted to two molecules of lactic acid by the
process of glycolysis. Given the thermochemical equations for the combustions of
glucose and lactic acid
$C_6H_{12}O_6(s) + 6 O_2(g) \longrightarrow 6 CO_2(g) + 6 H_2O(l) \qquad \Delta H = -2808 \text{ kJ}$
$CH_{3}CH(OH)COOH(s) + 3 O_{2}(g) \longrightarrow 3 CO_{2}(g) + 3 H_{2}O(l)$
$\Delta H = -1344 \text{ kJ}$

Let us take the example of the biological system, this is in a biological cell that have a plenty supply of oxygen a plentiful supply of oxygen and the glucose is oxidized completely to carbon dioxide and water muscle cells may be deprived oxygen due to the vigorous exercise and in that case one mole of glucose is converted to 2 moles of lactic acid by the process of glycolysis given the thermodynamic equation of the combustion of glucose and lactic acid is given here this is the; so, here I can see; this is glucose in presence of oxygen, it produces carbon dioxide water and change of enthalpy is 2808 kilo joules. Now when lactic acid, this is the lactic acid, when it burns it in presence of oxygen, it also produces carbon dioxide and water change of enthalpy is 1344 kilo joules.

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Problem (using Hess's law)	
calculate the standard enthalpy for glycolysis	
$C_6H_{12}O_6(s) \longrightarrow 2 CH_3CH(OH)COOH(s)$	
Is there a biological advantage of complete oxidation of glucose compared with	
glycolysis? Explain your answer.	
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Now, that calculate the what we shall have to do? We shall have to calculate the standard free energy change; standard enthalpy or glycolysis from glucose to lactic acid 2 moles of (Refer Time: 09:50) is the biological process the advantages to complete oxidation of glucose compared to glycolysis explain your answer. So, which one is more advantageous?

In the biological system energy point of view whether glucose should be converted to carbon dioxide and water or glucose should be personally converted to lactic acid. So, this problem deals with that now.

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Solution	
We need to add or subtract the thermochemical equations so as to rep thermochemical equation for the reaction required. We obtain the thermochemical equation for glycolysis from the following su	roduce the m:
ΔH /kJ	
$\begin{array}{c} C_{6}H_{12}O_{6}(s) + 6 O_{2}(g) \longrightarrow 6 CO_{2}(g) + 6 H_{2}O(l) \\ 6 CO_{2}(g) + 6 H_{2}O(l) \longrightarrow 2 CH_{3}CH(OH)COOH(s) \\ \hline + 6 O_{2}(g) \\ Overall: C_{6}H_{12}O_{6}(s) \longrightarrow 2 CH_{3}CH(OH)COOH(s) \\ \hline - 120 \\ \hline \end{array}$	
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So, previously we have seen this is the equation that we have. Now here what do we have we have? We have seen that that one mole of this glucose produce 6 moles of carbon dioxide and 6 moles of water it has this. Now 6 moles of carbon dioxide and 6 moles of water it can produce 2 moles of lactic acid and 6 moles of oxygen and that required the enthalpy 2 into plus because it was minus previously since it is reverse direction, it will plus the rate of formation will be; obviously, it was the rate of degradation.

So, it is plus the 134 point. So, if you see the overall reaction you have minor this, then this will be canceled, then I can write that one mole of glucose produce 2 moles of lactic acid and if you detect from this your free that enthalpy change is coming around 120 kilojoules per mole.

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So, what does it indicate it indicate that it follows the standard, it follows the standard enthalpy for the conversion of glucose to lactic acid during glycolysis is 120 kilo joules per mole is merely the 4 percent of the enthalpy of conversion of glucose because amount of heat enthalpy generated during combustion of a complete combustion of glucose to carbon dioxide water it will be 4 percent of that and therefore, full oxidation of glucose in metabolic is more useful than glycolysis because the former is more energy processed more energy become available for the performing the work.

So, if you energy point of view that glucose to carbon dioxide water is more attractive as compared to glucose to lactic acid.

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Now, I have taken another example that is that is the heat of formation of ammonia and the heat of combustion of ammonia and hydrogen is given here you can look it here, this is heat of this is the how ammonia is the heat of combustion how we can calculate heat of combustion of hydrogen, we can combo convert we can calculate like this and 3 moles of hydrogen combustion with a 3 into this.

So, as for this reaction we can calculate this one now if you if you look at; therefore, 2 moles of ammonia, we record one moles of nitrogen 3 moles of hydrogen the reversible. So, if this formation what is required we required if we if we if you subtract 3 from 1. So, we subtract this to this then we will find this equation this is 2 mole of ammonia and degraded nitrogen plus 3 moles of hydrogen. So, if you calculate from here you will find this is that this is the plus 188.58 kilo cals now this, but this is the ammonia degradation, but we want to calculate the heat of formation of ammonia. So, it will be reversible reaction the reverse reaction in other direction. So, it will be negative this is positive in case of degradation, but in formation.

It would be negative. So, heat of formation for pond 2 moles of ammonia is 188.58 kilo cals the pond mole of ammonia will be divided by 2 that is 94.29 kilo cals.

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Chem	ical Equilibrium
Wł wh cal	ien a reversible reaction is performed in a closed container, a state is reached en the rates of forward and backward reactions become equal. This state is led chemical equilibrium. Or
The pro	e state of a reversible reaction at which the concentrations of reactants and oducts do not change with time is called chemical equilibrium.
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So, we have we in the last lecture we discussed about the equilibrium of the kind of process that we have now another very interesting thing is that equilibrium that is largely applicable in the chemical process chemical process I particularly if you look at the biochemical reaction if we look at our metabolic pathway most of the reactions they are reversible in nature and when we carried out any kind of reversible reaction like A to A.

Reversibly give A to B. So, there is a forward reaction this is forward reaction and this is the backward reaction that we have. So, so under equilibrium condition the rate of forward reaction should be equal to rate of backward reaction. So, that is the under equilibrium condition through that that from that we can find out the equilibrium constant the state of reversible reaction in which the concentration of the reactant and product no change with time is called the chemical equilibrium when and that is exactly, I told you that when the rate of forward reaction is equal to the rate of chemical reaction, then we call it is equilibrium conditions.

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Characteristics of chemical equilibrium $A = B + C = E + B$
Reversible reactions attain a state of equilibrium from reactants or products side.
At equilibrium, reactants and products are both present and their concentrations
do not change with time.
The equilibrium is dynamic in nature, i.e. the reaction does not stop at this stage
but takes place in both the directions with equal speed.
Equilibrium state is not effected by the presence of a catalyst; it only helps to attain
the equilibrium state rapidly.
The state of equilibrium is disturbed when pressure, temperature of concentrations
(of reactants or products) are changed (Le Chatelier's principle), (
□ Free energy change ( $\Delta G$ ) is zero at equilibrium.
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Now, the characteristics of chemical equilibrium are several the reversible reaction attains a state of equilibrium from reactant and product side and at equilibrium the reactant and products both present.

And their concentrations do not change with this. So, if you look at the if you rate of suppose A to B; B to like this. So, this is the rate of this is the rate constant for the forward reaction is K; K and K. This is K minus 1. So, I can write what is the rate of forward reaction it is K 1 into C A and this should be this should be equal to K minus 1 into C B. So, this is at equilibrium condition.

So, if you if you if you consider the equilibrium constant capital K this should be equal to C B by C A or I can write this is K 1 by K minus 1. So, this is how you can calculate the equilibrium constant the equilibrium is the dynamic in nature and reaction does not stop at this stage, but take place in both the direction with equal speed now this is the equal speed.

It take place the equilibrium state is not affecting the presence of catalyst this is very important it only helps to attain the equilibrium state rapidly the purpose of the catalyst in a reversible reaction it did not change the equilibrium constant, but it will it will help to attain the equilibrium quantity at the faster rate the state of equilibrium be disturbed when the pressure temperature and concentration of reactant and products are changed according to the this is according to Le Chateller's principles the free energy change is 0 at equilibrium this I already explained in the last lecture.

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Equilibrium constant (K <sub>ea</sub> )
Let assume a reversible reaction
$aA + bB \Leftrightarrow cC + dD$
Rate of forward reaction = $k_f[A]^a [B]^b$
Rate of backward reaction $= k_b [C]^c [D]^d$
At equilibrium
Rate of forward reaction= Rate of backward reaction
$\frac{k_f}{dt} = \frac{[C]^c[D]^d}{dt}$
$k_b  [A]^a [B]^b$
IClc[D]d Inroduct
$K_{eq} = \frac{[S][C]}{[A]^a [B]^b} = \frac{[reactant]}{[reactant]}$

Now, I we can we can explain the reaction like this a A b B with. So, rate of forward reaction is explained like this because the backward reaction is. So, under equilibrium condition both are same. So, equilibrium constant basically this is equal to concentration of product divided by concentration of reactant the equilibrium constant; constant of a particular reaction is the concentration of product by concentration of reactant.

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Factors which do not influence equi	librium constant
<ul> <li>Concentration of reactant or product</li> <li>Pressure/volume</li> <li>Presence of a catalyst</li> <li>Introduction of inert gas</li> </ul>	B= the hadred

Now, one important thing is the what are the factors will not do not influence the equilibrium constant what is the concentration of reactant of product because you know that I can explain your K equal to a concentration of substrate and concentration of product. Now what do you mean that concentration suppose the concentration of product is changes the concentration substrate will be changed.

So, you know that change in the manner so that we can attain the equilibrium condition. So, this I write wrongly this will be product sorry this is a your product by substrate, sorry, I do not write it wrongly. So, as the product concentration increases the substrate concentration should be increased. So, that you know it K it remain constant.

Now one interesting feature is that suppose if we want to increase the product formation our what is the what is our goal our goal is to get more product if we want to get more product if we take out the product time to time and then more substrate will be converted to product to keep the equilibrium constant.

Now the examples are that the ethanol fermentation process a ethanol fermentation ethanol is a volatile component as the at the vacuum at a low temperature we can; this the ethanol now if you take out the ethanol more substrate will be converted to ethanol our productivity of the system will be increased the pressure and volume does not affect this.

So, concentration does not affect money as this changes this also changes then ultimately they will be constant the concentration do not affect the equilibrium much because and pressure and volume that also does not affect the equilibrium presence of catalyst that also does not equilibrium and introduction of inert gas that also will not affect the equilibrium.

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Factors affecting equilibrium constant	
<ul> <li>Temperature</li> <li>For endothermic reversible reaction, <i>K<sub>eq</sub></i> increases with rise in temperature and decreases with decreasing temperature</li> <li>For exothermic it is vice-versa</li> </ul>	
> The variation of $K_{eq}$ with temperature is given by Van't Hoff equation as	
tollows $k_{eq_2} = \Delta H (T_2 - T_1)$ $\Delta H \rightarrow \text{heat of reaction}$ $AH \rightarrow \text{heat of reaction}$	
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Now, we have if you look at the for endothermic reaction that K equilibrium increases with the rise of temperature and decrease with the decrease of temperature, but in case of exothermic reaction it will be reverse that equilibrium constant will decreases with rise of temperature and increases with decrease of temperature now if you if you burned off they explain the effect of temperature on this equilibrium constant by this equation lock the equilibrium.

Constant of e q 2 and e q 1 at 2 different temperatures it can be as well this is a change of interval with this is odd is the gas constant and this can be explained like this now.

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Gibbs free energy for reversible reaction	
Suppose a reversible reaction $aA + bB \Leftrightarrow cC + dD$ For this reaction $AG = cG_{a} + dG_{d} - aG_{b} = bG_{b}$	
Again $G_a - G^{\circ}_a = RTln([A])$ $G_b - G^{\circ}_b = RTln([B])$	u. alke
And so on Combining the above equations $\Delta G = \Delta G^{\circ} + RT ln \begin{bmatrix} C \end{bmatrix}^{c} \begin{bmatrix} D \end{bmatrix}^{d}$	051 4
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Now, how we can correlate this with the Gibbs free energy change for the reversible reactions. So, we have already find that change of free energy we can explain like this the change of the free energy of the product minus free energy of substrate that give the change of free energy and this is a G a is the a of and G minus g, it is this the standard free energy change, it can be explained by RT l n a concentration of a G b by G b 0 power 0 ln.

And this and this change of entropy can be a change of internal that a free energy change can be written as that standard free energy change plus R T ln concentration of product by concentration of substrate this can be explained like this and this is very important why it is very important because this is del G equal to del G 0 plus R T ln K ln ln K equilibrium constant; am I right. Now this since the equilibrium constant is constant for a chemical reaction reversible reaction. So, we can del G value also constant. So, if it is constant.

So, we del h value if we have you know a chemical reaction, we can find out easily, we can calculate the value of K e value and we can find out at what extent the reaction take place.

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So, this is one of the major purpose of the thermodynamics of the chemical reaction that tells you that to what extent that reaction take place. Now here del G equal to R T ln, this if you solve it here and if we add equilibrium if you if you if you find out that if you if you assume that the equilibrium del G the change of free energy changes 0 then standard free energy change equal to minus R T ln and in case. So, if we know in a particular chemical reaction if we have know the standard free energy change from that we can easily calculate the equilibrium constant.

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Standard Gibbs free energy and equilibrium constant				
When $K_{eq} > 1$ , the $ln(K_{eq})$ is positive and $\Delta G^{\circ}$ is negative When $K_{eq} < 1$ , the $ln(K_{eq})$ is negative and $\Delta G^{\circ}$ is positive				
,	$\Delta G^{\circ}$	K <sub>eq</sub>		
	$\Delta G^{\circ} = 0$	$K_{eq} = 1$		
	$\Delta G^{\circ} < 0$	$K_{eq} > 1$		
	$\Delta G^{\circ} > 0$	$K_{eq} < 1$		
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Now here the very interesting thing is that if we have K equilibrium constant greater than one then the log K ln is positive del G equal to negative the ant if this is less than one then log K is negative and del G will be positive. So, if del G this equal to standard free energy change is 0 then K equivalent is one, but if del G is less than 0 then K is greater than one and when del G is greater than 0 that is as positive then K is less than one. So, this is the; this is how there is a correlation between the Gibbs free energy change and the equilibrium constant it can be explained like this.

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Now this is the problem that we have this gives you some idea that how we can find out that equilibrium constant of that a reaction with the help of free energy change the problem says that at 200 Kelvin; a certain reaction that del G is 5.08 kilo kilo joules per mole what is the K equivalent equilibrium for this reaction at this temperature and I told you previously that that this Gibbs free energy change that correlation also help you to find out the equilibrium constant.

Now we I have we have the correlation of the free energy change standard free energy change equal to minus R T ln K u. Now K u K equilibrium constant and that you know that we this is not given, we have the rate constant 8.314. This is known to us and temperature is 2000 Kelvin and your change of free energy is this then we can find out that; that means, that means if K is K is fraction; that means, your del G as del G is less than 0 is greater than 0, then K is less than 1. So, this is this is justified even if you look

at sorry, you we have seen here if K is less than one then and this should be positive more than 0 that is only positive.

So, in this problem, it is cleared that this is and this is less than one the K is less than one. So, this should be positive. So, this is quite really relevance to this what we have we told you previously. So, in conclusion, I wanted to point out that what we get from the reaction thermodynamics reaction thermodynamics basically gives us couple of information first information we get that how the entropy influence the nature of the reaction I told you if entropy is positive then the reaction will be spontaneous.

And when entropy is negative that is not spontaneous and same thing happens to something we can correlate the free energies Gibbs free energy change how the standard free energy is related to the nature of reaction if the Gibbs free energy change is negative; that means, it is a exothermic reaction if it is positive it indicate the endothermic reaction. Now the Gibbs free energy change is equal to minus R T In equilibrium constant.

Since the equilibrium constant of a particular chemical reaction is constant so, but we can with the del G value that at a particular temperature that should be constant from that we can find out that what extent the reaction take place suppose if we know the free n h standard free energy change of a chemical reaction where biochemical reaction we can easily find out that equilibrium constant I have we try to solve one problem and you find out that how the equilibrium constant can be determined to be from the standard free energy change. So, basically that the thermodynamics gives the 2 different information's to us that what is the nature of reaction that take place second information that we have to what extent the reaction takes place.

Thank you very much.