Environment Engineering: Chemical Processes
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Module No # 01
Lecture No # 03
Gibbs Free Energy – Non Standard Condition- 1

Hello everyone welcome back so we are going have brief preview of what we discussed in the last session right.

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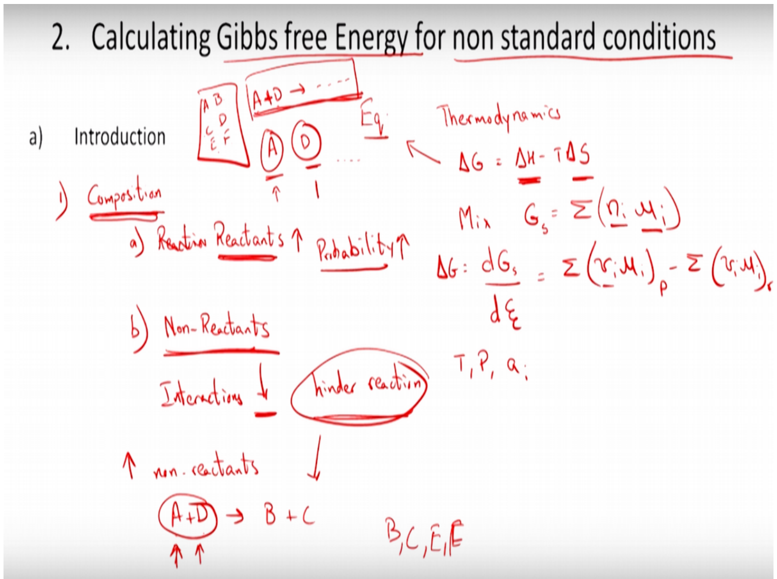

2. Calculating Gibbs free Energy for non standard conditions

a) Introduction

So I believe we were talking about equilibrium in greater detail right so we were talking about how equilibrium is defined by or it is driven thermodynamics. I believe you are trying to look at how delta G affects the particular reaction reaching equilibrium or not and we define delta G or delta H – T delta S and then we try to look at greater detail with respect to change in enthalpy and then change in entropy right then looked at Gibbs energy of mixtures right Gibbs energy or system of mixtures.

And then we calculated delta G value for the reaction which more or less sees the Gibbs energy of the system to the small change or infinite decimal change in the reaction right and then we calculate that as let me say if my memory also be right Vi Mu I of the products – VI Mu I of the reactants and then we discuss the relevant aspects of the applications right but this is the take home message now right.

And Gibbs energy of the system again it is what now summation of NI Mu I right and Ni is number of moles and Mu I is chemical potentials and Mu I is what not the stoichiometric coefficient. So here we are now going to talk about what do you say now the calculation of Gibbs energy of change in Gibbs energy or Gibbs free energy for non-standard conditions right. So in the previous cases classes we talked about how to calculate it at standard condition of temperature pressure and activity of the compound right.

So now let us move on standard conditions and first look at what are the aspects we need to consider now. The first aspect is the composition right composition of the system or you think of it and laymen terms of the concentration of the various compounds so better term if it dealt into greater detail could be composition. So there are two aspects composition is made up of I know we are not going to consider the reactance pardon me reactants and then the non-reactants. So I guess just for illustration purposes so let us say I have beaker or batch reactor here have compound A, B, C, D, E and F at difference concentration level let us say right.

But my reaction is something like A + D goes to so on let us see right you know various products here. So how do reactions takes place now when what do we say the compound A collides with compound D right there is physical coefficient that is why in general we have a reactions taking place is so in general the greater the concentration or composition pardon greater the concentration of the reactants the greater the probability for collision.

Probability of collision is going to be higher let us say and thus greater the concentration of the reactants the greater the chances of the reaction going through. So that is one aspect we are going to look at and the second aspect is obviously the effect of composition of the effect of the non-reactants in the solution now right. So here let say we are concern with the reaction A + D going to products let us say right or A and D colliding reacting with each other and going to products.

But here in solutions we also have C, B, E and F right so the either due to their charge right in general there will be charge or the sum of the compounds or most of the compounds will have a charge they can affect right the interaction between A and D right by interfering with either A or D usually due to charge right and their other aspects but we are not going to go into greater details here.

So these interactions right or inferences due to the non-reactance will in general tend to hinder your reaction now. So greater the concentration of your non-reactance you know that and such hindering your reaction now So here we talked about example again A + B going to products right or And D going to products so they greater the concentration of A and greater the concentration of let us say going to B + C right.

And let us say if greater the concentration of A and greater the concentration of D the higher the chances of collusion between the molecules of A and molecules of D and for the reaction to go through but let us say F greater the concentration of other non-reactants such as D, C E, and F they are going to effect the interactions between the A and D right and thus you are going to have hindrance to you reactions now.

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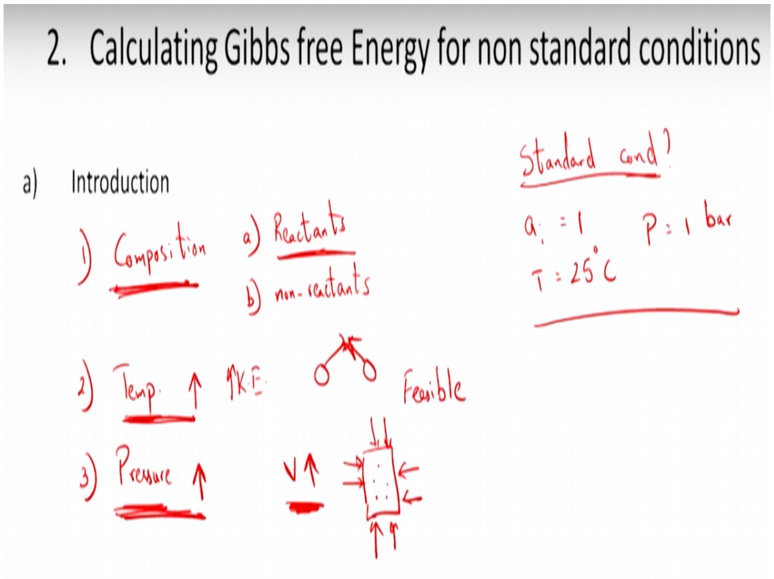

2. Calculating Gibbs free Energy for non standard conditions

a) Introduction

1) Composition a) Reactants
b) non-reactants

2) Temp. ↑ ↑K.E. Feasible

3) Pressure ↑ V↑

Standard cond?

$a_i = 1$ P = 1 bar

T = 25°C

So again this is generic background that we are going to look at so obviously composition of for particular system is an issue and let us see what else we have here and so we looked at composition and everything composition we looked at two cases composition of the reactants and composition of the non-reactants. And the second aspect which most people of aware of I guess is temperature the third aspects we consider I guess is pressure.

Again if you remember how did you look at or what did we define or try to identify when we talked about the standard conditions now right. So we said when the activity of the compound =

1 and also temperature = 25 degree centigrade right and pressure = 1 bar we said that the system is that standard conditions right. So we are just looking at the three aspects when the system deviates from these three standard conditions.

So initially we looked at composition right and then now we are going to look at new temperature. So in general greater the temperature let us say the greater the changes of collation the greater the kinetic energy or the system let us say greater the temperature greater the kinetic energy of your molecules pardon me and greater the chances of collation of one molecule with the other.

So in general again please keep in mind again we are talking about generics here going to look at specific cases later on the greater the temperature the greater the chances of the reaction going through right. so with respect to pressure greater the pressure for generic cases when let us say there is increase in volume let us say right if the volume is increasing think of this now if the volume is increasing to the reaction let us say you know two moles is going to 5 moles so on now.

Initially we have two moles and now let us say we have 5 moles but if you increase the pressure compare to the standard conditions right it pressure the change in volume. Yes so what is that mean in general if the pressure is increased it is not you know it is not favorable for the reaction let us say we are going to look at that how so it is going to hinder the reaction especially when there is a change in volume such that volume increases of your particular reaction these are the generic cases we are going to come back to that into look at that in greater detail.

So there are three cases so first we are going to talk about a composition here and reactants how the composition of the reactants affects your system.

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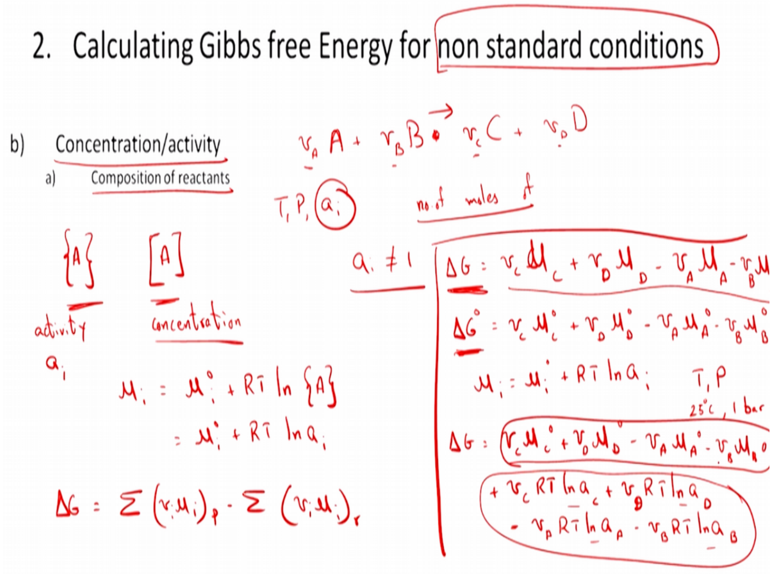

2. Calculating Gibbs free Energy for non standard conditions

b) Concentration/activity

a) Composition of reactants

$\nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D$

T, P, a_i

no. of moles

$\{A\}$ $[A]$

activity concentration

a_i

$\mu_i = \mu_i^\circ + RT \ln \{A\}$

$= \mu_i^\circ + RT \ln a_i$

$\Delta G = \Sigma(\nu_i \mu_i)_p - \Sigma(\nu_i \mu_i)_r$

$a_i \neq 1$

$\Delta G = \nu_C \mu_C + \nu_D \mu_D - \nu_A \mu_A - \nu_B \mu_B$

$\Delta G^\circ = \nu_C \mu_C^\circ + \nu_D \mu_D^\circ - \nu_A \mu_A^\circ - \nu_B \mu_B^\circ$

$\mu_i = \mu_i^\circ + RT \ln a_i$ T, P

25°C, 1 bar

$\Delta G = \nu_C \mu_C^\circ + \nu_D \mu_D^\circ - \nu_A \mu_A^\circ - \nu_B \mu_B^\circ$

$+ \nu_C RT \ln a_C + \nu_D RT \ln a_D$

$- \nu_A RT \ln a_A - \nu_B RT \ln a_B$

So let us move on to that particular aspects so concentration of the activity right is what we are going to look at. So composition of reactants right so in general think of this now let us say you have what is this now we have generic equation we have Mu A A Mu B B so stoichiometric coefficient here Mu A, B, C and D and A, B, C, D right. So this is out generic reaction so think of this now let us standard condition let say the system is that standard condition of temperature pressure and activity right.

And the reaction as gone through by a small extent let us say as infinite extent so now what is going to happen though the number of moles of your compounds are going to change right. So what is that mean the activity is now no more = 1 so right so then we are now entering the domain of the non-standard conditions right. So that is what we are going to discuss here so in general I guess we denote activity of a compound via the what do we say now of this brackets I guess and square brackets for concentration now.

So activity of a compound by third brackets I guess I am sure I am unable remember what we call them or activity of compound I in general when we use this square brackets we refer to that as the or we use them to refer to the concentration of a particular compound now right. So in general we are going to look at the chemical potential here of a particular compound.

This is a non-standard conditions obviously equal to the Mu I naught + RT natural logarithm of activity of compound A right or let us say for sake of writing it down and easier form let us say we are going to use a difference nomenclature here natural logarithm of activity of I of compound A right so we are going to use this and go ahead I guess and what do we know I guess delta G = what now the change in summation of Mu I of the products – VI Mu I of the reactants right.

And what will that be equal to I guess so we can now substitute here for this particular reaction and so delta G I guess = what now Mu C VC Mu C + Mu C – Mu A Mu A – Mu B right and this is what we have. So let us say we substitute for this is at the standard condition or such let us say and this is at the no standard conditions pardon me and we know that if it is at standard conditions let us go into B right this is what we have this delta G at the stand non stand condition and this obviously is that the standard conditions.

So let us try to expand this particular case here and also try to apply for what we just have the guess background information is Mu I at non stand conditions obviously = Mu I naught + RT natural logarithm of activity of I for the given or you know for the standard condition of the temperature and pressure which is 25 degree centigrade and 1 bar. So let us try to plug them in peace.

And what am I going to hit you I guess let us see if I can get that up okay so I guess without troubling you with the (()) (13:13) here of detail. So let me see if I can bypass some of the equations here right so what that be equal to that guess will be equal to VC Mu C naught + Mu D naught – Mu A U A naught – Mu B UB naught right + VC RT into national logarithm of VT of compound C + VC RT pardon me naught VC.

Now it is going to be VD RT natural logarithm activity of D – VA or Mu A pardon RT natural logarithm of activity of A – stoichiometric coefficient of B RT natural logarithm of activity of B right. So and again please note that this particular term or set of variable is nothing but delta G naught right and so again here we have national logarithm here right and so we can try to what do we say make this set of variables more concise right.

So let us do that in the next slide I guess so I guess I am out of space here so let me erase that here itself.

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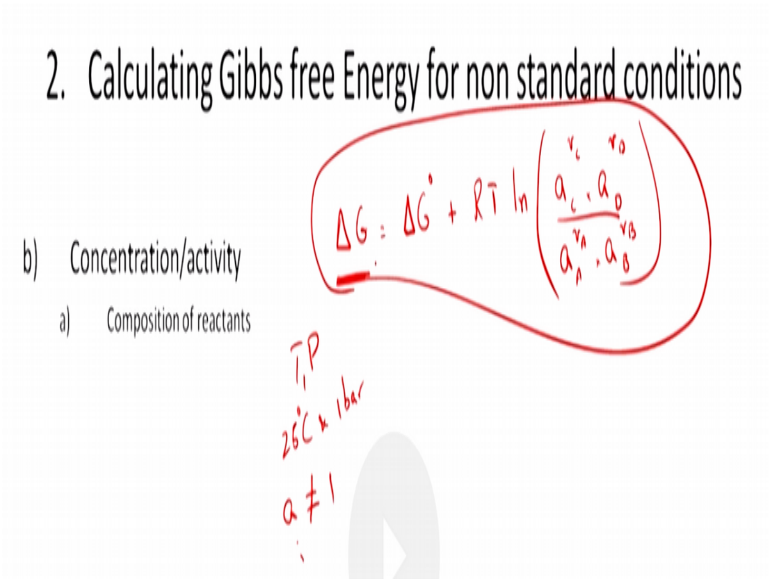

2. Calculating Gibbs free Energy for non standard conditions

b) Concentration/activity

a) Composition of reactants

$$\Delta G = \Delta G^\circ + RT \ln\left(\frac{a_C^{\nu_C} \cdot a_D^{\nu_D}}{a_A^{\nu_A} \cdot a_B^{\nu_B}}\right)$$

T, P

25°C & 1bar

$a \neq 1$

So now we have delta G = delta G naught right + RT into national logarithm of activity of C raise to the power its stoichiometric coefficient into activity of D raised its stoichiometric coefficient by activity of A raise to its stoichiometric coefficient into activity of B raise to its stoichiometric coefficient.

And so this is what we have here the delta G at non-standard condition standards as in the temperature and pressure are still at 25 degree centigrade and 1 bar but the activity is no more equal to 1 of the relevant compounds and so then we end up in this particular equation I guess anyway this is the take home message this is the do not need to mug this up in greater detail I guess right.

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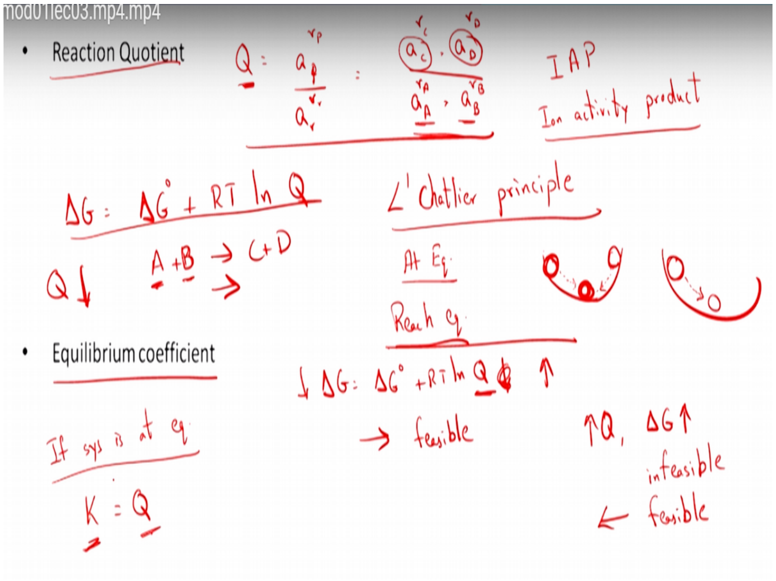
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- Reaction Quotient

$Q = \frac{a_p^{\nu_p}}{a_r^{\nu_r}} = \frac{a_C^{\nu_C} \cdot a_D^{\nu_D}}{a_A^{\nu_A} \cdot a_B^{\nu_B}}$

IAP

Ion activity product

$\Delta G = \Delta G^\circ + RT \ln Q$

L' Chatlier principle

$Q \downarrow$ $A + B \rightarrow C + D$ $\rightarrow$

At Eq.

Reach eq.

$\downarrow \Delta G = \Delta G^\circ + RT \ln Q \uparrow$

→ feasible

$\uparrow Q, \Delta G \uparrow$ infeasible

← feasible

- Equilibrium coefficient

If sys is at eq

$K = Q$

So now we are going to move on so here we have a new term which is called reaction coefficient I guess so reaction coefficient we define that as being equal to the activity of the products raise to the stoichiometric coefficient of the product by activity of the reactance raise to the what do we say now stoichiometric coefficient of the reactance which is in the earlier case was activity of C raise to the stoichiometric coefficient of C into activity coefficient of D raise to the stoichiometric coefficient of D by activity of the reactance which is in that case where A and B raise to their respective stoichiometric coefficients right.

So again thus this is called the reaction coefficient it is sometime also called as I on activity product Ion activity product people use them as of them as each other. So here please note that the system either be at equilibrium or not at the equilibrium. So again if we now rewrite delta G = delta G naught + RT natural logarithm of Q right. And this case now we are going to talk about a principal that people might have heard Le Chartelier's principle.

So I guess what does this mean now I guess it says that if a system at equilibrium let us say if equilibrium and its disturbed (()) (17:27) in any manner it will move or travel let us say I am using laymen's term again it will move or travel in such a way as to again reach equilibrium now right. So for let us say for your sake of understanding let us say I am trying to get this system and you have wall here let us say the system is that equilibrium now right.

Let us say we move the ball to the right and release it here it is again going to try to come to it equilibrium state right if I move it to the left and release it here again going to try to come back to it equal state of equilibrium you know more or less that is the principle of Le Chartelier's let us say. Right again what is that if the system is at equilibrium and its (()) (18:11) in any way because that it no more at equilibrium it is going to try to move back try to move in such a direction as to reach equilibrium again.

So what does that it mean so let us say if in this case let us say Q is decreased right so decrease in Q what does it mean now. So you end up adding A and B so we have A + B going to C + D and say decreasing means in general add more quantities of A and B right so what does it mean now from the Le chartelier's principle what does it mean let us say it is equivalent to moving the ball to the left here.

So earlier it was here now added more reactance of the ball is now here let us say it is going to try to move in the forward direction here or the reaction is going to go through in the forward direction and that is what you should see here in this case right again how do we relate to the equation that we describe that through delta G = delta G naught + RT natural logarithm of Q right.

So as Q decreases right you see that I guess the effect is such that delta G decreases to just meaning that forward reaction is feasible is again the inverse of it what would happen let us say if you end up increasing the Q though right that would mean that if you increase the Q that more or translates to delta G increase in 2 right. So that makes the reaction feasible or it means that reverse reaction is feasible right.

So that is what we have here right and the next aspect we are going to look at the term is equilibrium coefficient so let us say if the system is equilibrium right if the system is at equilibrium then K will be equal to Q right and that is what you want to understand here. So again keep in mind that we are talking about Q or K we need to define the relevant or the variable are activities are not concentration skill right.

So if the system at equilibrium that is one we will have Q which is the reaction coefficient being = K the equilibrium coefficient right and let us say why this important or why we need to discuss this in greater detail.

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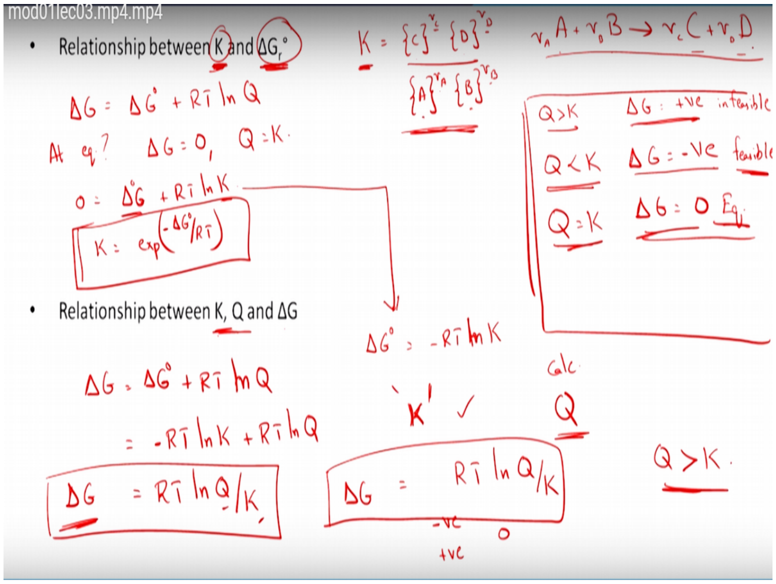

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- Relationship between K and $\Delta G_r°$

$K = \dfrac{\{C\}^{\nu_C}\{D\}^{\nu_D}}{\{A\}^{\nu_A}\{B\}^{\nu_B}}$

$\nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D$

$\Delta G = \Delta G° + RT \ln Q$

At eq? $\Delta G = 0$, $Q = K$.

$0 = \Delta G° + RT \ln K$

$\boxed{K = \exp(-\Delta G°/RT)}$

$\Delta G° = -RT \ln K$

$Q > K$ ΔG : +ve infeasible

$Q < K$ ΔG = -ve feasible

$Q = K$ $\Delta G = 0$ Eq.

- Relationship between K, Q and ΔG

$\Delta G = \Delta G° + RT \ln Q$

$= -RT \ln K + RT \ln Q$

$\boxed{\Delta G = RT \ln Q/K}$

K' ✓

Calc. Q

$\boxed{\Delta G = RT \ln Q/K}$

-ve

+ve

0

$Q > K$.

So I believe we will move on to this next slide so here we have we are trying to develop relationship between K right which is the equilibrium coefficient and delta G of your reaction again what is K I guess for reaction Ua A and this is the example reaction that we are using in our class so what is that equal to again when the system has reached equilibrium you will have relevant what do you say activities right.

So here I use the different terms right here again we have activates of the power right to their stoichiometric coefficient divided by activities of the reactants rise to their respective stoichiometric coefficient. So again when is this particular set off or these set of variables equal to equilibrium coefficient even through when the system is that equilibrium when is the equilibrium we will have relevant activities of the various compounds and then is when you calculate K.

So here I guess we are trying to develop a reaction pardon me relationship between K and delta right so try to write down what we know so far delta G = delta G naught + RT natural logarithm of Q right. So at equilibrium what do we know that delta G = 0 right and we also know that Q =

K yes plugging the relevant values and we get 0 = delta G naught + RT national logarithm of K or K = exponential – delta G naught by RT right.

So what does it mean so let us say if you have K you can calculate delta G naught or if you have delta G naught you can calculate K again what is delta G naught please change in Gibbs energy of the system during the reaction at standard conditions so you know once you. Once you have the relevant one variable you can calculate the other variable more or less that is going to be useful to you throughout the course of the class or in general our engineering systems 2.

So here I guess the second case is trying to develop a relationship is between K Q and delta G so let us what we have here. So guess here we have delta G – delta G naught + RT natural logarithm of Q right. So and we know that delta G naught = - RT national logarithm of K that is from more or less this particular equation here. So prime that in what is that mean here it is equal to – RT natural logarithm of K + RT natural logarithm of Q right and so that is equal to that translates to delta G = RT natural logarithm of Q / K right.

And so this is relationship we are going use widely right so you do not need to mug up any here everything is logical here right. So these are the take home messages here and let us we get what we just discuss now right so we were able to calculate K given delta GR naught or you know vice versa. And again we see that we have relationship between delta G and Ion activate product equilibrium coefficient.

So what does this mean though in general in your standard tables or such you will have the K values or equilibrium coefficient K is the capital K here equilibrium coefficient given for most of the relevant reaction now right. So let us say if you know if you can calculate the Q at any particular point in time let us say right you know the relevant activities or concentration and calculate Q right.

And then you end up calculating RT national logarithm of Q by K right and then what will give idea about it will thus give an idea about delta G. So you can calculate delta G in negative is delta G positive or is delta G 0. So what happens here Q is greater than K what does mean right so I am going to work that out here so then Q greater than K as you look at this relevant reaction that translates to delta G being positive right.

And when Q is less than K what does that translates to? It translates to delta G being negative and obviously when Q equal to K what was that means it mean delta G = 0 or the system is that equilibrium. So in the same case again when Q is greater than K you know that the reaction is feasible right it is in feasible that is what delta G is positive and again say when Q is less than K delta G is negative so the forward reaction is feasible and again we have here the 3 cases here right.

So when Q greater than K forward reaction as we have defined at feasible when the reverse fee as an C and D going or reacting to form B and A is going to be feasible right and A less than K the forward reaction is feasible as in written as A D react into form C and D and so on when C = K obviously the system is at equilibrium or delta G is 0 and then there is not further change in the system right.

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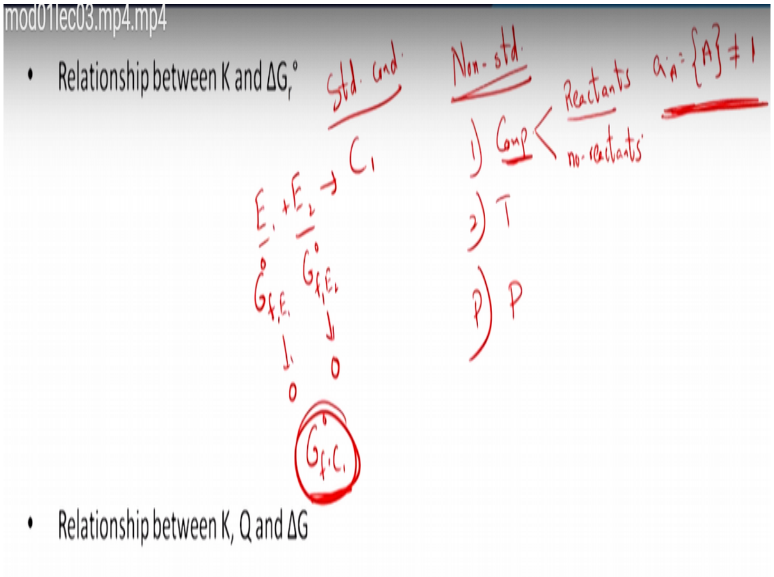
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- Relationship between K and ΔG_r°
- Relationship between K, Q and ΔG

So let us try to summarize what we have looked at so for and then wrap it up for this session so I believe we started talking about you know the calculation of the relevant aspects or Gibbs energy at non-standard conditions and the previous classes we talked about how to calculate at standard conditions and how did we calculate at standard conditions we let us say we have elements 1 , 2 reacting to form compound 1 we have defining the Gibbs energy of formation of these particular elements right Gibbs energy of formation of this elements.

We are setting those the references and they have being zero so from that you can calculate the Gibbs energy of formation of the relevant compounds at the standard conditions and that is how we went about that and obviously you know most of these will be in your standard tables now. So it fits at non-standard conditions obviously you will need to calculate that non-standard condition three cases what are that we look at non conditions we look at temperature we look at pressure.

So today we have discussed the issues with respect to composition especially with respect to reactants the activities or activity of A not being 1 I guess right. So we discussed how would that situation or scenario change of the activity of the relevant compounds or not or reactants or not one. So in the next class we are going to talk about composition of non-reactance and so on so I guess with that I will bit favorable and thank you.