## Environment Engineering: Chemical Processes Prof.Dr. Bhanu Prakash Vellanki Indian Institute of Technology – Roorkee

# Module No # 01 Lecture No # 02 Equilibrium – Process feasibility, GIBBS Energy – Standard Condition

Hello every one welcome back to my course so in the previous section we looked at or we introduced ourselves to the concepts of the equilibrium and kinetics and also i believe we looked at some of the aspect about identifying which particular state or characteristics such as kinetics is very important for example we looked at trying to identify is the system under equilibrium control kinetic control or mixed control and so on.

So during the course of the next few sessions we are going dealt into greater depth or detail with respect to equilibrium now right.

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So believe we already looked at some of the aspect for example relevant to the importance of equilibrium I believe one example we looked I think in the previous session was that we looked at trying to identify maximum heavy metal removal at a certain PH let us say try to identify the maximum heavy metal removal at a certain PH let us say right say.

Heavy metal can be precipitated out and given the relevant PH and like an concentration you can you know estimate a great degree of accuracy the greatest possible removal or you know the high percentage removal of the relevant heavy metal or mixture of heavy metals is that is one particular example but that is applicable in an equilibrium is applicable into any particular engineer or particular systems.

So we are going to move on and I believe we are going to also discuss about you know what you know drive or defines equilibrium right I want to know let us say is particular system feasible or not feasible in first case. So I believe we started discussing the aspect called GIBBS energy or GIBBS free energy or change in GIBBS energy now right. So let look at the definition first right and most people are aware of this so delta G = delta H - T delta S right.

So delta G change in GIBBS free energy change in GIBBS energy of particular system delta H change in enthalpy more or less gives you an idea the heat energy being released or being taken to the system and delta S gives you an idea about the change in enthalpy more or less let us say right the greater the disorder the greater in entropy now. And in general delta G is the state variable what is this mean right.

So in general we know let us say if this is G how to reaction occurs let us say you can vigilance them as if it is going from state G1 to G2 right so they are going to fall down the ladder you can visualize them right from state G1 to G2. So what when we say delta G or you know GIBBS free energy is the state variable is what is that mean? It does not depend on the path it takes to go from one to right.

It is independent of path it takes to the system to go from state one to state two that is what we understand when we say when we call it is call GIBBS energy state variable right and again one another aspect consider the two other minor aspect is that delta G changes in same direction as a G changes in same direction as H or change in enthalpy but delta G changes in the opposite direction as change in entropy right.

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So that is something to keep in mind which we are going to discuss later on is so let us move on and I guess we are going to talk about process feasibility now. So what defines how can we understand let us say or relate the change in GIBBS free energy to equilibrium or the relevant concept that we come across in nature or in engineering systems right.

So you want to know let us say particular reaction is it feasible I mean I would go forward and ignore right. So for that in general we always have learnt to look at the delta G right and what is that equal to I guess we know that equal to delta H - T delta S and in general I guess this is common knowledge so whenever delta G is less than 0 or in negative we say that the process in feasible.

When delta G is greater than 0 we say that the process in in feasible and when delta G is equal to 0 we say that the system is that equilibrium. So let us just try to understand is aspect for the second I guess so in general we again go back to previous figure that looked at so if I have G here and let us say if I am trying to indicate the two states so the initial state is G1 and final state is G2 right and obviously here the change delta G = G2 - G1.

And as you can see state G2 or state 2 is that the lower energy stoichiometric to state one or G1 right thus it is negative and you can see you know if you can vigilize that it is falling down the ladder right the system. So thus process is feasible right this is feasible and obviously though the

second aspect that we looked at or we just have we have written down here let us say G2 is it a higher energy state and G1 or (()) (05:54) state 1 is at the lower energy state.

So delta G right which is G2 - G1 let us say is going to be poised right so system cannot move up the ladder right again for visualization purpose again saying it is moving up the ladder. So obviously that means that the system is in feasible but as you can visualize the system can go from G2 to G1 though right the reverse reaction is feasible this is what we can understand from here.

So this indicates that the reverse reaction is feasible but the reaction which goes from 1 to 2 is in feasible right and obviously the third aspect I guess is self-explanatory so when both the states are at the same energy states let us say or energy levels which ever you want to understand that there is no what do we say for the intensive to move up or down the ladder pardon me move down the ladder.

So we can say that the system as reached the maximum extent possible at that particular conditions of temperature and pressure so it as this travel the so we looked at the equilibrium as how far the system can go right at the given conditions of temperature and pressure so when G1 and G2 are the same it means the system has reached equilibrium or travel the far and extent possible right or reach the maximum possible and the given terms and condition of temperature and pressure.

So again so delta G = delta H - T delta S right and now we are going to look at the individual terms in greater D2RO pardon me I guess okay.

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So again we have delta G = delta H - T delta S so again let look at how this apply to let us say delta H and delta S and so on let us say right. So in general H obviously as we talked about delta H is decrease in enthalpy means it favors the reaction right so what does it mean though. So decrease in enthalpy delta H is negative when delta H is negative right that promotes delta G being negative right and that is what you can see from this particular reaction when delta GH is negative that promotes delta G being negative that means it favors the reaction now right.

So what does delta H negative been let us say again if I draw have here again this is just for visualization purpose right. So here let us say H1 and H2 right so heat energy will released in this process delta H = H2 - H1 right and as you see that is negative is so what does it mean though the energy that stored in state 1 let us say is going to be released as heat energy here.

So whenever delta H is negative what does that means it is exothermic reaction and obviously what is that mean release of heat energy yes and obviously again increase in entropy and what does it mean delta S being positive and delta S being positive right promotes delta G being negative is and that favors the reaction now right. So let us look at an reaction here I have an example here let us look at what does it means.

So in general entropy I guess gives you an idea about the degree of disorder in the system so again I am using lot of layman's terms here so that people it is easier for the students or the audience to understand what I am talking about? So for example let us say for solid is change in

phase or transforming to liquid phase with degree of disorder entropy will increase and again if liquid again for the transforms into the gaseous phase or gas let us say or gaseous phase pardon me.

So it is again going to increase the degree of disorder in the system or if there is an increase in number of modes let us say of the system. So what does it mean so let initially being one more and that either due to combustion or other relevant reaction which we are going to discuss in greater detail you know now transforms into 2 or 3 or so moles.

You see now you have increase in number of modes but more or less means greater degree of disorder in the system right and that means again delta S is positive right in the second state there are more number of modes right. So delta S is positive right and again that means delta H delta G will intend to be negative and that obviously again favors the reaction as we define the deltas right reaction defined as in this case I believe we have been taking about going from state 1 to state 2 right.

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So again one final example here so we have NACL in solid form what you say disassociating it to NA + NCL - when dissolve in water obviously aqueous space AQ stands for aqueous space which we in general indicate when we have a compound dissolve in water now right and here we have let us say let us look at the delta S value at the standard condition this here particular nomenclature indicates standard conditions.

So change in entropy at time conditions when the value that have here is 43.4 joules per kelvin right and obviously someone asked you to what do we say guess what is the sign here you can obviously say it is going to be positive right + 43.4 joules per kelvin. Why is that obviously now we have the solid face and it is disassociating into what do we say aqueous spaces and more importantly initially one mode and now you have 1 + 1 2 modes so the disorder or greater the disorder we know the delta S is going to be positive.

So that is one example that you see guess so the example that I have is 2 NO2 in the gaseous space you know and that seems can be equilibrium with N2O 4 in the gaseous space. So now if I look at the change in entropy of this system and the magnitude looks like is 175.83 joules per kelvin now right and someone asked you know to think of what sign is going to be. So here both of the gaseous space so we cannot really draw many conclusions from there.

But if we look at particular aspect as in initially have number of modes have been 2 and then i have one mole here so right the degree of disorder is less so what is that mean delta S is going to be obviously negative here and this in general would not favor the reaction to go through right obviously you need to look at the standard change in enthalpy to be able to give final call or take a final call about delta G either being positive or negative right.

Anyway a few examples that we looked at so let us see what we have next okay so we talked about the driving forces for you know equilibrium let us say or for system to reach equilibrium pardon me right we looked at GIBBS free energy.

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= 
$$\sum n, \overline{G}$$
,  
c) Application to reactions  
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Heo the capacity to descenthing.  
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So now we are going to move on to look at applications too reactions now right. So you now let us see you want to you now calculate delta G values but you are going to look at it great detail about how to relate that to a particular system or let us say a system is going from state 1 to state 2.

You want to able to rewrite that so again before we go further through obviously we need to look at what is the GIBBS energy of a mixture right here keep in mind we are not talking about a change but we are just talking about the GIBBS energy of a mixture what is that and how do I calculate like that so let us say in the mixture I have compound A, B, C, D and so on I number of compounds.

So how do I calculate that let us see right and that obviously you have calculate by summation of NI GI bar NI is number of moles of compound I right GI bar a new concept I guess is GIBBS energy per mole of compound I and that is actually also = Mu I which again is a new term to C chemical potential of component or compound I right. So now we have a new term what do we say Mu I chemical potential of I.

So we are going to discuss that in a bit more detail right so what would you understand when let us say somebody says someone as let us say person A as potential right and here again we are talking in laymen's terms so what do you understand let us say some body as potential now right so it means the person or the system let say as the capacity right again this are all layman's terms we do no need to note them down obviously capacity to do something let us see a very generic term to do something right.

Again so I think a better example to look at a potential energy let us say so higher the potential higher the capacity to be able to something worthwhile let us say. So you can draw a (()) (16:53) here or look at the analogy here right and you can think of chemical potential in the same way as an mixture or in with respect to reaction or either going forward or backward let us say. As we know how the reactions go through let us say we know that G1 and G2 so we know that the system would fall down the ladder from G1 to G2 right.

And we know that the G of the mixture let us say what is that equal to I guess summation of NI GI bar which is also we have looked at NI Mu I I guess we have even arrived it I guess and what is that mean now you see that whenever the chemical potential is high let us say right the greater potential for the system to fall down the ladder and for the reaction to proceed through.

So greater to potential of the system it has the greater tendency or it can let us say go down the potential and make the reaction favorable you know that just for you purpose of understanding now right. So again the minor aspect that we are going to look at so in general we call or we can say potential equal to right what is this equal to I guess D G of the system or mixture right by D NI and that would be equal to as we just looked at here I guess what is that equal to I guess D gardon me summation of NI Mu I / DNI and that obviously =Mu I I guess.

So that is what we are trying to look at potential chemical potential that is how it comes about is again it take home message is that the higher the chemical potential is that the particular chemical that more or less relate to higher energy state or GIBBS energy of the mixture and that would mean a greater tendency or potential for reaction grow through or fall down the ladder which more or less translates to the reaction going forward right.

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So let us see what we have next I guess so next aspect I guess we have is applying this to the GIBBS energy change for chemical process or obviously for a reaction now right. So here we are going to look at what we say trying to so very small change let us say or infinite decimal change in reaction let us say I want to be able to calculate the change in GIBBS energy how this GIBBS energy going to be affected by small change or infinite change in reaction now right or in the reaction as gone through but small extent now right.

So first let us take an example of a reaction here a generic example so here have stoichiometric coefficient of A times compound A is stoichiometric B going to C say here we have a stoichiometric coefficient Mu A, Mu B and Mu D right say A + B goes to C + D pardon and moles of A guess stoichiometric coefficient we have that let us say. So this is the general reaction now so let us define a term let us say saying that small change in reaction right is the great term Z right I guess my hand writing is very poor okay Z.

So for a small change in the reaction let us say I want to be able to equate that to a change in moles of compound A, B, C and D right let us say the change in number of moles of A, B, C and D. So how do I do that let us see because I am still missing a few terms right how do I do that let us see. So obviously as people may (()) (21:23) you can normalize that by picking at the stoichiometric coefficient right.

And obviously because A and B are being last and C and D are being formed we are going to have to use to the relevant (()) (21:29) right. And so that say something that we have here and we are going to use this later on so let us say I am going to call this equation one let us see right. So next aspect is you want to look at for a small change in reaction what problem you are looking at GIBBS energy of the system how is this changing.

So obviously we first need to calculate the GIBBS energy of the system of the mixture initially right. So what is that equal to I think we looked at that earlier equal to NI Mu I right and that again is equal to what now anyway we do not need to go into detail here or I guess it is worthwhile and A Mu A + N B Mu B right + N D and C Mu C + N D Mu D right yes and we have that here.

And so obviously here again water will looking wet this is the initial what do we say GIBBS energy of the system or the mixture this as an this particular term or set of variables here and what do we want though we want to observe for a small change in reaction and how the GIBBS energy changing right and we have already defined for a small change in reaction and the Z right.

So if I take the derivative here DG of the system DZ and that is equal to what now D/DZ = D/DZ of NA Mu A + NB Mu B + NC Mu C + ND Mu D right. And now I guess right to get this right here and that would be equal to what now here please Mu A into D by NA of Z + Mu B into D and the DZ + Mu C D and C / DZ + Mu D into derivative of what now number of modes of D for a small change in extend in reaction here so right and what do we see here let us try to simulate these particular terms to what we just calculate here in this equation one right.

And what do we get here I guess we are going to get D and A by DZ derivative of number of modes of A by number of small change in reaction is going to be equal to – Mu A right. So that obviously is going to be – Mu A UA + again what is this stoichiometric coefficient and this is the chemical potential of A right and again not plus here – Mu B + Mu C + Mu T + Mu D right. So instead of going to a fresh page and then losing of track of what we are up to here let us summarize what we have looked at (()) (24:48) here.

And so obviously this is the take home message so I am do that here in this part okay so here we have here now DG of the system DZ = what now summation of NI Mu I of the products not NI

pardon me so obviously that is a bit of mistake there summation of stoichiometric coefficient I guess right did we mess something up here let me have a look at this now Mu A seems fine here Mu I of the products – summation of Mu I of the reactors here right.

So this what we have here and so let us look at let us review what we are up to we are trying to calculate the change in GIBBS energy for reaction for a small change in reaction or reaction as gone through a small extent so that we define by DC and we try to relate that change in the number of moles of your particular compound here right and we are in reaction one we normalize by the stoichiometric coefficient is so here are trying to define the change in the number of moles of each compound with the extent of the reaction.

And then obviously because of the calculating the change in GIBBS energy we first need to define or calculate what the initial GIBBS energy of the mystery that we have looked at it earlier and so upon expansion this is what we have here is and this is what we are trying to calculate all around ahh change in GIBBS energy of the system for a small extent in change in reaction and so guess we have the here and a transformation here looking at equation 1 we came up with this now.



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What is that again let us go on to next page and then write that up again so DG of the system DZ or more less change in GIBBS energy of the system for a small extent in or infinite decimal change in the extent of reaction = what now stoichiometric coefficient of I VI Mu I of the

product – Vi Mu I of the reactors. Again right and so obviously this is equal to what now delta G right.

So obviously if you look at it when will delta G be negative obviously when this term is going to be greater than this term again the higher the chemical potential I guess they would like to fall down the ladder so that is what we are here so greatly applicable here but the analogy I am trying to draw here right. So when this term is greater than this so that is what we are going to have here when that is going to be native and where did we have here that I guess here.

A and B are the reactors and C and D are the products here right so let us try to have this in a graphical format so that we can understand this better right. So here we are going to have a particular figure here and here we are going to have G of the system and X is the extent of the reaction and example let us say this is how the system can behave right and this is what we have here and so let us say we are trying to look at delta G or more or less DG by DZ.

So more or less what is DG by DZ it means the sole of this particular graph or system here so let us say I am identifying particular aspects here right and this case as you see delta G or delta DG by DZ is going to be negative so it is negative here it is = 0 and here it is going to be positive right. So what do we understand here in this particular phase let us say when delta G is going to be negative or the slope is negative let us say here going to have a reaction that is feasible again we have here the GIBBS energy of the system in on the Y axis extent of the reaction X on the X axis.

So think of this let us say again for (()) (29:09) purposes so if this is G1 it can fall down to G2 right and that is how the reaction can go through right and that is where you see delta G being negative or DG by DZ being negative. So obviously when it is equal to or the slope is equal to 0 at this particular point let us say it has reached equilibrium yes and there is not tendency for the system either I guess from G1 to G2 or so on it has reached the maximum extent possible.

Again what is happening here though here let us say G2 is that the higher energy state let us say again I am using laymen terms please and G1 for the system cannot go from G1 to G2 or if it is want to not if wants to the reaction that takes the state from 2 to 1 is feasible but not from 1 to 2 though right that is what you can understand here when we say delta G in this region here is

positive again you see the positive slope here and again you can relate that to what we just looked at earlier DG of the system by DZ right and so that is what we just looked at here.

So hopefully this could give the good idea about what we are talking about so again you do not need to what we say mug this up and this is for an understanding of basic principles involved here right. So again we are going to try everything up delta G negative means the reaction is feasible delta G being positive means is the reaction is not feasible or the reverse reaction is feasible and delta G = 0 means the system is that equilibrium right okay.

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So let us move on and what we have next okay we are going calculate the GIBBS energies now right. So you are trying to calculate the delta G's right or we have learnt how to look at delta G until now and how to lead that to reactions how to relate that to mixtures and again to take a bigger view not a bigger view pardon me holistic view right look at the bigger picture what are we talking about let us say just summarize briefly.

So we have we introduce ourselves to equilibrium kinetics and then we started (()) (31:34) to the concepts of equilibrium and there we introduce the concept of change in GIBBS energy delta G and in that aspect we are applied that to reactions and we also applied that to mixtures right. And now we are going to further talk about how to calculate GIBBS energy of the systems now right and we will talk about kinetics later on may be a few session down the line.

Again I am giving you this information so you will have an idea about what is that we are talking about in relation to the bigger picture again still talking about equilibrium here right. So how to you calculate GIBBS energy I guess before we go further we need to you know understand that two aspects involved now once the standard conditions and the other would be the non-standard conditions right.

So obviously we are going to first discuss the relevant aspects how to calculate GIBBS energies at the standard conditions and then we are going to move on to the normal standard conditions. So standard conditions how to do you define them so we could say that when the temperature is 25 degree centigrade and when the pressure = 1 bar and now we have a new term called activity of the particular compound = 1.

For example understand activity as concentration for now right we are going to go through that later activity or not the same or equivalent to concentration but for now think of activity as ideal measure of ability of compound to react. So gives an idea about the particular compound to react right in general let us say. We are going to you can for now think of it as concentration of particular compound but we are going to see why we need to look at activity later on.

So when do we so standard condition what are the again please temperature being 25 degree centigrade pressure is 1 bar which is more or less equal to I guess one atmosphere but not so you can root this up and when we say activity or let us say activity which we were can approximate by concentration in some cases = 1 right. So again we need to calculate GIBBS energies right. So in general we are always concern with delta G values though.

So what is this here so looking at difference here G 2 pardon me G1 - G2 right so for that we obviously need the reference right. So it is calculating the means sea level right in the railways stations you would have come across as particular term called MSL below the name plate or you know where you have the relevant sign let us say you would have seen a particular term MSL and so.

I guess obviously it is a mean see level that I guess they said the sea level as the reference in the same case here in our delta G or you now when we are looking at changes in the GIBBS energy need to set a reference too. So here we set that the GIBBS energy or formation of elements you

know = 0 so here we have the two aspects I guess we are coming across new terms. So GIBBS energy of formation of a particular compound or element a standard conditions.

So in this case though we are setting a reference as GIBBS energies of formation of elements at the standard states we are setting that as being 0. So what is that means or how will that help us now.

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Let us say I have elements 1 and element 2 you know forming compound I guess right and since we set the GIBBS energy of the system of the elements to be 0 at the standard conditions and if you want to calculate delta G of this particular reaction that is equal to what now I think we looked at this now right NI GI bar of what not the products – NI GI bar of the reactant so right so that would be equal to what now.

So here let us say we have number of moles of stoichiometric coefficient are 1 here for all the three cases here so that is more or less equal to the GIBBS energy of formation of compound I – GIBBS energy of formation of this element one – GIBBS energy of formation of element 2 right so but as we just discussed said this two terms as being 0. So this will not give us the delta G of the reaction would give us the GIBBS energy for formation of again all these are standard conditions so that keep this in mind here right of compound I.

So at the standard condition if you can measure the change in GIBBS energy you will thus be able to calculate the GIBBS energy of formation of your compounds in general all this available in you standard tables in most text books certain in the reference that we talked about right and if you are not sure which one implement or which one say compound which will again refer to those standard tables and there you will have the relevant information.

So here I believe one example and lets us look at that so here let us say we have graphite carbon in the form of graphite let us say and 2 H2 gas going here to form methane CH4 in the gaseous phase. So how do I calculate the so these two are elements here and this is a compound here right so I am just trying to draw a (()) (37:49) here.

So how do I calculate here the GIBBS energy say I guess the relevant compounds delta G naught change in GIBBS energy of reaction at standard conditions = as we know VI MU I or pardon me that is not Mu I here we are talking about the GIBBS energy we will talk about GI a bar of GIBBS energy of the products – the summation of VI GI bar of the reactants.

So that is equal to what now here so here GIBBS energy G of formation of which more or less in this case is equal to more or less GIBBS energy GI I guess of CH4 - 1 into what is that1 into stoichiometric coefficient here right 1 into what do we have here the GIBBS energy of formation of graphite – two times GIBBS energy of summation of hydrogen right the gaseous space obviously hydrogen gas pardon.

So as we just discussed these two are elements and so hydrogen and graphite are elements and GIBBS energy of those elements we set as 0. So these two terms would now be 0 and so the delta G reaction is standard condition same as GIBBS energy of formation of methane. So if you can calculate these so you can calculate CH4 or such. So what will this (()) (39:26) from the elements again I am coming back to equation you calculate the GIBBS energy of formation of most of the compounds right.

So once you have the most of the compounds let us say C1 and C2 and so on then you can again. So now let us say you have the GIBBS energy is formation of C1 and C2 right C3 and C4 so then you can go ahead and without measuring it I guess calculate delta G value at standard conditions of your relevant reaction. (Refer Slide Time: 40:02)



One last example before we wrap up the class so here I guess we have CH4 + 2O2 geos to CO2 + 2 H2O. So delta G naught or change in GIBBS energy systems at standard conditions = sigma of Mu I GIBBS energy of formation of 5 product – summation of Mu I GIBBS energy of formation of 1 standard condition of the react right.

So delta G naught or delta GR naught whichever way I guess = GIBBS energy of formation of carbon dioxide right at standard conditions and + 2 times GIBBS energy of formation of H2O at standard conditions – GIBBS energy of formation of what now methane its standard conditions and two times GIBBS energy of formation of the hydrogen gas right and we can identify which of these are implements I guess and you already have the GIBBS energy of formation of some of the compounds and then you can end up calculating the delta G of the reaction right.

So I guess we will summarize what we have been up to for today right so we are started talking about the equilibrium in greater detail and then we talked about how it depends upon delta G and we looked at delta G being negative positive and 0. 0 equates to obviously equilibrium and then we looked at some drive in forces as in standard or change in enthalpy and entropy. Enthalpy gives us an idea about the heat energy or let us say MG in the system and entropy about the degree of disorder.

So again we try to link change in enthalpy or change in entropy to change in GIBBS energy and I believe then we have moved on to talking about GIBBS energy of the mixture. So G system or of the mixture right what is the equal to leave it summation of NI GI bar GF bar and that we said is also the same as sigma of NI Nu I is the chemical potential right and then we believe again we try to link that to change in GIBBS energies of during a reaction right I believe we have calculated DG by DZ.

And then we looked at the relevant changes and so on right so I guess with that I will wrap up the class for this sessions and thank you.