Environment Engineering: Chemical Processes
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Module No # 01
Lecture No # 04
Gibbs Free Energy – Non Standard Condition- 1I

Again hello everyone so we are back here I guess so we are continue our sessions so we are again briefly going to look at what we discussed in the last class and then quickly move on the out current lecture.

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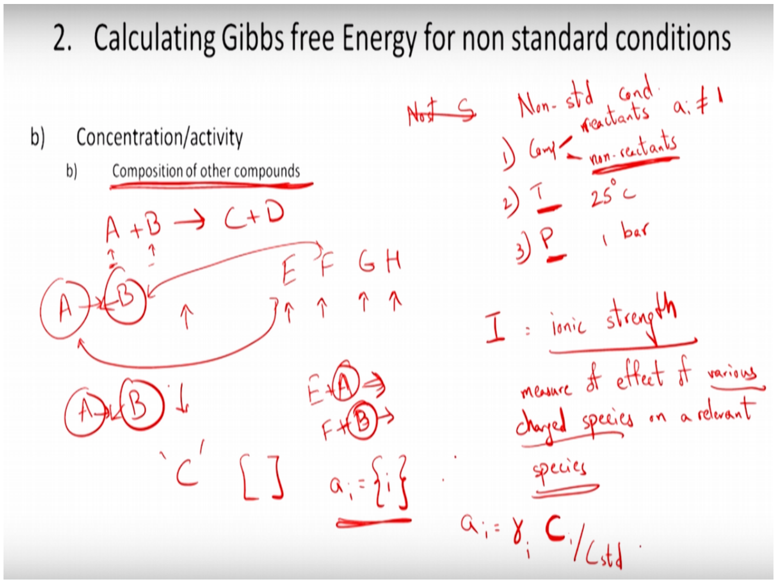

2. Calculating Gibbs free Energy for non standard conditions

b) Concentration/activity

b) Composition of other compounds

So what you have been looking at in the last class I believe we are trying to calculate the change in Gibbs energy right and that too for non-standard conditions for non-standard conditions is and so there are three aspects we have consider in that what are they the composition temperature and pressure so in the last class we talked about composition with respect to reactants.

So do we go about calculating the real two variables relevant variable when your activity of component is not equal to 1 right. So today we are going to continue talking about the non-reactance what will be effect of the composition of the non-reactance or the concentration of the non-reactance or our relevant reactions or the relevant variables and also the effects of temperature and pressure when they are either 25 degree centigrade or 1 bar right.

So let us move on I guess so again as we discuss here if we have A + B reacting to form C + D and let us say you also have V, F, G and H in your system. So how do reactions proceed I guess when molecule A collides with molecule B that when your reaction proceed right. So in general the greater then concentration of your what do we say molecules reactants pardon me the greater the chances of your reaction going through.

But in this case let us say when we are talking about composition of other compounds right especially ionic compounds charge (()) (02:20) and let us say your concentration of charge species is relatively high then they are going to have their own interactions right with relevant reactants right yes and so the let us say the probability of what do we say A reacting or colliding with B would decrease.

So in general the higher the composition of the other compounds right you are going to have what do we say a detrimental effect on your particular reactions right these are the composition just need not been reacting with A or F reacting with D right just due to the charge itself relevant interactions due to charge species on your reactants you can have detrimental effects. Since we are going to look at what it is that they are right.

So obviously we are going to calculate what do we say variable and that is going to be equal to R (()) (03:21) right and so what will this give you an idea about this let us say. It is going to give and idea about a measure of I believe effect of various charge species various charged species on relevant species more or less what is the effect of non-reactants on your reactions or your reactants right.

So before we go further in this case obviously we cannot concentration right concentration again which we said the use the square bracket is to look at that. So we say that we are going to look at a new term called activity may be most probably most of you have not yet come across it. Say activity of your particular component so we are going to look at what it is and how that is going to be equated to your concentration let us see right.

So activity of any compound I would be equal to an activity coefficient right times the concentration of the dimensionless concentration. So make the dimensionless we are going to divide your concentration of the compound by the standard concentration.

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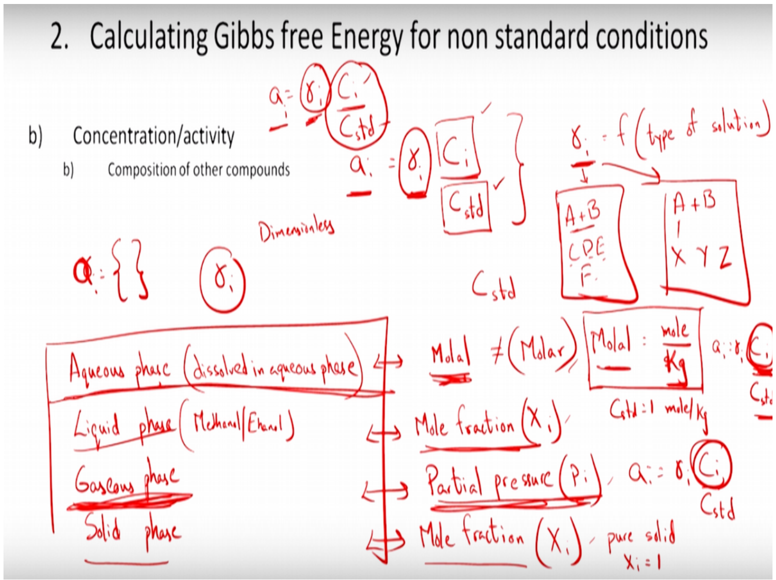

2. Calculating Gibbs free Energy for non standard conditions

b) Concentration/activity

b) Composition of other compounds

So let us look at what we discussed we just defined activity – activity coefficient of that compound or component in particular solution we are going to come back to this into that concentration of that particular component or compound by the standard concentration. In general activity is dimensionless activity is dimensionless right so concentration of the particular compound or component you will have that you know and standard concentration you are going to define such a way that you know this variable is going to dimensionless.

Again here we have an new term what is this now the activity coefficient so this obviously depends upon or let us say I can I am going to call that as function I guess obviously of the type of solutions so it is changes from one solutions to the other. So thus we need to redefined whenever you know we have a particular solution with different kinds of species. For example let us say I am looking at A and B reacting and I have C, D, E and F here.

So I am concerned about what are the effects of C, D, E and F you know on this particular reaction here let us see and in another solution let us say A reacting with B and now let us say I have X, Y and Z compounds here. So and so I am concerned about what are the interaction between XA, YB, YA, ZA, ZB and so on. So what i am trying to hammer whom is that this activity coefficient various from solutions to the solutions to solution right.

So in general again we need to talk about the four phases which we usually come across with respect to calculation of this activities will go further into greater (()) (06:45) with respect to activity coefficient later on. So first we are going to discuss activity in bit more detail so in general we look at four phases what are they? We have the aqueous phase so when something is dissolved water let us say and then we have liquid phase.

So for example we have methanol, ethanol and so on various proportions or such right and we have also obviously come to the gaseous phase and then again what else we come across I guess the solid phase so for all these three cases we need to define the standard concentration I guess right. So what is it going for the aqueous phase it is going to be the molal concentration or molal units I guess.

Molal units it is not similar to molar is something different right it is not the same as molal it is going to be the error of 3 or 4 % I believe so what is molal I guess? What do we define molal units you calculate by saying mole per KG molal units mole per liter in general molal units moles of your compound KG of your aqueous or water in this or water I guess right so molal units.

And so obviously whenever you are calculating your activities right so activity of I = activity coefficient into CI for the CI needs to be in molal units and obviously C standard is going to be defined as what do we say C standard = 1 in molal units mole per KG and thus you are going to have a dimensionless value here right. So again moving on to the liquid phase we are going to have a term called mole fraction.

Fraction of moles to your component to the total number of moles here going to have fraction of moles right and mole fraction is your relevant aspect or relevant what do we say unit you are going to look at here and again gaseous phase we are going have partial pressure and that you know that you relate to that to again to what is now the mole fraction so on.

And again the units of CI no when you write down CI / C standard right the units need in terms of mole fraction whenever you are looking at concentration or reaction in the gaseous phase right. And again coming back to the solid phase we again look at mole fraction again mole number of moles of your solids by total number of moles of the other solid into 1 right. So these are aspects that we need to keep in mind but in general most of our lives at least not lives pardon me it is in engineering system we usually come across the aqueous phase.

So keep in mind that you need to look the molal concentration when you write that and in the gaseous space which is something that we come across usually so you need to define your concentration in terms of the partial pressure this is the take home message here. So now we are going to move back to your activity coefficient or how to calculate activity coefficient. So we are trying to calculate activity here right.

And for that we just looked at how to calculate this particular this C standard = 1 for this difference kinds of what do we say concentration units we just discussed and CI you need to obviously define that in molal units if it is aqueous phase in mole fraction if it is liquid phase in partial pressure if it is liquid phase again in mole fraction if it is a solid phase right. So the next variable that we are going to look at it calculation of your ahh activity coefficient.

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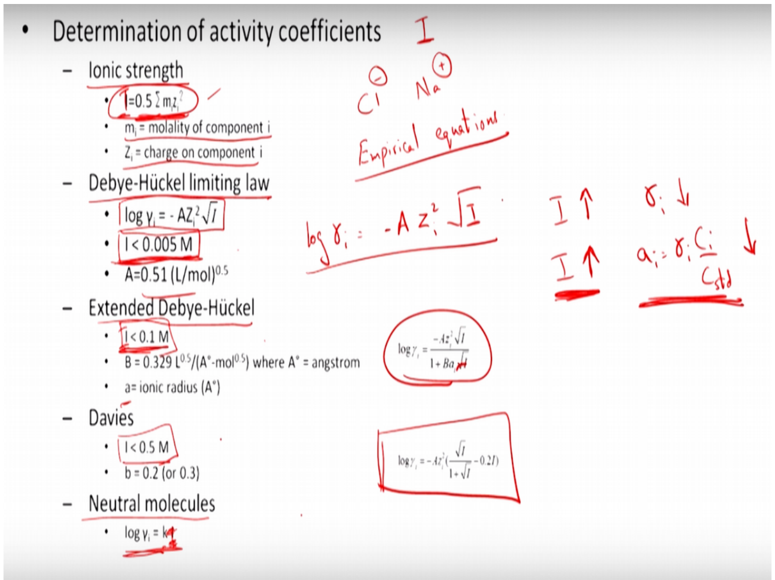

- Determination of activity coefficients
  - Ionic strength
    - $I=0.5\sum m_i z_i^2$
    - m_i = molality of component i
    - Z_i = charge on component i
  - Debye-Hückel limiting law
    - $\log \gamma_i = -AZ_i^2\sqrt{I}$
    - $I < 0.005$ M
    - $A=0.51\ (L/mol)^{0.5}$
  - Extended Debye-Hückel
    - $I < 0.1$ M
    - $B = 0.329\ L^{0.5}/(A^\circ\text{-}mol^{0.5})$ where A° = angstrom
    - a= ionic radius (A°)
  - Davies
    - $I < 0.5$ M
    - b = 0.2 (or 0.3)
  - Neutral molecules
    - $\log \gamma_i = kI$

$$\log \gamma_i = \frac{-Az_i^2\sqrt{I}}{1+Ba\sqrt{I}}$$

$$\log \gamma_i = -Az_i^2\left(\frac{\sqrt{I}}{1+\sqrt{I}}-0.2I\right)$$

So moving on to the next slide it is activity coefficient as we just discussed earlier it is going to be depend upon your ionic strength. So let us look at that particular value here ionic strength I I guess here we have the relevant terms 0.5 into summation of MI into ZS square MI is the morality of the particular component ZI is the charge on your component right the charge on your component right or the charge.

And here you can end up calculating the ionic strength so once you calculate the ionic strength then they are difference empirical equations so we are going to look at that obviously you do no need to mug them up so I think the most usual usually used law is the Debye Huckel limiting Law but keep in mind this is only applicable when the ionic strength less than 5 into 10 per – 3 molar right or 5 milli molar.

So let us look at what we have here so we have log gamma I = -A constant here I guess charge square into square root of I right. So what do you see here as ionic strength increases right I believe the activity coefficient decreases yes that is what you see here and so what is this mean now as you ionic strength increases where activity which is = gamma I into CI / C standard that also decreases.

So that is what you see now so right as a ionic strength which will give an idea about the various charge species your particular solutions as they increase the activity or the ability of your particular compound or component to decrease to react will decrease so that is what you see here so obviously it limited to ionic strength is less than 1005 molar so let us look at the other thresholds.

So other threshold is with respective of the ionic strength is being less than molar right and here we have the extended Debye Huckel. So again more or less another empirical equation here you do not need to mug this up they will be available in lots of textbooks. So again we have ionic radios and those variables here am not going to go into the greater detail so depending upon ionic strength is we are use this relevant what do we say empirical equations.

So again ionic strength is less than 0.5 molar though we have another empirical equation here yes and that is what you see here. And believe lastly for neutral molecules to you are going to have an effect right and that is what you see here log gamma = K which is a constant believe and times the ionic strength here. What is the effect of ionic strength and the neutral molecules to so that is what you see here.

Again different what do we say threshold with respect to ionic strength right and so once we calculate the ionic strength then choose which particular log to use and so on right okay let us move on.

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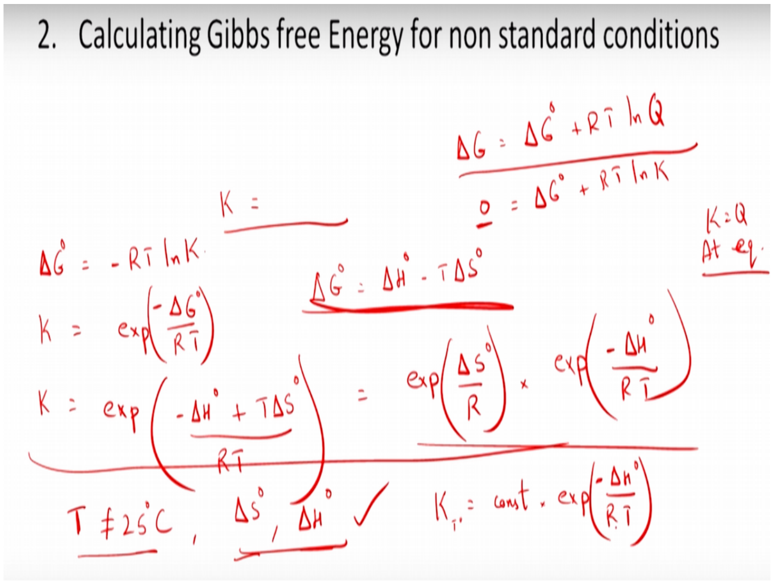

2. Calculating Gibbs free Energy for non standard conditions

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

$$0 = \Delta G^{\circ} + RT \ln K$$

$K = Q$ At eq.

$K =$

$$\Delta G^{\circ} = -RT \ln K$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$K = \exp\left(\frac{-\Delta G^{\circ}}{RT}\right)$$

$$K = \exp\left(\frac{-\Delta H^{\circ} + T\Delta S^{\circ}}{RT}\right) = \exp\left(\frac{\Delta S^{\circ}}{R}\right) \times \exp\left(\frac{-\Delta H^{\circ}}{RT}\right)$$

$T \neq 25^{\circ}C$, ΔS°, ΔH° ✓ $K_{T'} = \text{const} \cdot \exp\left(\frac{-\Delta H^{\circ}}{RT}\right)$

So looks like we are going to now move on the aspect where the temperature is no more equal to 25 degrees centigrade. So until no we have discussed composition of both the reactants and the non-reactants right and we have done with both two aspects and we going to move on the next aspects when temperature is no more equal to 25 degrees centigrade right and how do we calculate the relevant values right of the equilibrium coefficient of the delta G values.

So I will start from a fresh page right so for temperature I guess here we need to look at the original equation that we developed so let us see what is K – I guess so I think let me go back to delta G = delta G naught + RT natural logarithm of Q and just trying to recalculate between the K and delta G naught and so if this system is at equilibrium = 0 or delta G obviously 0 delta G naught + RT natural logarithm of K.

And K = Q at equilibrium which is something we discussed in the previous class right so now we have K being = what naught or delta G naught = - RT natural logarithm of K and that translates K = exponential of delta G naught – delta G naught by RT right and here we will go back to the initial concept that we are aware off delta G naught is obviously = change in enthalpy and change in entropy relevant equation here.

So let us try to plug thus here so the K equilibrium coefficient = exponential of what now – delta H naught right + T delta S naught / RT is and that could be equal to exponential of what is it please delta S naught / R into exponential of – delta H naught by RT so this is a equation that we have here right. So let us keep this in mind here and so here we are going to proceed with one assumption that even if the temperature is not at the standard condition of 25 degree centigrade we can assume that we are assuming that delta S naught and delta H naught are not going to change.

And this you know in general we are going to look at it the error associated with the assumption is relatively minimal and we can go through with this as a assumption and what are we assuming again delta S naught and delta H naught do not change when we change the temperature I guess. So does this particular equation transform into so K will be equal to a constant of KT naught let us say = constant into exponential of – delta H naught by RT right so that is what we have here.

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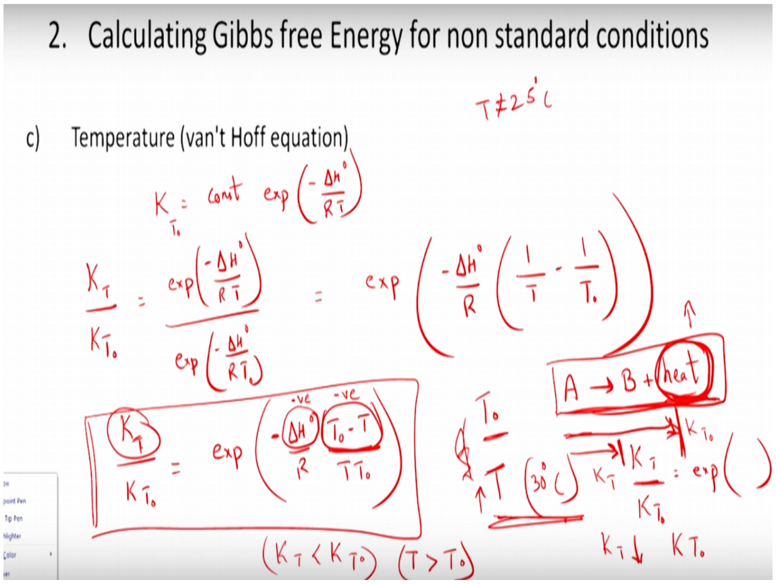

2. Calculating Gibbs free Energy for non standard conditions

$T \neq 25^\circ C$

c) Temperature (van't Hoff equation)

$$K_{T_0} = \text{const} \exp\left(-\frac{\Delta H^\circ}{RT}\right)$$

$$\frac{K_T}{K_{T_0}} = \frac{\exp\left(-\frac{\Delta H^\circ}{RT}\right)}{\exp\left(-\frac{\Delta H^\circ}{RT_0}\right)} = \exp\left(-\frac{\Delta H^\circ}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)$$

$$\boxed{\frac{K_T}{K_{T_0}} = \exp\left(\frac{-\Delta H^\circ}{R}\,\frac{T_0 - T}{T T_0}\right)}$$

-ve -ve

$(K_T < K_{T_0})$ $(T > T_0)$

$A \rightarrow B + \text{heat}$

T_0

$\uparrow T$ $(30^\circ C)$ K_T K_{T_0}

$$\frac{K_T}{K_{T_0}} = \exp(\;)$$

$K_T \downarrow$ K_{T_0}

So let us take this on to the next page in this page itself I will try to work this out please and what do we just have we had I believe let me recall that K = constant KT naught = constant and exponential – delta H naught / RT right. So now if I want to look at the change right when temperature is no more 25 degree centigrade right so I can look at the ratio of K by temperature T which is not at standard condition by KT naught.

So that is equal to constant cancel out exponentials of what now exponential of – delta H naught by RT / exponential – delta H naught / RT naught right. So what will that translate into now exponential of so if I take out – delta H naught by R has been common so that is going to be 1 / T

– 1 / T naught I believe right so that if we simplify further hopefully what do we end of with I guess KT / KY naught = what now exponential of – delta H naught / RT naught / T / TT naught right and this is what we have here right.

So now let us try to understand the system so this is the final equation that we are looking at right so let us try to look at the case what would happen let us say we have an exothermic reaction as an A goes to B + heat this is what you can what do we say represent the exothermic reaction as. So for this case let us say that we are increasing in temperature so let us say this can go through at the standard condition and also at a temperature let us say we are talking that to be 30 degrees or 40 degrees centigrade and so on.

So what is the effect going to be on delta G or your KT now so we take a moment plug this in and look that up I guess. So here we have two aspects to consider so T naught – T is now going to be a negative value right because we increase the temperature here and we also know it is exothermic reactions delta H naught is also negative right. So we are going to end up with KT / KT naught as being exponential of so on the relevant terms.

So it is going to decrease right so that is what you are going to see here as you increase the temperature compare to the standard conditions you see that the KT is going to decrease KT compare to KT naught. So I guess how do you understand this system now right let us again take a quick look at what we just had so this is our equation KT / KT naught = exponential of so on.

And so on we looked at a specific example of a exothermic reaction A + B going to heat right and we saw that we put at or you know plugged in the values KT is going to be less than KT naught when T is greater than T naught right this is not we observed. So let us try to apply that what we see here so think of this now so let us say at standard condition A goes to B + heat and you increase the temperature what does that more or less translates into.

It translates into U providing more of the product right you can let us say approximate that visualize that of product now. So if you increasing the heat content of the temperature right compared to the standard conditions so what does this mean you have more of your products initially now. So reaction would not for example let us say if the reaction go to can go to this extent though right but not because if you are increasing or temperature or your part here the equilibrium is going to shift towards the left and it is not going to go to the previous value.

So this is let us say KT naught and let us say this is KT if I guess I am writing over writing too much let us again look this up.

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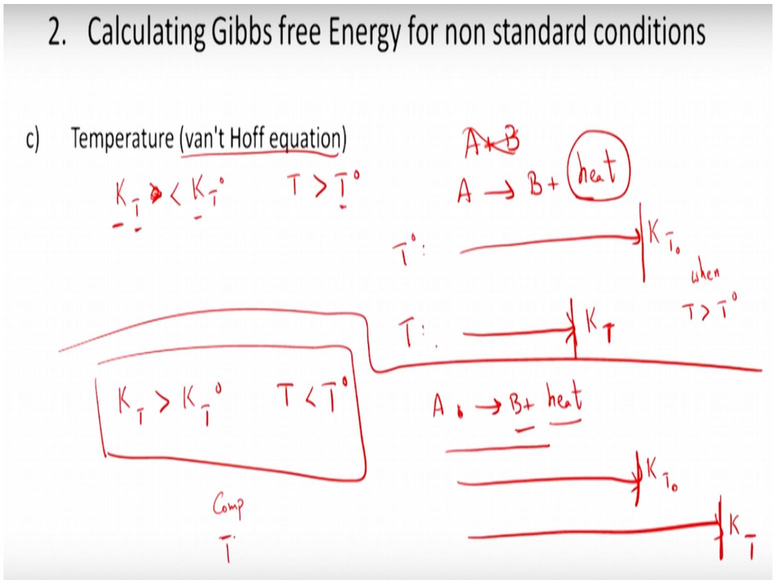

2. Calculating Gibbs free Energy for non standard conditions

c) Temperature (van't Hoff equation)

So here we said that KT will be greater than pardon me less than KT naught when temperature is greater than T naught what are this K please what are the K equilibrium coefficient T is that higher temperature of that T naught which is 25 degree centigrade and what example do we used though I guess for a exothermic reaction. So what does this mean so at T naught condition let us say for example the aquarium can proceed till this extent let us see right and this is my KT naught let us see.

But because if I am providing or you know increase in the temperature to T or what is that translating to in this exothermic reaction and already providing some of the product here let us say. So the reaction would not proceed to that particular extent is going to shift the equilibrium is going to shift to left so it is going to stop you know laymen’s terms so this is for your ahh purposes of understanding and that is the Van’t H off equation is guess.

But obviously the (()) (23:39) when K or when T is less than T naught what will that mean though KT will be greater than KT naught right. So what is going to happen here again let us look at this particular reaction A goes to B + heat so now let us say in depth of your products right the temperature is lesser so instead of it going till KT naught now your KT is going to move to your equilibrium is going to shift to the right.

Because now have lesser temperature so that is what it would translate into so here now we are going to have KT greater than your KT naught and the equilibrium is going to shift to the right. So obviously if it is an endothermic reaction you can do the relevant calculations and check accordingly right so we are done with composition and we are done with temperature so now we are going to move on to pressure i guess.

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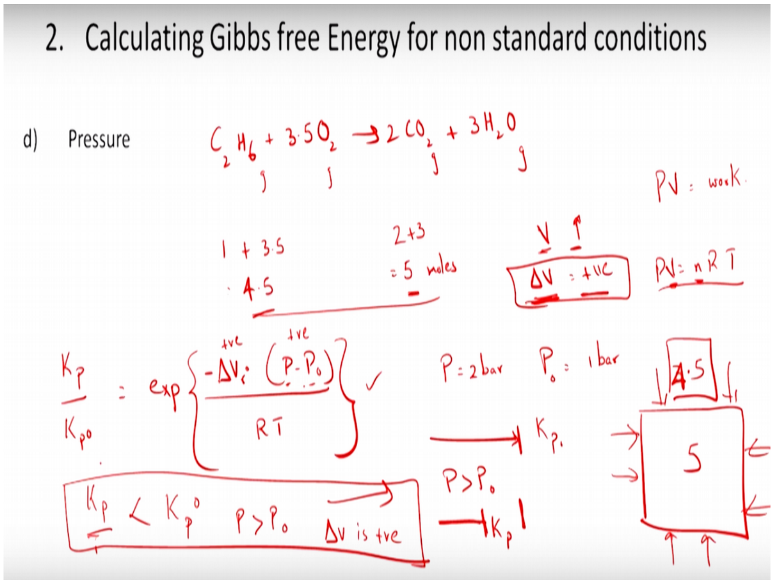

2. Calculating Gibbs free Energy for non standard conditions

d) Pressure

$C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O$

$1 + 3.5 = 4.5$

$2+3 = 5$ moles

$V \uparrow$

$\boxed{\Delta V = +ve}$

$PV = $ work

$PV = nRT$

$$\frac{K_p}{K_{p0}} = \exp\left\{\frac{-\Delta V_i \cdot (P - P_0)}{RT}\right\}$$

$P = 2$ bar $P_0 = 1$ bar

$\longrightarrow K_p$

$P > P_0$

$\longrightarrow K_p \downarrow$

$\boxed{K_p < K_p^0 \quad P > P_0 \quad \Delta V \text{ is +ve}}$

So let me look up the relevant equation that I have here so we are going to look at this particular equation C2 H6 + 3.5 O2 goes to 2CO2 + 3H2O right. So in general here we assume that all are gases everything is in the gaseous phase and what are the moles here initially we have 1 + 3.5 and that is = 4.5 moles and we end up with that is equal to 5 moles right.

So what does it mean? It means that the volume has increased or delta V is positive yes in general any change in increase in volume means PV means OR right so work needs to be done yes and PV = NRT you know one mole of any particular compound will occupy the same volume now right. Anyway keep that in mind that is why as the moles are increasing PV = NRT we know that volume is also going to increase delta V is going to be positive.

So rather than going to the same derivation again similar to the KT / KT naught here we can come up with KP / K naught = exponential of – delta VR naught into P – P naught / RT right. So here we are trying to look at what is the effect on your equilibrium coefficient when your change in pressure so pressure at standard conditions is 1 bar and let us say we are increase in the pressure now to two bars let us say.

So how it is going to change we can first we will later on look at the equation so first let us try to understand the equation system let us say here you are trying to change your volume by increasing it right. So let us say now earlier you had 3.5 moles and now you are ending up with 3.5 pardon me earlier and now you are ending up with 5 moles now so the volume is increasing right.

But let us say compare with the standard conditions you are increasing the pressure so earlier it was one bar now let us say its two bar now. So as you know the pressure would increase the pressure would restrict the change in this particular volume or increase in volume so what does its mean though. So earlier let us say if you are KP naught is to this extent right but because you are increasing the pressure because P is greater than P naught the reaction would not go to that particular extent but is at equilibrium is going to shift to the left right.

So you are going to have an equilibrium its sooner compare to KP naught hopefully that makes sense right. So again let us try to apply that to your equation and let us see if you set to the same conclusion now. So here we have P – P naught P is greater than P naught that means this term is positive right and delta V naught we know that delta V in this case especially when the volume is not especially when the volume is increasing is positive.

So when you end up increase in the pressure over the standard condition of 1 bar we see that KP and being less than KP naught and this is what we just discussed now right. So when T is greater than P naught and the case is that delta V is positive right. So this is your take home message right so with that am going to end today session so we will have a quick review though so what have you looked at so far and before what have you looked at today's class I guess.

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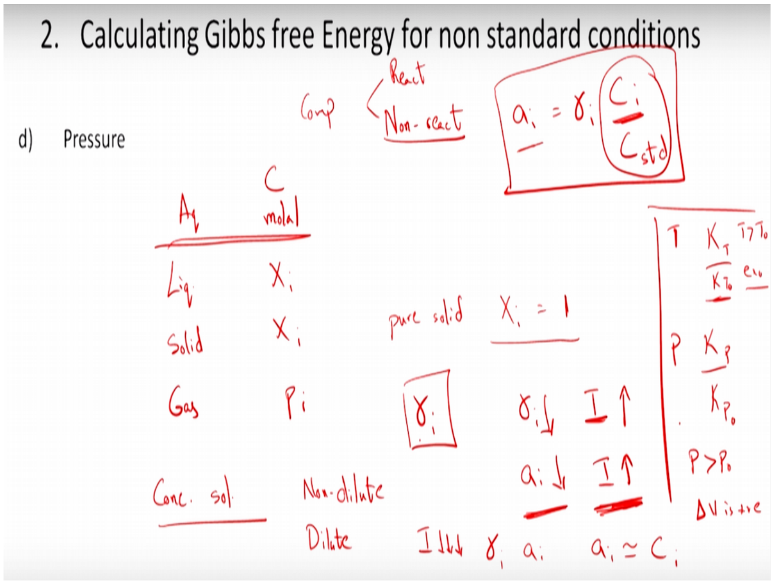

2. Calculating Gibbs free Energy for non standard conditions

d) Pressure

Right we looked at I believe non reactants in the earlier class we looked at reactants and today we looked at non reactants I came across the terms of activity = activity coefficient into the dimensions less concentration so for that we define different what do we say units of concentration for different phases and what are the phases I guess for aqueous phases I said the concentration units need to be molar right and what next liquid phase let us say we said the units had to be mole fraction right number of moles of your particular components by the total moles.

And same case with the solid phase we are again going to look at mole fraction but for the gaseous phase we are going to look at the partial pressure right. So what is that mean whenever you are calculating activity let us say it is in gaseous phase we need to use the partial pressures there right. So again obviously I guess just for your understanding let us say if it is pure solid there are only one solid that precipitate out what is the mole fraction going to be equal to 1 right.

There is only pure solid or only one solid now so this is what we have discussed and then looked at various empirical equations to calculate gamma I right and we saw that it is not proportional I guess inversely proportional to ionic strength as we increase the ionic strength I guess the gamma I decreases right and in effect means the activity of your compound decreases as the ionic strength decreases.

What is this mean? So when you have more of your non reactance present the ability of your compound to react decreases. So if you are look at in the aqueous phase what does this mean so when you had concentrated solutions let us say concerned solution which are non-dilute. So in this cases we need to be remarkably careful to be able to look at the activity of your compounds.

But obviously if these are dilute system when your ionic strength is very low right you do not need to look at what do we say activity coefficient or calculating activities you can approximate activity as C = concentration right. So this is something we need to look at in mine and then I believe we looked at the effect of temperature effect of pressure on the equilibrium coefficient and so on.

And then we looked at KT / KT naught and KT / KT naught we looked at two examples when I guess what we look at when T is greater than T naught for an exothermic reaction which looked at what the effects are and when T is greater than P naught when delta V is positive what are the effects so this is what we looked at in today session and I believe I am done for this session thank you.