

Engineering Thermodynamics
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Lecture – 54

Phase and Chemical Equilibrium: Equilibrium constant. Phase equilibrium.

This is the 2nd lecture on Chemical and Phase Equilibrium. In the 1st lecture, we derived a criteria for chemical equilibrium and came across the notion of the equilibrium constant. In this lecture, we will take the idea of equilibrium constant further and see what its implications are, then we will examine what the equilibrium constant depends on and how it influences systems.

That will bring us to the end of chemical equilibrium after which we will move on to phase equilibrium.

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STANDARD STATE GIBBS FUNCTION CHANGE

$$\Delta G_T^\circ = \sum_{j \in P} (\nu_j \bar{g}_{j,T}^\circ) - \sum_{i \in R} (\nu_i \bar{g}_{i,T}^\circ) \quad \Delta G_{mix,T}^\circ$$

$$\Delta G^\circ(T) \quad \text{or} \quad = \sum_{j \in P} (\nu_j \bar{g}_{j,T}^\circ) - \sum_{i \in R} (\nu_i \bar{g}_{i,T}^\circ)$$

Define

Equilibrium constant, K_p

$$K_p \equiv \frac{\left(\frac{p_C}{p^\circ}\right)^{\nu_C} \cdot \left(\frac{p_D}{p^\circ}\right)^{\nu_D} \dots}{\left(\frac{p_A}{p^\circ}\right)^{\nu_A} \cdot \left(\frac{p_B}{p^\circ}\right)^{\nu_B} \dots}$$

\leftarrow Products
 \leftarrow Reactants

A
B
C
D

$T, p.$

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So, to recap the derived equilibrium constant as K_p which is a product of the partial pressure of the reactants, the product species to the standard pressure, raised to the power stoichiometric coefficient. So, C D E F all this would be product species and in the denominator would be A B C D which are the reactant species and this is for a mixture where all these species are present together. So, we say that if I have a mixture like this in which I have some A, some B, some C and some D, then this tells you what is the equilibrium constant for this particular system which is at a temperature T and P.

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$K_p :$
 $p_i = y_i \cdot p = \frac{N_i}{N_{\text{mix}}} p$

$K_p = \frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} \cdot \left(\frac{p}{N_{\text{mix}}} \right)^{\Delta \nu}$

$K_p = \frac{y_C^{\nu_C} \cdot y_D^{\nu_D}}{y_A^{\nu_A} \cdot y_B^{\nu_B}} \cdot \left(\frac{p}{p^\circ} \right)^{\Delta \nu}$

$\Delta \nu = \sum_{j=P} \nu_j - \sum_{i=R} \nu_i$

p : system total pressure
 p° : standard state pressure

Now, we rewrite this constant the equilibrium constant define that p_i is y_i into p or in the partial pressure y_i is the molar fraction N_i by N_{mix} which is the total number of moles in the mixture.

So, either we can write mix or we can write total. So, K_p then becomes the molar, the number of moles of each species to the power of its stoichiometric coefficient. The reactants are the products are in the numerator, reactants are in the denominator multiplied by p upon N_{mix} . N_{mix} as we have saying is total this whole thing raised to the power $\Delta \nu$. $\Delta \nu$ is ν_C plus ν_D like that for the products minus ν_A minus ν_B for the reactants.

So, in a summation form $\Delta \nu$ is summation of the number of the stoichiometric coefficients of each of the product species minus sum of the stoichiometric coefficients of the reactant species. So, it is this minus one can call this as this. So, this is rewritten again as y_C to the ν_C into y_D to the power ν_D . Similarly for the products multiplied by p over p° to the power $\Delta \nu$ remember p is the system pressure total pressure and p° is the standard state pressure. So, we have two more expressions coming up from our earlier definition of the reaction, the equilibrium constant. One could be in terms of the moles and the other in terms of the mole fractions. They are all equivalent as long as the substance in gaseous state.

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EQUILIBRIUM CONSTANT, K_p

∴ chemical eqm at constant T and p is

$$\Delta G_T^\circ = -R_u T \ln K_p \quad \Delta G^\circ(T)$$

or $K_p = \exp\left(-\frac{\Delta G_T^\circ}{R_u T}\right)$

Also, $\Delta G_T^\circ = \Delta H^\circ - T\Delta S^\circ$

$$\Rightarrow K_p = \exp\left(-\frac{\Delta H^\circ}{R_u T}\right) \cdot \exp\left(\frac{\Delta S^\circ}{R}\right)$$

$K_p > 1$ i.e. $R \rightarrow P \Rightarrow \Delta H^\circ < 0$ i.e. exothermic reactions.

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Now, we put this expression back in the relation that we had. Now, delta G 0 becomes minus RuT ln kp where that it was this big expression over there in this equations there.

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$$\sum (dn_i \cdot g_i(T)) + \sum (N_i dg_i(T)) = 0$$

$$d(\ln p_i) = \frac{dp_i}{p_i} \quad \& \quad \sum dp_i = 0$$

Total pressure constant

$$dG_{mix,T} = 0 = \sum_i dn_i \left[g_i^\circ(T) + R_u T \ln\left(\frac{p_i}{p^\circ}\right) \right]$$

$$dn_i = \nu_i \sum_j \nu_j \quad \begin{array}{l} -\nu_j \text{ for } R \\ +\nu_j \text{ for } P \end{array}$$

$$-\sum_R \nu_i \cdot g_i^\circ(T) + \sum_P \nu_i \cdot g_i^\circ(T) = R_u T \ln \left[\frac{(p_1/p^\circ)^{\nu_1} \dots (p_P/p^\circ)^{\nu_P}}{(p_R/p^\circ)^{\nu_R} \dots (p_Q/p^\circ)^{\nu_Q}} \right]$$

$K_p > 1$ i.e. $R \rightarrow P \Rightarrow \Delta H^\circ < 0$ i.e. exothermic reactions.

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This is what we had. All of this was RuT ln all of this which was d G mix T. So, now we know that this whole thing it become K p and our expression becomes much more elegant. The delta g T at 0 or you can even some cases we write this as delta g 0 at temperature T is minus RuT ln kp. So, we now get a new expression that K p can be

expressed; the equilibrium constant as exponential of minus delta G 0 T upon R u T; R u being the universal gas constant.

This is an important expression in all of reaction, chemical reactions. We can express delta G T 0 as in terms of enthalpy and entropy and then K p is exponential minus delta h 0 upon R u T minus exponential delta s 0 upon T. So, this is get on their expression we get which is same as from there. So, what it tells us is that if K p is greater than 1, that means reactants are headed towards becoming products. This implies that delta h 0 is less than 0 which means that the reaction is exothermic. So, this is the type of implications that we can see from this expression.

Now, we will look at K p in more depth and the case of ideal gas mixtures.

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* partial pressures:

$$K_p = \frac{\left(\frac{p_C}{P^0}\right)^{\nu_C} \left(\frac{p_D}{P^0}\right)^{\nu_D}}{\left(\frac{p_A}{P^0}\right)^{\nu_A} \left(\frac{p_B}{P^0}\right)^{\nu_B}}$$

molar fractions

$$= \frac{P^{\nu_C + \nu_D - \nu_A - \nu_B}}{P^{\nu_A + \nu_B}} \left(\frac{P}{P^0}\right)^{\Delta z}$$

$\Delta z = \nu_C + \nu_D - \nu_A - \nu_B$

* Standard state Gibbs functions.

$$K_p = e^{\left(-\frac{\Delta G^0(T)}{RkT}\right)}$$

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So, what we have is that K p could be expressed as partial pressures in terms of partial pressures. So, all of that is done or in terms of the molar fractions that not rewrite this expression. We already have these before us and that K p can also we have written in terms of the standard state Gibbs function as K p is equal to e to the power minus delta z 0 T upon R u T. This is the same expression that we are got earlier.

So, the two ways in which we are able to express K p once as partial pressures or in molar fractions or as standard state Gibbs function. What it tells us that if we know delta G 0 T from thermodynamic data, we can calculate K p or here if you know partial

pressures of the molar fractions, then we can get K_p . So, the two different ways that take us to the value of K_p .

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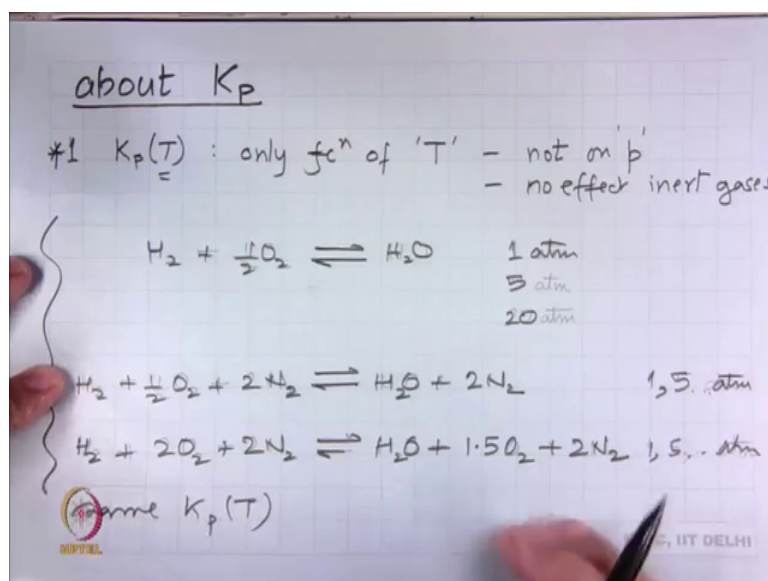
K_p
* in moles

$$K_p = \frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} \left(\frac{p}{N_{TOTAL}} \right)^{\Delta \nu}$$

And the third one in terms of moles that K_p was N_C to the power ν_C ; N_D to the power ν_D upon N_A to the power ν_A and N_B to the power ν_B multiplied by p upon N_{total} to the power $\Delta \nu$.

Now, what we will do is we look at these expressions and say what can we interpret from them.

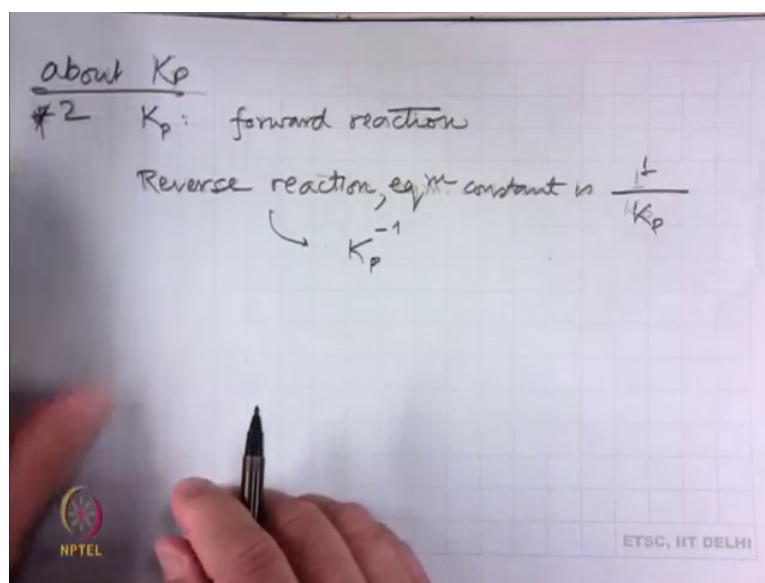
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So, the several characteristics of this K_p that we will come out that first K_p which is a function which is unique value at every temperature is not only a function of T is only a function of temperature and is not a function of pressure. So, in expression like this H_2 plus O_2 ; H_2 plus half O_2 equilibrium at this is same at 1 atmosphere, 5 atmosphere or 20 atmospheres. Then in this expression if we added inert gas like nitrogen, then also the K_p value does not change and it does not matter whether this mixture is at 1, 5 or any other pressure.

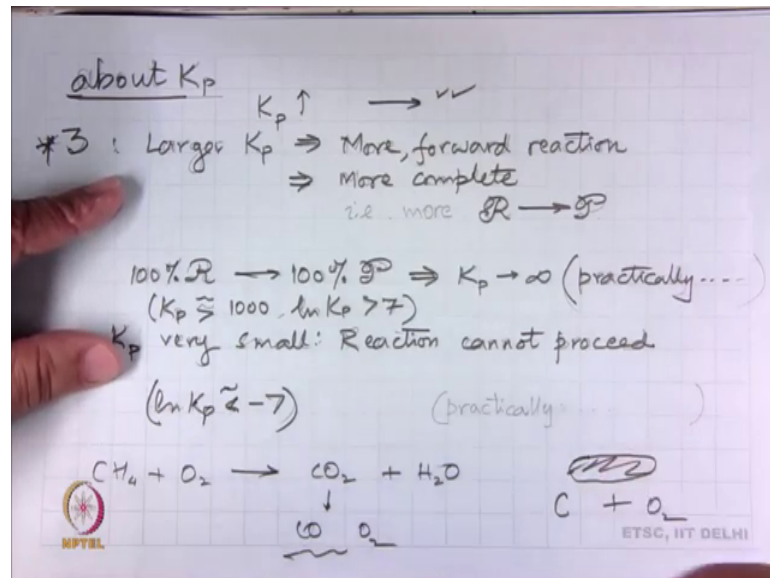
And even if this is expression if the in this particular case where H_2 and O_2 are in the elemental states H_2 plus $2 O_2$ plus $2 N_2$ living an excess of oxygen on the right side; in the products this also at any pressure, then all these reactions at any pressure they have the same K_p T . So, this is one characteristic about K_p .

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The second thing is that K_p as we have defined is the equilibrium constant that comes from the forward reaction. For the reverse reaction everything is just instead of left to right, right to left the equilibrium constant for the reverse reaction is 1 upon K_p . So, the reverse reaction equilibrium constant is K_p to the power minus 1 .

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Then the third thing about K_p is that as K_p is large or is big or greater or increasing; the forward reaction we will go to a large extent. So, larger the value of K_p this implies more forward, more of the forward reaction will take place and which tells us basically that the reaction will proceed more towards completion. The reaction will become more complete that is more of the reactants become more of the products.

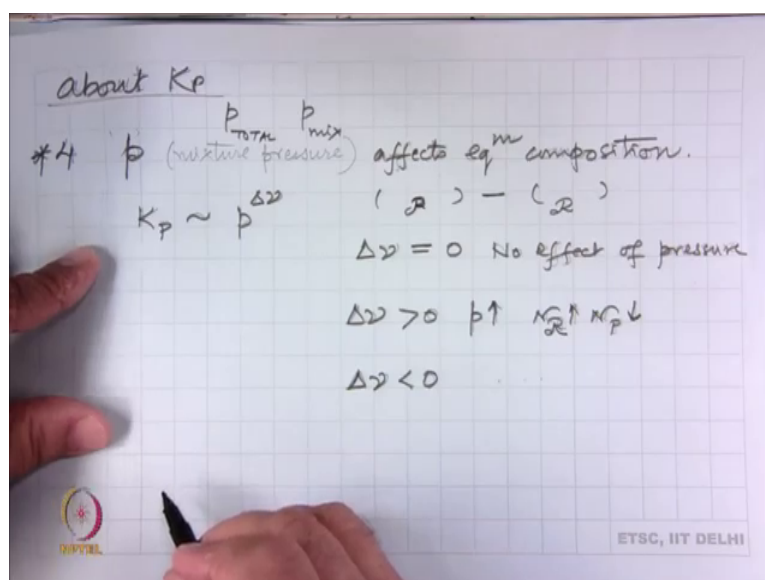
If you want 100 percent of the reactants to become 100 percent of the products which basically would require that K_p should tend to infinity which means that in some cases we say that it reaches pretty much there, but not exactly there. So, it never exactly goes there. For example, if you are always looking at methane burning and we always said that this always produces CO_2 plus H_2O under the reverse did not happen, in practical situations earlier we would say that yeah this is what happens when we are worried about emissions where we have to worry about the fact that some of this could get decomposed and form CO and O_2 and so, the exhaust or the emissions would include carbon monoxide.

So, K_p although it has gone to a very large extent in burning out all the fuel, this is always a very small amount which is still not completely is burned. So, what you are saying is that if K_p is of the order of or greater than 1000; which says that $\ln K_p$ is more than 7, then we can say that practically almost all the reactants are converted into products. On the other hand if K_p is very small, the equilibrium constant is very small. It

means that the reaction cannot proceed and it is the opposite of this that if $\ln K_p$ is of less than of the order of minus 7, then we say that practically the reverse reaction will not happen. The reaction itself will not happen.

So, this could be an example that we just take a piece of say carbon and keep it in atmosphere and we say look I have carbon, I have oxygen in the atmosphere is this reaction taking place, but the answer is yes because of K_p being very very small, this reaction is produce the equilibrium which is very small and it is not going to be proceedings much faster than this.

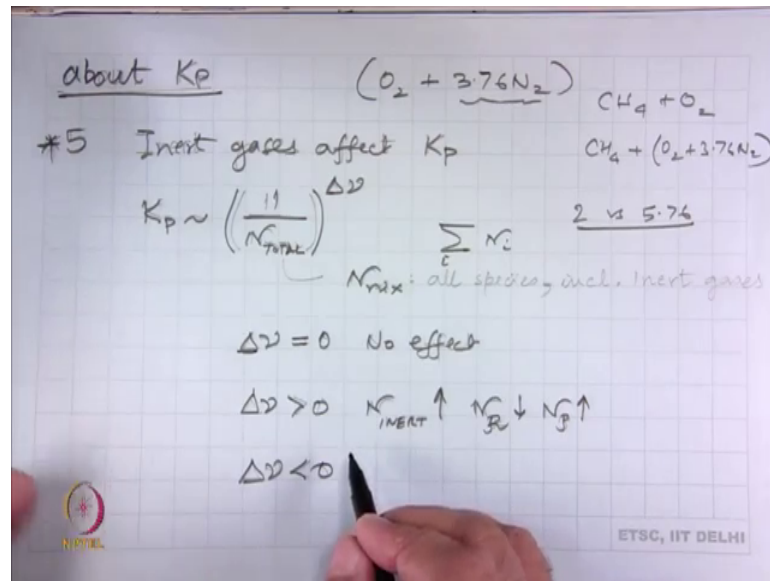
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Then the four thing about the equilibrium constant that the pressure of the mixture that is p total or p mix; this affects the equilibrium composition. And that is because in these expressions that we have derived K_p is the function of p to the power Δn . Δn you recall is the sum of the stoichiometric coefficients of the products minus sum of the stoichiometric coefficients of the reactants.

If Δn is 0 or very close to 0 or very small, then pressure does not affect K_p . So, there is no effect of K_p , but if Δn is greater than 0, that means more moles are being added. That means, number of reacted moles is going up and number of product will go down. So, as pressure increases, more products will be formed and less is more reactants will be there and less products will be there. Opposite is the case when Δn is less than 0.

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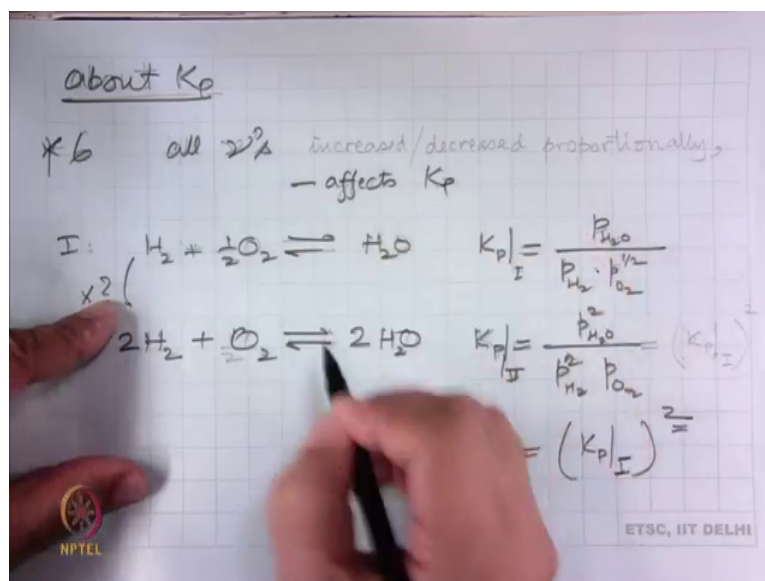


Now, we are looking at the effect of inert gases and this is of interest because air as the oxidant is always got very large amounts of nitrogen which for practical purposes we treat this as an inert gas. So, if you have burning CH_4 plus O_2 what will how will it be different from $CH_4 + O_2 + 3.76 N_2$?

This is the question that before us and what we say is that inert gases affect the value of the equilibrium constant. Why so? Because we seen earlier in the expression that we have K_p is proportional to $1/N$, the total number of moles in the mixture; so this is nothing, but N_{mix} which is summation of N_i for all the species that are there in the mixture. Now when you have only this, you have 1 plus 1.2 moles where you have this. You have 1 plus 1.2 plus 3.76; 5.76 moles. Earlier you had 2 and now you have 5.76. So, this is what is changing.

And in what will happen in this case? Is it is raised to the power of the same $\Delta \nu$, the difference in reactant and product stoichiometric coefficients; if $\Delta \nu$ is equal to 0, the presence of inert gas has no effect. If $\Delta \nu$ is greater than 0, then as the number of moles of inert gas is goes up, this comes down and the products moles goes up and the opposite will happen if $\Delta \nu$ is less than 0. So, there is some effect of the inert gas depending on the $\Delta \nu$ factor.

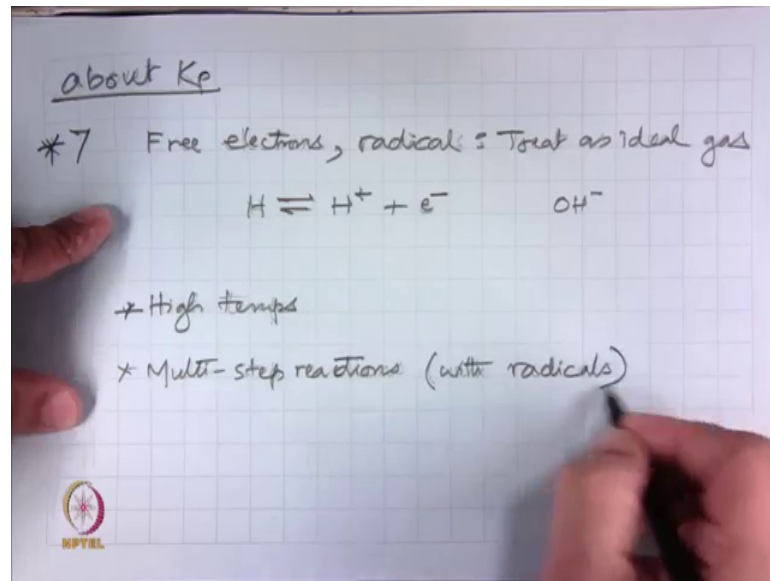
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Then what if we have the same reaction, but written in different moles such as H₂ plus half O₂ going to H₂O, but now we multiply everything by 2. So, this is reaction 1 and we say now the reaction 2 is H₂ plus O₂ goes to 2 H₂O; is the equilibrium constant in both cases

What will happen is K_p for this reaction will be partial pressure of H₂O upon p H₂ and oxygen partial pressure to the half. But in the second case this will be p H₂ O square upon p H₂ square upon p O₂ which is K_p for the first reaction square. So, if you the multiplication factor for the number of moles in the reaction, so this is whatever x into something that shows up as a exponent over here. If it is three times here this will become cube; it is half, this will become half. So, what we have seen is that all nu's are increased or decreased proportionally, then this affects the equilibrium constant p.

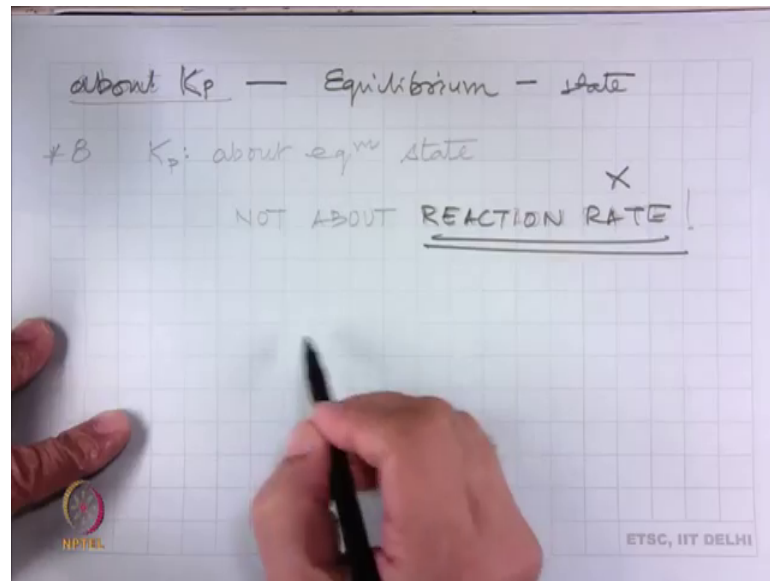
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And then visible what does it applicable to? Because in many chemical reactions there are lot of radicals being formed and in some cases even free electrons. So, of an reaction like H becoming H plus plus e minus or there are radicals like say O H minus radical in a chemical reaction, then free electrons and radicals; if they are present in the reaction, we can treat them just like an ideal gas.

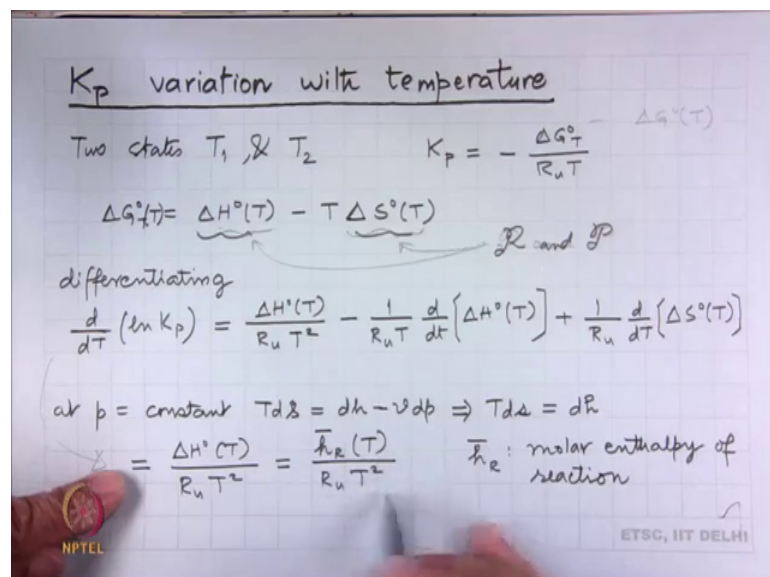
This is particularly the case we have to we cannot ignore this particular type of reactions at high temperatures. For example, when a spacecraft is entering the earth atmosphere or for that matter leaving the earth atmosphere, this is an important situation and in combustion reactions which are all multi step reactions there will be radicals and so we will have to account for it in the same way.

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And last point to note about K_p is that this is only about equilibrium and this is the equilibrium state and it tells us nothing about the reaction rate. So, if you want to ask the question what is the rate at which this reaction will take place, K_p is not the one to tell us what is going to happen. So, we do not know anything about this from K_p , then there are effects of catalysts that we can factor in.

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And finally the fact that K_p depends only on temperature; so question is how does it vary with temperature? So, if you are two states at T_1 and T_2 and K_p defined in the

same way, then we can rewrite this in terms of G , H and $T S$, where this and this are for reactants and the products and differentiating we get this expression and at constant p which we get $T ds$ is equal to dh . This expression becomes \bar{h}_R times $T R$ upon T^2 . \bar{h}_R is the molar enthalpy of reaction. So, we end up getting a nice elegant expression from here.

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van't Hoff equation

for small $T_2 \rightarrow T_1$:

$$\ln\left(\frac{K_{p2}}{K_{p1}}\right) \approx \frac{\bar{h}_R}{R_u} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$K_p - \bar{h}_R$

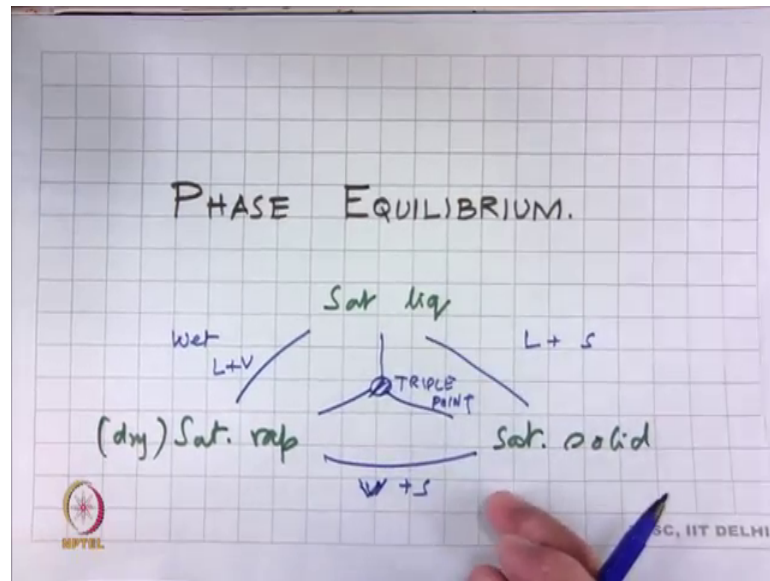
$T_2 \uparrow \quad K_{p2} \downarrow \Rightarrow$ Exothermic reactions less complete.

And what it tells us is that for small changes of T_2 to T_1 $\ln K_{p2}$ over $\ln K_{p1}$ where K_{p2} is the equilibrium constant at T_2 . This is equilibrium constant at T_1 , this \bar{h}_R over R_u $1/T_1$ minus $1/T_2$.

So far we can get a very quick idea about the heat of reaction from this and it tells you that as T_2 increases if K_{p2} decreases, then we have exothermic reactions and it will be less complete. So, this is an interesting equation which connects equilibrium constant to their molar enthalpy of reaction. So, one side you have K_p and the other side you have \bar{h}_R ; this is called the Vant Hoff equation.

So, that brings us to the end of chemical equilibrium and we have seen that we have the equilibrium constant and what are all it depends on and how it is influenced by different parameters. We now come to the topic of phase equilibrium.

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And we are now looking at situations where we have three phases which can possibly exist in equilibrium with one another saturated liquid, saturated vapour or even call it dry saturated vapour and saturated solid.

So, we have several possible combinations. These two could exist in equilibrium liquid and vapour which is what we called earlier as a wet state. This could also be existing there together liquid and solid and the third one is vapour plus solid. So, what is the 3rd thing that is there is when all of them are there together and that is the triple point. So, this was liquid plus vapour, liquid plus solid vapour plus solid and then a triple point.

So, now let us see what is the condition that tells us that equilibrium will exist when two phases are present simultaneously; first in a single component system, then very briefly we will look at multi component systems.

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PHASE EQUILIBRIUM: SINGLE COMPONENT

Saturated states

for $\frac{\text{sat. liq.}}{(f)} + \frac{\text{sat. vapour}}{(g)}$

$$G = m_f g_f + m_g g_g$$

change: sat. liq. \rightarrow sat. vap. (or vice versa)

$$(dG)_{T,p} = g_f d(m_f) + g_g d(m_g)$$

equal, opp. sign

$$= (g_f - g_g) dm_f \Rightarrow \text{At eq}^m \underline{g_f = g_g}$$

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So, we are looking at we will take the case of saturated liquid with subscript f saturated vapour subscript g consistent with what we have learnt so far and g for a mixture. So, this is a mixture a system in which there is this much of the liquid f, this much is the vapour g, then the Gibbs function for this mixture is $m_f g_f$ which is specific Gibbs function plus $m_g g_g$. So, we are assuming g as subscript to denote the vapour phase.

Now what will happen if there is the small change from saturated liquid to saturated vapour or vice versa? So, this will result in a small change in the Gibbs function dG at T, p . This we can then write this as g_f into $d m_f$ a small mass of a liquid that disappeared plus g_g $d m_g$ and this will be the minus sign because this would have decreased. And since the liquid became vapour, the two masses in quantity are the same; so they are equal and of opposite sign.

So, we can simplify this to write as g_f minus g_g into $d m_f$ and which tells you that at equilibrium this parameter has got to be 0 which means that g_f is equal to g_g .

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* Two-phase mixture; in equilibrium, when each phase has same value of Gibbs function.
eg. $g_f = g_g$ (or $\bar{g}_f = \bar{g}_g$)

* Three-phase mixture:
i.e. $g_f = g_g = g_s$

$(f-s, g-s)$
mixtures
 p, T, h, s
 $u = h - pv$
 $g = h - Ts$
vap \rightleftharpoons liq
 $g_g = g_f$
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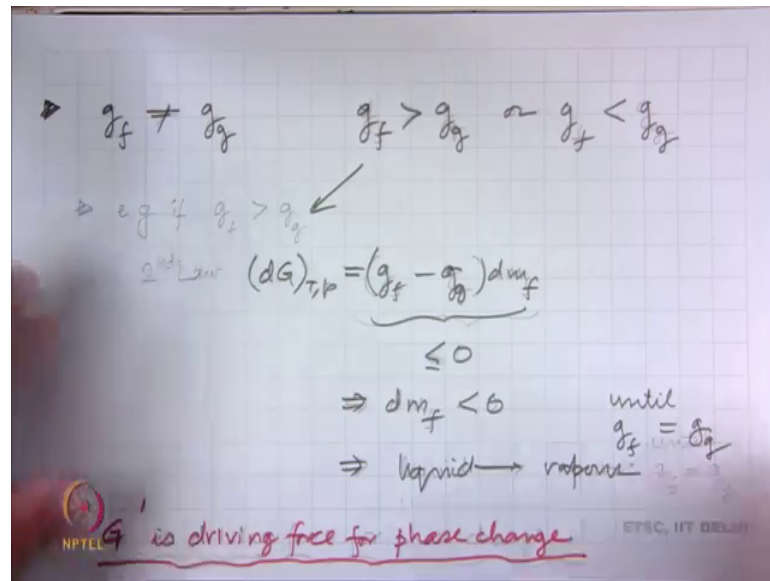
So, this is something we can say that is come out called explicitly that for a two phased mixture in equilibrium the each phase has two of the same value of the Gibbs function that is g_f is equal to g_g or in molar terms \bar{g}_f is equal to \bar{g}_g and this is true for any of the other combinations of mixtures also.

So, what it basically tells us here is that if you look at the property data that we had looked at right at the beginning at the pure properties of a pure substance, in the property table what was listed was p, T, h and s , in some cases u was also listed. So, by and large g was not listed, u was not listed because u could be calculated as h minus $p v$ and g can be calculated as h minus $T s$.

So, what this thing is telling us? That if we take a saturated state and get these data from the table for the vapour phase and get these data for the liquid phase and do the calculation and get g_f, g_g for vapour and g_f for liquid, these two values will turn out to be equal. This we can verify for any substance. In three phases, this logic gets extended and the only way you can have equilibrium is g_f is equal to g_g is equal to g_s . Again you can look up the property data and verify this for yourself.

So, what will happen if these were not equal?

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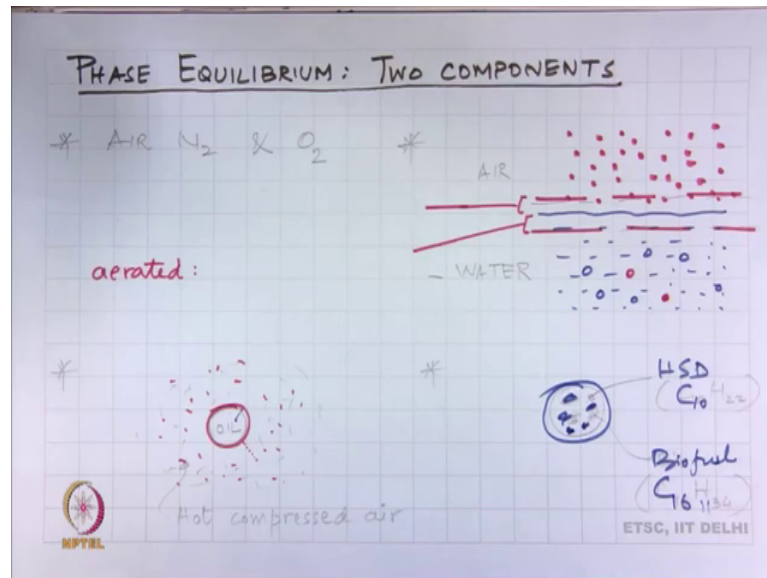


So, we say if g_f is not equal to g_g and say g_f is greater than g_g or we have the second case with g_f is less than g_g , then according to say you take this case. The second law says that dG at T and p this is equal to g_f minus g_g dm_f . This is less than 0, this has to be less than 0 this part.

So, which tells you that dm_f has to be less than 0 which implies that some of the liquid will become vapour and it will do so until g_f is equal to g_g . So, in some sense what we are saying is that we are able to get the direction in which phase change will take place this way or that way by looking at the value of g .

So, we get another important conclusion coming here that g is the driving force for phase change. So, this is a simple thing that has come out, but this have got far reaching implications and we look at engineering of complex systems; this is what we will end up using. So, that was simple for a single component phase. The g_f is equal to g_g that the phase Gibbs function for each phase is the same, then we have equilibrium.

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Now, let us say look at the more complicated case of two components and what are the examples of that? There is water and there is air over there and we are interested in finding out what happens in a small layer over here and a small layer over there.

So, what we are asking is in the air which is just above the surface of the water, how much water is there and we have equilibrium. And we ask the opposite that how much is the small layer just below the surface of the water, how much air has come over there. So, this has got many applications and implications in nature we have oceans and waters where this thing is happening. So, we have some air always getting dissolved in water and by the type of equilibrium calculation that we will just look at; we can estimate how much air is dissolved in water and when you say air is dissolved in water, it basically means that as we have oxygen molecule or a nitrogen molecule.

So, that means that water got is slightly aerated and we know from experience that this is enough for the seas and the lakes and the rivers to sustain marine life. This is very important. This is also fact that the water we drink has air in it, but the same water what to be used in any process where steam is being used that what you learnt in the rankine cycle, then as you heat it, what will happen to this oxygen and nitrogen is that begin to get out then this oxygen will react with say many of the elements which forms the material of the tubes and the other surfaces start reacting and that is not nice.

Another example could be that if instead of air we have carbon dioxide and we pressurize it. So, now what we have done is pushed carbon dioxide molecules into the water we got what we call a carbonated drink. So, this is the type of applications that we can look at. Some other things is applications are that if we have an oil drop sort of a fuel which has been sent into an atmosphere which like happens at the end of a compression stroke in CI engine, then you have very high pressures and high temperatures over there.

One thing we would we were looking at is that these molecules will go out there, mix with air and start burning, but now you got to worry about some things that is the pressures are sufficiently very high and the properties of the oil ascertain then some of these air we will start going into the oil and alter the properties of the dropped surface.

And without that we will not be able to accurately predict how this particular fuel will burn. And this is especially then this is another application in that if you are trying to have something like biodiesel where you have HSD and some biofuel, some sort of an oil or a vegetable oil which is the much heavier molecules C16; C20 something like that was HSD which is C10, then these two are not going to exactly mix with one another.

And they will how they will behave and what will be their equilibrium behavior like this is something we would like to know. So, these are the type of applications that we are looking at for two component in two phases.

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No driving force between different phases of each component, i.e.

$$g_{f,i} = g_{g,i} \quad i = 1, 2, \dots, k \quad \text{No. of components.}$$

and for $(f-s), (g-s)$

$$g_{f,air} = g_{g,air}$$

* NH₃ + H₂O vapour & NH₃ + H₂O liquid.

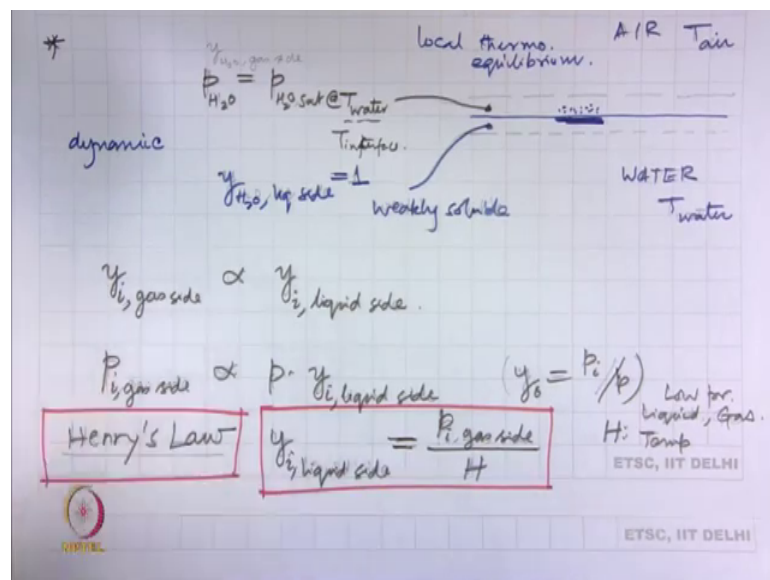
(Air) O₂ + N₂ : any composition at "low" temperatures
77 K - 120 K

ETSC, IIT DELHI

So, we are saying that we are not considering a situation, there is no driving force between different phases of each component $g f i$ is equal to $g g i$; that means, for each species $g f$ say for air would be $g g$ for air.

So, this is what we would do when you are looking at ammonia water mixture in the vapour phase and ammonia water mixture in the liquid phase or at air mixture of oxygen and nitrogen air which is at very low temperatures, temperatures of the order of 77 K to maybe 120 K where some of this oxygen and nitrogen may start becoming liquid. So, this is one assumption we start with and what we say is that in this case say water air thing.

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So, this is water on this side and the above that there is air. This is at T_{air} and this is at T_{water} which need not be the same.

And now what we are saying is water is what is the equilibrium condition over here and for that we might have already used this in some cases that the partial pressure of water in the air just above the water surface will be equal to the saturation pressure of water at the water temperature or strictly at the interface temperature is the two temperature is not very much different. That does not make much difference, but is they are very widely different, then we have to worry about the interface temperature.

What we are saying is that the liquid just at the surface or below the surface over here and the vapour here are in local thermodynamic equilibrium, but that does not mean that this is the static system like chemical equilibrium; phase equilibrium is also dynamic which means that at any instant, some molecule is leaving the liquid phase and coming into vapour phase, at the same time the molecule from vapour phase is going back into the liquid phase. So, this going back and forth is happening, but if we take a snapshot of the entire macro level system, it is invariant.

Then what happens on the water side? We know from experience that air is weakly soluble in water. So, y_{H_2O} on the liquid side will be practically 1, the mole fraction of air in water is going to be extremely small. So, one of the key ideas here is that y_i in the gas side is proportional to y_i in the liquid side. This is important thing from which lot of things will come out. First p_i on the gas side is proportional to p times, y_i on the liquid side where y_i is the ratio of partial pressure to the total pressure. So, we can modify this slightly and get an expression that y_i on the liquid side is equal to p_i on the gas side divided by h which is the constant and this is called Henry's Law.

So, for a limited class of problems, we have Henry's law telling us what is the equilibrium condition at the interface. This is valid at very low pressure and for mixtures of liquid and gas. So, here is one important expression we got to predict what will be the composition of these layers. The same expression when it can be recast becomes p_i on the gas side is equal to h times y_i on the liquid side.

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$p_{i, \text{gas side}} = H \cdot c_{i, \text{liquid side}}$ $H = ?$
Table/Data
L + Gas
different temp.

- Concⁿ gas dissolved in liquid $\propto \frac{1}{H}$
- As $T \uparrow \Rightarrow H \uparrow$
 \Rightarrow concⁿ of dissolved gas in liquid \downarrow (de-aeration)
Water + O₂/Air
~80°C
150°C
- Concⁿ of dissolved gas in liquid \propto partial pr. of gas
i.e. $p \uparrow$ dissolved gas concⁿ \uparrow

NPTEL Only for weak solutions (at interface) IIT DELHI

So, the question is how do we get the value of H? And for that there is lot of data has been tabulated for different combinations of liquids and gases at different temperatures. So, we can look up the problems say in this case you are looking at air and water, we can look up air water data and from there gets the value of H, use it here and start predicting these things.

So, what this expression tells us is that the concentration of gas dissolved in the liquid is proportional to 1 upon H. Larger the value of H, less with the concentration of the gas dissolved, then as T increases, the data will show from the tables that H increases. So, if you look at this point here, that means if H increases, concentration of gas dissolved in the liquid goes down. So, the implication now is that concentration of dissolved gas in liquid goes down.

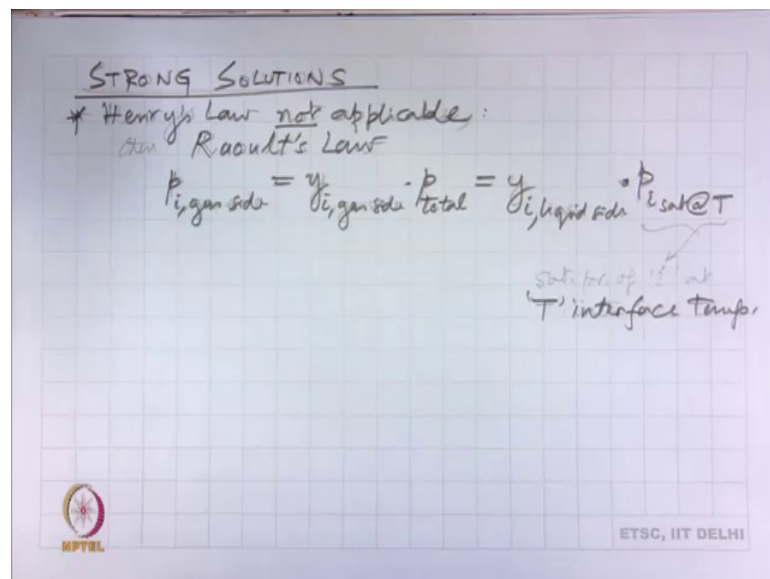
So, this is something which is important when you look at practical engineering. A power plant cycles of steam base steam within steam as a working substance especially at higher pressures and temperatures if you look at this relation, then for water with say oxygen or nitrogen in it or air at temperatures of like 80 degrees C and definitely around 150 degree Celsius.

If you just warm up the water and keep it; lot of the oxygen and the nitrogen or the air that will dissolved in water has been expelled in that, if you put something marine life, it will not be able to sustain at 150 degree Celsius; the driving out of oxygen from water is

much more in the concentration of dissolved gases far far less. This process of say heating water and driving of the dissolved gases is called the opposite of what we saw by putting it in de-aeration. And this is very crucial in steam systems especially large power plants and that is the way one does it. Then we have seen that concentration of dissolved gases in the liquid is proportional to partial pressure of the gas.

So, what a partial pressure of the gas which is the surrounding total pressure, so if p goes up dissolved gas concentration goes up and that is the idea of aerating water that you increase the pressure and dissolved some gas into it. The gas could be carbon dioxide which is what we have actually in aerated drinks, then this entire idea is applicable only for weak solutions at their interface. In that if we want to predict the concentration oxygen deep into this sea, this is not going to give us the correct answer. This is good enough for a small layer near the surface of the water.

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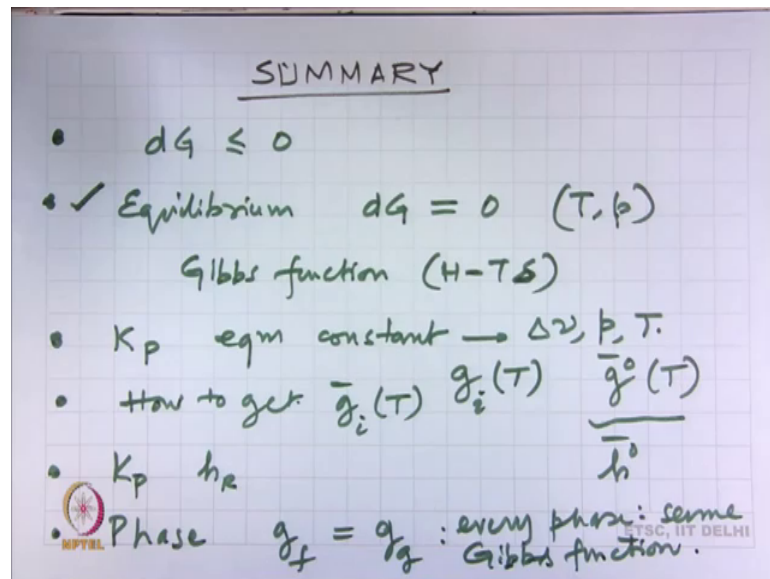


So, what we do? We have learnt a limited application of two phase two component equilibrium. What if we have strong solutions? And this is what we have counter and things like the burning of biodiesels or solutions in vapor absorption systems. In all those cases, we cannot apply Henry's law; then there are more advanced techniques that we have to use one of which is Raoult's law. We will not go too much into the detail of these where says that p_i on the gas side is equal to y_i gas side multiplied by the total pressure

which is y_i on the liquid side multiplied by p_i at saturation partial pressure of i th component at T .

And again here T is some sort of a interface temperature. So, we will leave this at that and that brings us to the conclusion of phase and chemical equilibrium. So, we can now summarize what we have.

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We started off by looking at three different systems and for all cases we said that ΔG less than 0 is where the processes will take place. And the condition for equilibrium whether reacting system, a two phase single component system or a two phase multi component system, in all cases we are looking at dG equal to 0 for a given temperature and pressure this is the condition that we will ensure there is equilibrium.

So, that is what we learnt was a new property the Gibbs function and not just H minus TS , but its implication on the processes that bring about equilibrium. Then we developed the idea of an equilibrium constant and so what all; how it is affected.

In doing that we also require values of g_i which is the Gibbs function for any material at a particular temperature. And this data we can get as the g^0 data from the same tables where we have looked at h^0 data and from there we can use this in these equations. So, we also knew what is the method, how to get g of i at any particular temperature or g or g bar.

And then we finally saw that K_p depends on various parameters. It is affected by Δn , how it is affected by p and how it is affected by T . And you know very limited case we came across Vant Hoff equation which correlates K_p to the heat of reaction ΔH_R . And finally, we looked at phase equilibria and we said that g_f is equal to g_g which means that in the equilibrium state, every phase must have the same Gibbs function.

So, with this we can now apply this knowledge to predict equilibrium conditions for various applications. In all these cases, we will require some data and those tables are available in some case various books and website will have that data. So, we will have to pull that data from there and solve the equation in problems. So, that brings us to the conclusion of the 4th part of Thermodynamics 2; where we have learnt about phase and chemical equilibrium.

Thank you.