Corrosion – Part I
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Lecture - 11
Relation between Free Energy and Equilibrium Constant

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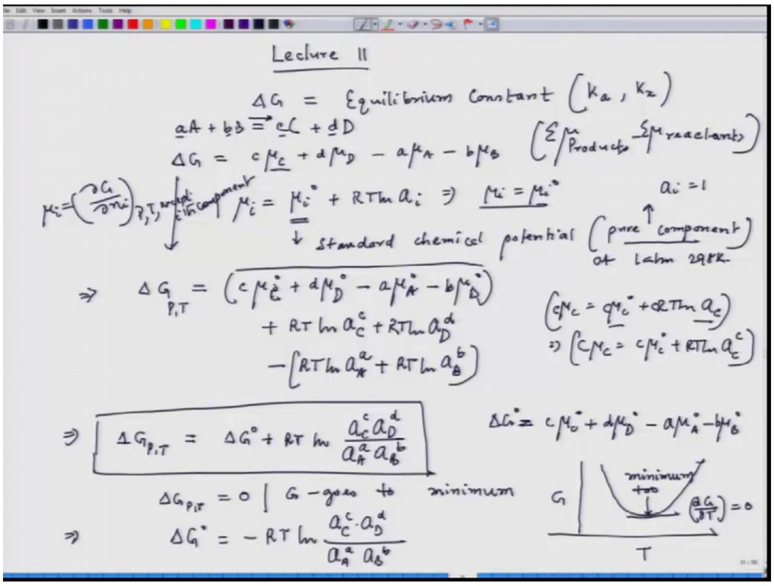

Lecture 11

ΔG = Equilibrium Constant (K_a, K_x)

$aA + bB \rightleftharpoons cC + dD$

$\Delta G = c\mu_C + d\mu_D - a\mu_A - b\mu_B$ $\left(\sum \mu_{Products} - \sum \mu_{reactants}\right)$

$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T, \text{except } i\text{th component}}$ $\mu_i = \mu_i^\circ + RT\ln a_i \Rightarrow \mu_i = \mu_i^\circ$ $a_i = 1$

standard chemical potential (pure component at 1atm 298K)

$$\Rightarrow \Delta G_{P,T} = \left(c\mu_C^\circ + d\mu_D^\circ - a\mu_A^\circ - b\mu_D^\circ\right) + RT\ln a_C^c + RT\ln a_D^d - \left[RT\ln a_A^a + RT\ln a_B^b\right)$$

$(c\mu_C = c\mu_C^\circ + cRT\ln a_C)$

$\Rightarrow \left[c\mu_C = c\mu_C^\circ + RT\ln a_C^c\right)$

$$\Rightarrow \boxed{\Delta G_{P,T} = \Delta G^\circ + RT\ln\frac{a_C^c a_D^d}{a_A^a a_B^b}}$$

$\Delta G^\circ = c\mu_C^\circ + d\mu_D^\circ - a\mu_A^\circ - b\mu_B^\circ$

$\Delta G_{P,T} = 0$ | G – goes to minimum

$$\Rightarrow \Delta G^\circ = -RT\ln\frac{a_C^c \cdot a_D^d}{a_A^a a_B^b}$$

Hello everyone, today we will start our lecture 11. And we will continue our discussion on Relation between Free Energy and Equilibrium Constant. This equilibrium constant depending on whether we are taking mole fraction as our concentration of the species or activity, accordingly it has got it is name K a when we talk when we take care concentration, activity of the species in a particular chemical reaction or K x when we take mole fraction to be our concentration of those species in the system.

Like that way we can have a different connotation for this equilibrium constant. And this equilibrium constant is arising because, whatever process we are considering for the corrosion; that means, a redox reaction this is also a chemical reaction though this is this has electrochemistry associated with it, but it is also chemical reaction.

Now, as we talk about in our last lecture that delta G for a particular reaction a A plus b B equal to c C plus d D this all those are number of moles associated with different species. And actually if we take reaction is going towards this then we can write in this form c chemical potential of c plus d chemical potential of D minus a chemical potential of A minus b chemical potential of B. Because, it is products chemical potential of product minus chemical potential of or I would say summation of chemical potential of product minus summation of chemical potential of reactance. So, that is what we have put here this equation.

Now, from our discussion we have also seen the concept of chemical potential. The chemical potential is nothing, but the change of free energy of the system or a system means of a particular phase when we have a small quantity which is one mole of the a particular component in that particular phase is added or taken out. This is a basically the rate of change of free energy of the system.

And that is written as chemical potential equal to let us say I consider the ith component in that particular system i 0 plus RT ln a of i. Here I am taking activity since we are considering condensed system and there we are not assuming that it is a dilute solution or something.

So, once we have this and now we have to understand this part. This is nothing, but standard chemical potential of that particular phase and this indicates the chemical potential of pure component at one atmosphere pressure and 298 Kelvin. This is a standard value and when we talk about chemical potential it immediately points that a i is equal to 1 and if we put a i to be 1 then of course, mu 1, mu i equal to mu i 0. So, this is the standard chemical potential of that particular component.

Now, we can break this and then write accordingly delta G which is the free energy change of the system for this particular reaction. And since we are considering in terms of chemical potential and at the same time chemical potential is nothing, but delta G delta n i constant pressure, constant temperature and all the components are kept fixed except the ith component.

So, that is what I would say that except ith component. So, this is the concept so, that is what this is also P T because we are fixing pressure and temperature. Now, this becomes c chemical potential of i 0 plus d chemical potential sorry this is C, this is D, 0 minus a chemical potential of A minus b chemical potential of B, with their standard value this is the one part.

See for example, if we write this mu C in terms of standard potential, chemical potential of c which would be for example, mu C would be it is a nothing, but mu c 0 plus RT ln a c. So, accordingly we have broken all those chemical potentials into their respective standard and the other part which contains the activity. And then the rest of the part would be plus RT ln a c c because, when I am put c then it would become C chemical potential c so it will turn into this, so then let me write accordingly RT ln a d D, minus RT ln a A to the power a plus RT ln a B to the power b.

Next step we can write, I can write the entire term this entire term as delta G 0 and then plus RT ln a C c, a D to the power d, a A to the power a, a B to the power b. So, this is my relation where delta G 0 equal to C mu c 0 plus d mu D 0 minus a mu A 0. Now, question is when I write this particular equation I do not know the system whether system has reached equilibrium or not. Now, when it reaches equilibrium then as per our classical thermodynamics this goes to 0 or it has got another Rayleigh connotation that means, G goes to minimum.

For example, let us say I have reaction coordinate and G. So, if I try to see this graph a schematic representation at this point I see that delta G, delta if I consider this axis to be T would be equal to 0 so, this is the slope which is 0. But at the same time you see the variation of G with temperature this point is minimum 2 so, this is the equilibrium. So, then from this I can write delta G 0 equal to RT minus becomes the relation we get this relation in case of equilibrium.

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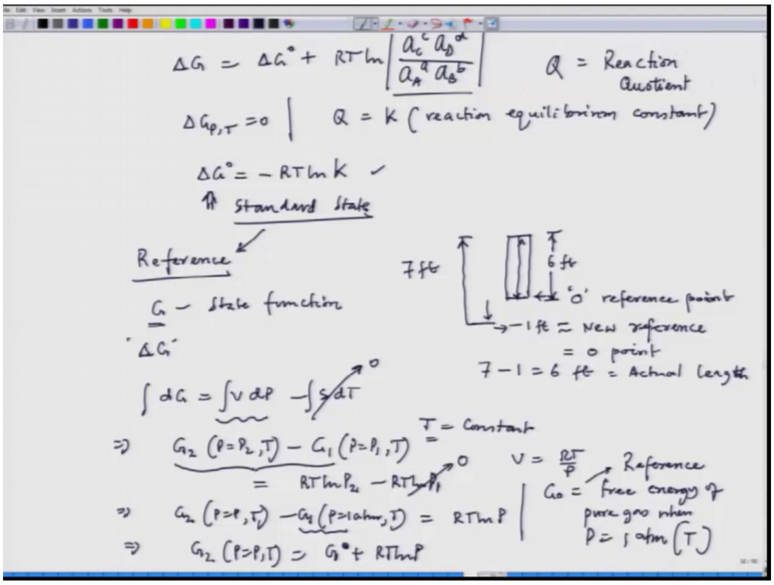

$$\Delta G = \Delta G^\circ + RT\ln\left|\underline{\frac{a_C^{\,c}\, a_D^{\,d}}{a_A^{\,a}\, a_B^{\,b}}}\right| \qquad Q = \text{Reaction Quotient}$$

$\Delta G_{P,T} = 0$ | $Q = K$ (reaction equilibrium constant)

$\Delta G^\circ = -RT\ln K$ ✓

⇑ Standard State

Reference

$\underline{G}$ – State function

'ΔG'

7 ft

6 ft

'0' reference point

→ −1 ft = New reference = 0 point

7 − 1 = 6 ft = Actual length

$$\int dG = \underbrace{\int V\,dP}_{} - \int \cancel{S\,dT}^{\,0}$$

T = Constant

$$\Rightarrow \underbrace{G_2(P=P_2,T) - G_1(P=P_1,T)}_{} = RT\ln P_2 - \cancel{RT\ln P_1}^{\,0}$$

$V = \frac{RT}{P}$

$$\Rightarrow G_2(P=P,T) - \underbrace{G_1(P=1\,atm,T)}_{} = RT\ln P$$

$$\Rightarrow G_2(P=P,T) = G^\circ + RT\ln P$$

G_0 = free energy of pure gas when P = 1 atm (T) ↗ Reference

Now, if we write the same equation once again, this term we can term it as Q which is nothing but the reaction quotient. Now, when delta G P T equal to 0 then this term becomes Q becomes K, which is the reaction equilibrium constant, so delta G 0 equal to minus RT ln K which is the equilibrium constant.

Now, here we are talking about the standard state, before going to the next stage let us put let us discuss little bit on the standard state remember standard state is nothing but the reference state it is a reference nothing, but it is a reference. Now, what do you mean by a reference? Let us have a crude example. So, if I try to measure height of this pillar or length of this pillar so, if the length is let us say 6 feet, whenever I am talking about 6 feet the length of this pillar I always try to measure from a particular datum point; that means, we have to take something as 0. So, this is let us say 0 point, which is the reference point.

Now, if we change the reference point would there be any change in my actual length of this particular pillar. Now, let us say I take reference point to be minus 1 so; this minus 1 feet which is going downwards is my new 0, new reference so, this becomes my 0 point. So, height becomes 7 feet but is that actual length of this particular object 7 feet? No, it is 6 feet, but even if we take this new reference to be 0 point still we can get the actual height of this particular pillar. Because, when I try to find the actual length of this pillar what I will do, I will just do 7 minus 1 so, 6 feet, so this is my actual length. So, whether

I take my reference state to be this one or this one it does not matter the difference would always be the same, because if I try to find out the difference between difference of this particular length of this particular pillar would beside.

Same thing happens here when I talk about G which is a state function whether I take one particular point to be 0 or different other point to be 0 finally, we cannot measure absolute value of G. We always measure delta G which is the difference. So, once we get this difference whether I take something to be 0 or other my other part to be 0, it does not matter it will give me the same value. Now, let us see we can also have some connotation with reference to classical thermodynamics.

Now, we have seen this particular relation. This is a very popular relation in thermodynamics and there if I do this particular treatment at a constant temperature if T equal to constant, then I do integration. So, it becomes G 2, P equal to P 2 temperature minus G 1 P equal to P 1 temperature equal to and V if we take ideal gas then V would be equal to RT P because P V equal to RT for one mole of gas. So, then it becomes RT ln P 2 minus RT ln P 1. So, this term, so this would be go to 0, because T is a constant.

So, then we have to find out these difference. Now, when I try to find out this difference I need to know P 1 as well as P 2 and then we will be able to find out. Now, question is can you simplify this so, if we do it G 2 P equal to P temperature and G 1 P equal to 1 atmosphere and T then it will become RT ln P.

So, this P 1 equal to 1, so this would also go to 0 this term. So, this particular quantity we write in the term of we write as G 0 plus RT ln P. Now, this G 0 is basically the free energy of a pure gas when the pressure is 1 atmosphere when pressure is 1 atmosphere and then at any temperature could be anything.

So, now whenever we have the P equal to 1 atmosphere we take it as a superscript 0 is put which is the standard value this is the standard or this is called reference. So, standard is nothing but the reference now, it is up to you what you want to take it as standard.

Now, this has there is an advantage, advantage is once you take P equal to 1 atmosphere at any other temperature any temperature wherever you would like to put this as standard. So, then you do not have to deal with one more pressure. So, only one pressure the final pressure is important for you, the other pressure you do not have to worry because already you fix that particular pressure.

Now, question is you can also take P to P 1 to be 2 atmosphere, if you want to do that still you will see the difference would become say if you consider P 1 to be 3 atmosphere no problem. So, it is up to you, but the convention is as per the convention everybody follows pressure is considered to be one atmosphere so, that is what this is called standard. So, pressure is important temperature I can have standard value at 273 Kelvin, 273 Kelvin, I can have standard value at 100 Kelvin, I can have standard value at 1000 Kelvin.

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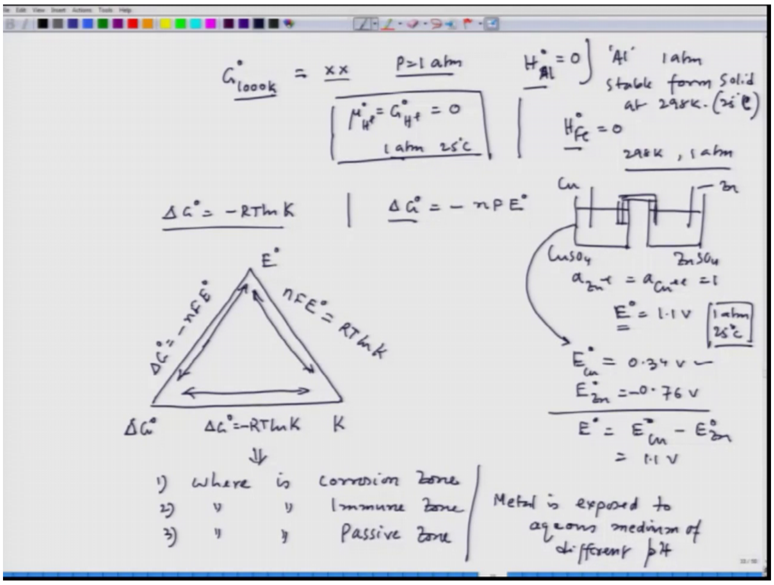

$G^\circ_{1000K} = xx$ $P = 1$ atm

$\mu^\circ_{H^+} = G^\circ_{H^+} = 0$ 1 atm 25°C

$H^\circ_{Al} = 0$ 'Al' 1 atm stable form Solid at 298K. (25°C)

$H^\circ_{Fe} = 0$ 298K, 1 atm

$\Delta G^\circ = -RT\ln K$ | $\Delta G^\circ = -nFE^\circ$

$a_{Zn^{++}} = a_{Cu^{++}} = 1$

$E^\circ = 1.1\,V$ 1 atm 25°C

$E^\circ_{Cu} = 0.34\,V$

$E^\circ_{Zn} = -0.76\,V$

$E^\circ = E^\circ_{Cu} - E^\circ_{Zn} = 1.1\,V$

1) where is Corrosion Zone
2) " " Immune Zone
3) " " Passive Zone

Metal is exposed to aqueous medium of different pH

That is what in text book you see that sometimes this G 0 is put like this connotation people do in textbooks G 0, 1000 Kelvin equal to some value, ok. It means that the standard value the pressure equal to 1 atmosphere at 1atmosphere free energy of that particular phase at 1000 Kelvin is this much. So, that is the way one has to read for example, enthalpy, enthalpy also has got standard value.

For example, in case of enthalpy we let us say aluminium in case of aluminium if we take one atmosphere pressure and that case the solid is the stable form at 298 Kelvin or 25 degree Celsius stable form. So, at that temperature stable form of aluminium is solid and then H aluminium is considered to be 0.

For example, iron H 0 iron equal to 0, when we consider 298 Kelvin and 1 atmosphere pressure. So, these are already some fix some value which we generally assigned to the enthalpy value. So, until unless we assign this value to some particular value assign some particular, this particular enthalpy at one atmosphere pressure we cannot calculate the change in enthalpy.

For example, a gaseous system, in the gaseous system for example, oxygen, if it is a pure oxygen at 25 degree Celsius the stable form is gaseous form. So, that case the enthalpy of pure oxygen at 298 Kelvin one atmospheric pressure would be 0 so, that is the convention.

Now, in case of electrochemistry also we have some convention. The convention is chemical potential or the standard free energy value of hydrogen ion is taken as 0, 1 atmosphere pressure and 25 degree Celsius. So, this is a reference value we do not know whether actually this value the hydrogen ion chemical potential of hydrogen ion is 0 at 25 degree Celsius, 1 atmosphere pressure, but we already assign this value.

And this assignment helps us in finding the change in enthalpy or change in free energy or change in entropy. So, that is about the standard state which is nothing, but the reference state remember this and the pressure is very important we can have standard state at any other temperature.

Even temperature we can change, but that part, that discussion is not part of this current discussion just we thought that we should rebrush brush up this particular knowledge of standard state. Now, coming back to this quantity since we have taken delta G 0 equal to minus RT ln K which is the equilibrium constant relation between equilibrium constant and free energy change at standard condition

Now, we also saw another relation delta G 0 equal to minus n P E. Now, this delta G is we have not specified whether it is a standard state or not. Now, if you recall when we talk about this particular cell copper and this is basically my solve bridge this is copper and here you have copper sulphate and here have zinc sulphate and this is zinc. So, that time we saw that if activity of zinc plus plus equal to activity of copper plus plus equal to 1, then we saw the cell potential becomes 1.1 Volt at 1 atmosphere pressure and 25 degree Celsius.

Now, this also we see that it is also standard value, this is standard value. Now, if we change this temperature this will not become this will also be standard value, but it is at a different temperature, but the pressure is one atmosphere. So, this standard value we can have separately, for this particular cell standard value is plus 3 4 Volt copper side zinc side is equal to 0.76 Volt minus. So, that is what we got E equal to E 0 copper minus E 0 zinc is equal to 1.1 Volt we have seen this.

Now, there another condition is since the activity is 1, so you will see later on that why this activity part is important, when activity goes to 0, this will become this only then this becomes this otherwise it will be a different value. Now, since we are taking standard conditions we can also write this.

So, now, I can have a triangle, where I can put delta G 0 at one side, G at one end and E at one end, E 0 at one end. So, we are talking about standard conditions. Now, let us see the relation delta G 0 equal to minus n F E 0, here delta G 0 equal to minus RT ln K and on this side we can have n F E 0 equal to RT ln K.

So, now, we have the relation between these two, relation between these two, and the relation between these two. And this triangle would enable us to understand at what pH or at what potential in aqueous medium I would get corrosion or I would get protection or I would get there is one particular term first time you are listening which is called passivity we will get passive region.

So, this triangle will be able to let us know where is corrosion zone, where is immune zone and third is where is passive zone for a situation when metal is exposed to aqueous medium of different pH. So, from this we would we are very clear that we have a relation between free energy change with potential change or the cell potential as well as equilibrium constant of the reaction that is taking place in the cell. So, we will stop here we will continue in our next lecture.

Thank you.