Corrosion - Part II
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Lecture - 38
Construction of Ellingham Diagram (I)

Hello everyone, today we have lecture 38 and topic.

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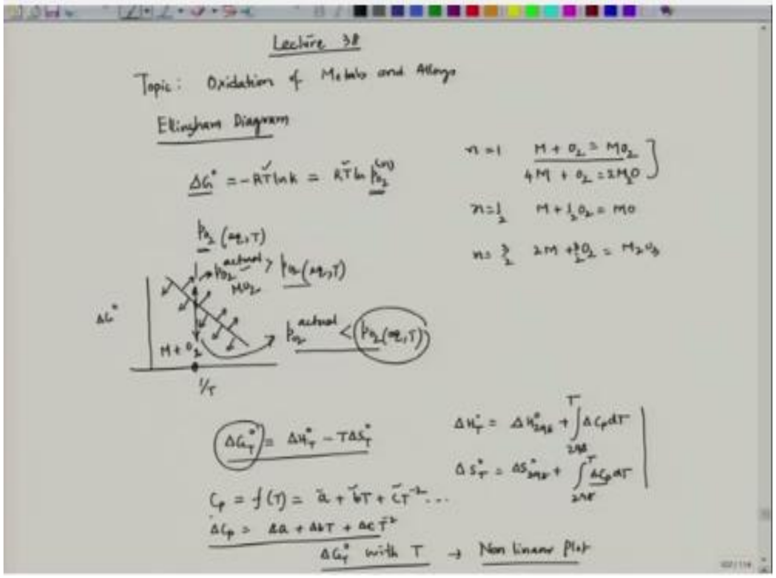

Lecture 38

Topic: Oxidation of Metals and Alloys

Ellingham Diagram

$\Delta G^\circ = -RT\ln K = RT\ln p_{O_2}^{(n)}$

n = 1 $M + O_2 = MO_2$
$4M + O_2 = 2M_2O$

n = 1/2 $M + \frac{1}{2}O_2 = MO$

n = 3/2 $2M + \frac{3}{2}O_2 = M_2O_3$

$p_{O_2}(eq, T)$

$p_{O_2}^{actual} > p_{O_2}(eq, T)$

$p_{O_2}^{actual} < p_{O_2}(eq, T)$

$\Delta G_T^\circ = \Delta H_T^\circ - T\Delta S_T^\circ$

$\Delta H_T^\circ = \Delta H_{298}^\circ + \int_{298}^{T} \Delta C_p dT$

$\Delta S_T^\circ = \Delta S_{298}^\circ + \int_{298}^{T} \frac{\Delta C_p}{T} dT$

$C_p = f(T) = a + bT + cT^{-2} \ldots$

$\Delta C_p = \Delta a + \Delta bT + \Delta cT^{-2}$

ΔG_T° with T → Non linear plot

We will continue our discussion on oxidation of metals and alloys and today we will talk mainly Ellingham diagram. Now if you see in the last class, we have seen relation between standard free energy change for oxidation of pure metal forming pure oxide and that too stoichiometric oxide. And that

$$\Delta G^o = -RT\ lnK = RT\ lnP_{O_2}^{(n)}$$

So this pO2 to the power n could be 1 or could be half or could be some fraction depending on how the reaction oxidation reaction is taking place. So now in the last class we have seen we have come across this important relation when an oxidation reaction reaches equilibrium which is RT this is minus RT ln pO2 to the power n. So this n is 1 when oxidation reaction is like this

$$M + O_2 = MO_2$$

or

$$4M + O_2 = 2M_2O$$

So this is in those both the cases I will have n equal to to 1 n would be half when we write the equation like half O2 equal to MO n equal to 3 by 2 when we write

$$2M + \frac{3}{2}O_2 = M_2O_3$$

So that case n becomes 3 by 2, so like that way n would vary. Now from this equation we could get to know that pO2 what you are getting here is equilibrium partial pressure of oxygen at temperature where we are carrying out the oxidation.

And this temperature is fixed temperature, so that means and at the same time since delta G0 is a function of temperature only as well as K is a function of temperature only. So that is what this partial pressure of oxygen becomes equilibrium partial pressure at that temperature. Now at the same time we have experienced that if we plot delta G0 with 1 by T, we get a plot like this and then we have to stay down this way when that time we get M + O2.

And if we go that direction then we have a MO2 that also we have seen at a particular temperature. Let's say if this is the temperature we are considering beyond this line we have a MO2 to be stable. Because the partial pressure of oxygen at that temperature which is in equilibrium for the reaction and here we are taking this reaction and that time this beyond this line partial pressure of oxygen which is actual is greater than pO2 equilibrium temperature.

And this is the temperature what we are considering and if we go downwards here we get this is the, have a situation pO2 actual less than pO2 equilibrium temperature. So in this case at that temperature system always would like to attain equilibrium if it is a closed system. And then in order to achieve this equilibrium partial pressure of oxygen at that temperature metal oxide would reduce to form more amount of oxygen.

But in this case since this is more than this equilibrium partial pressure of oxygen more amount of oxidation would take place, that information we had. Now then we realize that we have also started talking about Ellingham diagram we just mentioned that next class will be doing analysis on the basis of Ellingham diagram. So in order to do Ellingham diagram let's see how del G T at a temperature.

So this temperature I am talking about is related to del H0 T minus T del S0 or this is 0 or node, so these equation I can write, okay. Now del H this one can be written as from the Kirchhoff's law, this we can get at the same time we can also get del S. And this del Cp is the difference between product minus reactant the Cp of product minus Cp of reactant that is the del Cp. So now we get this and Cp is having a function of temperature which is a kind of polynomial function of temperature which can be written as like that.

Now if this is these are constants and then I can write $\Delta Cp = \Delta a + \Delta b\, T + \Delta c\, T^{-2}$. So that means I could see that this particular value that is del G T 0 is having a complex relation with temperature. Now that means I would also say that if I try to plot del GT with temperature, I will have a non linear plot**.**

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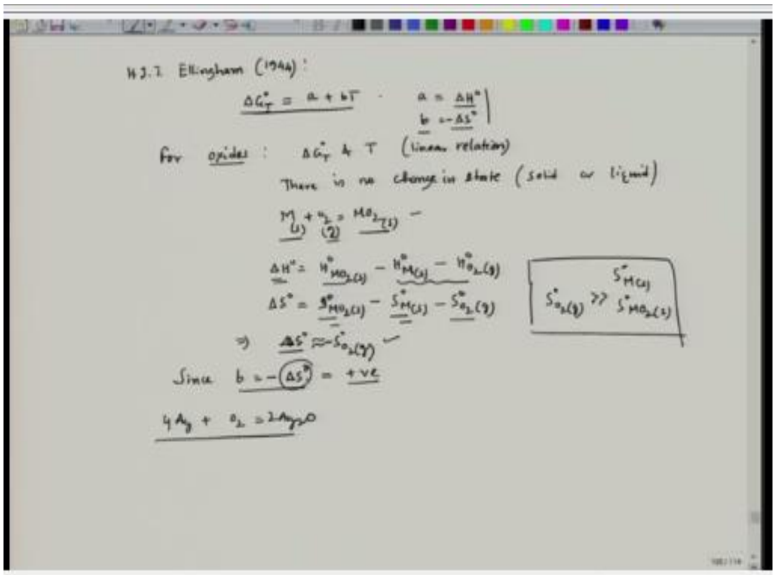

H.J.T. Ellingham (1944):

$\Delta G^\circ_T = a + bT$ · $a = \Delta H^\circ$, $b = -\Delta S^\circ$

For oxides: ΔG°_T & T (linear relation)

There is no change in state (solid or liquid)

$M_{(s)} + O_{2(g)} = MO_{2(s)}$

$\Delta H^\circ = H^\circ_{MO_2(s)} - H^\circ_{M(s)} - H^\circ_{O_2(g)}$

$\Delta S^\circ = S^\circ_{MO_2(s)} - S^\circ_{M(s)} - S^\circ_{O_2(g)}$

$\boxed{S^\circ_{O_2(g)} \gg S^\circ_{M(s)}, S^\circ_{MO_2(s)}}$

$\Rightarrow \Delta S^\circ \approx -S^\circ_{O_2(g)}$

Since $b = -(\Delta S^\circ) = +ve$

$4Ag + O_2 = 2Ag_2O$

But H. J. T. Ellingham, he has shown in 1944 and he was also shown that in a paper which titled reducibility of oxides and sulfides in metallurgical processes which was published in journal of society of chemical industries. And there he mentioned that del G, this factor this value which is the free energy change in standard state at a particular temperature for oxidation process can be written as this form, okay, that can be written as this form.

So that means if I see this form, so and where a $=\Delta H^o$, b = $-\Delta S^o$. So for oxides as well as for sulfides since we are talking about oxidation, so we will talk about oxides. So del G0 T has linear relation with temperature provided condition this is a linear relation. So now provided there is no change in state, change in state means it remains solid all the time or it remain liquid all the time any species.

For example, if I consider

$$M + O_2 = MO_2$$

This is solid, this is gas, so this will remain solid, this will remain gas, so there will be no state change. So that case over a temperature range this linear relation can be true. Now this is the standard entropy change, this is the enthalpy change standard enthalpy change. And now since this is a simple linear equation, if I take oxidation process this process I can write

$$\Delta H^o = H^o_{MO_2(s)} - H^o_{M\,(s)} - H^o_{O_2(g)}$$

And del S0 can be written as this is the product these 2 are reactants, so now

$$\Delta S^o = S^o_{MO_2(s)} - S^o_{M\,(s)} - S^o_{O_2(g)}$$

Now if we see the value of this 2 quantities they are almost equivalent since they are solid state, their entropy is very low. But if I try to see this entropy in comparison to these 2 entropies, so I can say that this value is very large as compared to or S0 MO2 solid.

So that can allow me to have a kind of approximation, this approximation is possible because of this situation. And then I could see that the entropy of gas is always positive and there is a negative sign in front of it, so this becomes negative. And when I take b since b is minus del S0, so then b becomes positive because this becomes negative, so there is a negative sign, this becomes negative from this relation and since there is a negative sign so it becomes positive.

So that means the slope of this linear plot is positive, so if I try to plot let's say taken an example and this example is taken from Gaskell the book by Gaskell. So there it is taken as Ag oxidation, so this oxidation is taken this reaction.

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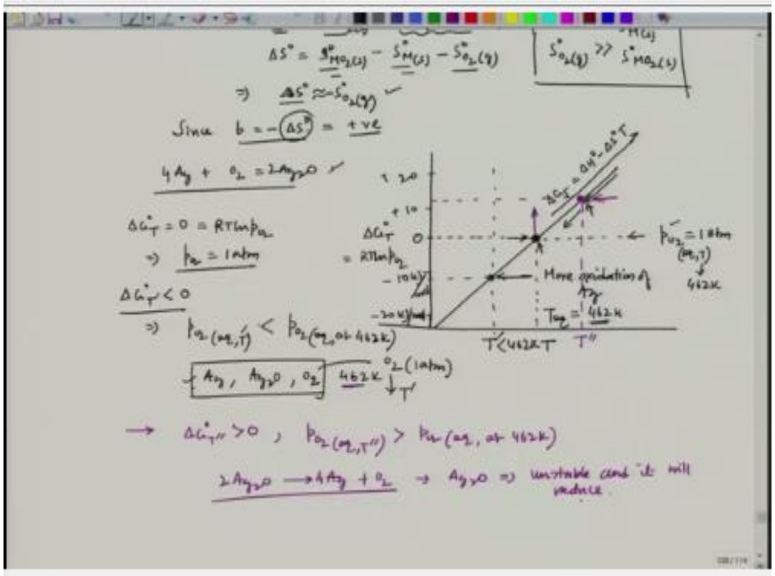

$\Delta S^\circ = S^\circ_{MO_2(s)} - S^\circ_{M(s)} - S^\circ_{O_2(g)}$

$S^\circ_{O_2(g)} >> S^\circ_{MO_2(s)}$

$\Rightarrow \Delta S^\circ \approx -S^\circ_{O_2(g)}$

Since $b = -\Delta S^\circ = +ve$

$4Ag + O_2 = 2Ag_2O$

$\Delta G^\circ_T = 0 = RT \ln p_{O_2}$

$\Rightarrow p_{O_2} = 1 atm$

$\Delta G^\circ_T < 0$

$\Rightarrow p_{O_2(eq,T')} < p_{O_2(eq, at\ 462K)}$

$\boxed{Ag, Ag_2O, O_2}$ 462K O_2 (1atm) ↓T'

→ $\Delta G^\circ_{T''} > 0$, $p_{O_2(eq,T'')} > p_{O_2(eq, at\ 462K)}$

$2Ag_2O \rightarrow 4Ag + O_2$ → Ag_2O ⇒ unstable and it will reduce.

And there if you plot temperature with

$$\Delta G_T^o = RT\ ln\ ln\ p_{O_2}$$

and since it is a linear a plus b T mod, so this relation becomes like this. And now it has a 0 value minus 10 kilo joule per mole and here it is minus 20 kilo joule per mole of oxygen. Now here if I draw a parallel line with T at 0 value, so this is 10, this is 20 and here of course it is a minus sign this is plus 0 value. So this value indicates pO2 to be 1 atmosphere and this is also equilibrium at that temperature.

And now this point is the equilibrium temperature, so this is T equilibrium and here it is 462 Kelvin. So at this temperature when this del GT line, this line is drawn like this wherever it cuts that point belong to pO2 equilibrium at temperature, so this temperature I can write as 462 Kelvin. So now delta G 0 T equal to 0 which is nothing but for this equation RT ln pO2 hence pO2 equal to 1 atmosphere, okay, so this is the equilibrium partial pressure.

Now if I go at a temperature let’s say T which is less than 462 Kelvin, so that time delta G 0 T is less than 0 which means that pO2 equilibrium temperature which is let’s say T prime. So this is T prime should be less than pO2 equilibrium at 462 Kelvin. Now interesting part is this any point on this line this particular line any point is indicating equilibrium standard free energy change at that temperature.

So that also indicates equilibrium partial pressure of oxygen, now if I take Ag, Ag2O and O2 in a closed system. And then if I keep it at 462 Kelvin and if I maintain O2 as 1 atmosphere then this system will be at equilibrium. Because I know if this is a closed system that means if pO2 is maintained as 1 atmosphere pressure and at the same time we also know that pO2 equilibrium at 462 Kelvin is 1 atmosphere. So that time pure Ag, pure Ag2O as well as O2 will be in equilibrium.

Now this particular system if the temperature T prime since the P equilibrium pO2 at equilibrium at T prime is less than 1 atmosphere. So that times you have more oxygen than the required equilibrium partial pressure of oxygen at T prime, so Ag will oxidize and form Ag2O. So that means here if I go to T prime at this location, if I start from this location I will have more oxidation of Ag.

Now similarly if I consider temperature let's say I take a temperature T double prime this is the point where it reaches equilibrium. So at this location delta G0 T double prime and here it is T prime greater than 0. Because this is the 0 value and corresponding value is greater than 0 and here corresponding value was less than 0. So then of course pO2 equilibrium at T double prime should be greater than pO2 equilibrium at 462 Kelvin.

Now similarly if I start with a system where I have pure Ag, pure Ag2O and O2 at 1 atmosphere pressure that partial pressure of oxygen is 1 atmosphere that time it reaches equilibrium. But once I take this temperature to T double prime that means this temperature this point it is taken to this particular point. Then I see that the requirement for pO2 to reach equilibrium for that reaction this reaction is more than what atmosphere pressure.

But in the closed system we are not supplying any oxygen from outside, so how does it get oxygen extra oxygen to reach equilibrium. So that time Ag2O will convert to Ag plus O2, so this reaction the reverse reaction will start. So that time I could say that Ag2O becomes unstable and it will reduce. So there are 3 situations rather if we have a closed system where we have these 3 spaces and oxygen partial pressure is 1 atmosphere, system will reach equilibrium and that equilibrium temperature is 462.

Now this equilibrium system is taken to 1 time it is taken to T prime which is less than 462. So that time I could see that partial pressure of oxygen at T prime is less than 1 atmosphere. So it will try to reduce the oxygen content in the system, so more oxidation would happen. And since it is a closed system we are not supplying any oxygen from outside or we are not taking any oxygen from inside to the surrounding.

So whatever happens it should happen within the system, similarly if it is taken to this particular state is taken to this particular position is taken to this position. Then of course I need more oxygen for the system for the reaction to reach equilibrium and then more oxygen will come from the reduction of Ag2O. So this is the very concept of this Ellingham of this particular del G T plot with temperature, now this is the Ellingham diagram for that oxide.

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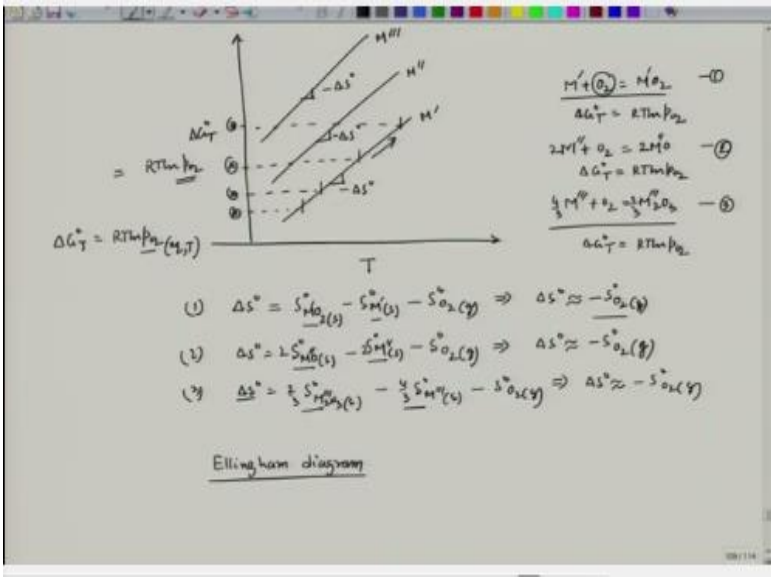

$M' + O_2 = MO_2$ —①

$\Delta G^\circ_T = RT\ln p_{O_2}$

$2M'' + O_2 = 2M''O$ —②

$\Delta G^\circ_T = RT\ln p_{O_2}$

$\frac{4}{3}M''' + O_2 = \frac{2}{3}M'''_2O_3$ —③

$\Delta G^\circ_T = RT\ln p_{O_2}$

(1) $\Delta S^\circ = S^\circ_{MO_2(s)} - S^\circ_{M'(s)} - S^\circ_{O_2(g)} \Rightarrow \Delta S^\circ \approx -S^\circ_{O_2(g)}$

(2) $\Delta S^\circ = 2S^\circ_{MO(s)} - 2S^\circ_{M''(s)} - S^\circ_{O_2(g)} \Rightarrow \Delta S^\circ \approx -S^\circ_{O_2(g)}$

(3) $\Delta S^\circ = \frac{2}{3}S^\circ_{M'''_2O_3(s)} - \frac{4}{3}S^\circ_{M'''(s)} - S^\circ_{O_2(g)} \Rightarrow \Delta S^\circ \approx -S^\circ_{O_2(g)}$

Ellingham diagram

So per Ellingham diagram is nothing but plot between

$$\Delta G^o_T = RT\ ln\ ln\ p_{O_2}$$

with temperature for different oxides. Now in this case one important factor is we are considering all the time pO2 that means 1 mole of oxygen when it is consumed for the oxidation of a pure metal and going to form pure metal oxide. Now for example if I consider

$$M + O_2 = MO_2$$

that time it is very straight forward would be equal to

$$\Delta G_T^o = RT\ ln\ ln\, p_{O_2}$$

Now if it is

$$2M + O_2 = 2MO$$

$$\Delta G_T^o = RT\ ln\ ln\, p_{O_2}$$

So that time we will consider like this, so then also it will become. Now if it is, so that time we will consider this one as so I will consider that way just a minute 4 by 3 and yes. So it will be like this,

$$\frac{4}{3}M + O_2 = \frac{2}{3}M_2O_3$$

So that time also it becomes

$$\Delta G_T^o = RT\ ln\ ln\, p_{O_2}$$

And if I plot make it as M1, M2, M3 sorry if I put it that way then it will be confusing. So I can say that this is M prime metal M double prime metal L triple prime metal, so this is prime, double prime, triple prime, so that means M prime, M double prime, M table Prime all are different metals.

So now if I try to plot del GT with temperature for all 3 cases I will get a plot like this, I am just drawing arbitrary plot, okay. And interestingly if this is for M prime, this is for M double prime, this is for M triple prime I could see that they are almost parallel to each other. So that means they have some slope which is nothing but del S0 that is the slope for every case here also del S0 minus here also minus del S0.

Now if I try to calculate their corresponding del S0, in this case it will be let's say this is equation 1, this is equation 2, this is equation 3 reaction. So case 1

$$\Delta S^o = S^o_{M'O_2(s)} - S^o_{M'(s)} - S^o_{O_2(g)} \approx -S^o_{O_2(g)}$$

Which I can write this. Case 2, for the equation minus I can write

$$\Delta S^o = 2S^o_{M''O\,(s)} - 2S^o_{M''(s)} - S^o_{O_2(g)} \approx -S^o_{O_2(g)}$$

So I could see that, so they are slopes and similarly third case

$$\Delta S^o = \frac{2}{3} S^o_{M_2'''O_3(s)} - \frac{4}{3} S^o_{M'''(s)} - S^o_{O_2(g)} \approx -S^o_{O_2(g)}$$

So now you could see that these quantities, this entropy of solids whether it is 2 by 3 or 2 they will not make much of difference to the overall entropy change. And overall entropy since the gas entropy is very very high as compared to the solid entropy and that is what we can roughly say that that all the 3 cases that the slope becomes similar.

Because all the cases slope is nothing but minus S0 O2 which eventually become plus S0 O2 and entropy of a substance is always positive. So that is what their slopes are almost similar and that is what you will see an Ellingham diagram you will see that all the oxide lines are parallel nearly parallel to each other. Now this is nothing but Ellingham diagram, now from this Ellingham diagram one can calculate partial pressure of oxygen which is an equilibrium at any temperature.

For example, if I consider this line then at different temperatures I can calculate partial pressure of oxygen by simply noting down those delta GT values at different temperatures. So I can find those values and simple calculation

$$\Delta G^o_T = RT \ln \ln p_{O_2\,(eq,T)}$$

So this pO2 is nothing but equilibrium at the temperature of consideration. So that is one way of calculation of partial pressure of oxygen which is an equilibrium for that oxidation reaction.

So there is one more way to calculate if you see Ellingham diagram we will see that on the side of the right and the bottom side we see that there are some partial pressure of oxygen lines. And those lines if we continue and we find that those line meet delta G T axis at 0 when T equal to 0 Kelvin. So that is one way graphically one way to find out partial pressure of oxygen equilibrium in equilibrium at a particular temperature of consideration for any oxidation of metal.

So that part we will do in our next lecture and also in the next lecture we will show how to what is the logic behind getting those radiating line from delta G T equal to 0 at T equal to 0 Kelvin. And then wherever that line crosses any of the oxidation lines and that crossing point is the partial pressure of oxygen for that particular oxide line at that temperature where it crosses. So we will do that in our next lecture, so let’s stop here.

We will continue our discussion on Ellingham diagram and try to see a complete Ellingham diagram plot and understand how to read Ellingham diagram and also we will understand that what is the importance of Ellingham diagram, thank you very much.