Corrosion - Part II
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Lecture - 37
Thermodynamics of Oxidation

Hello everyone now will start lecture 37.

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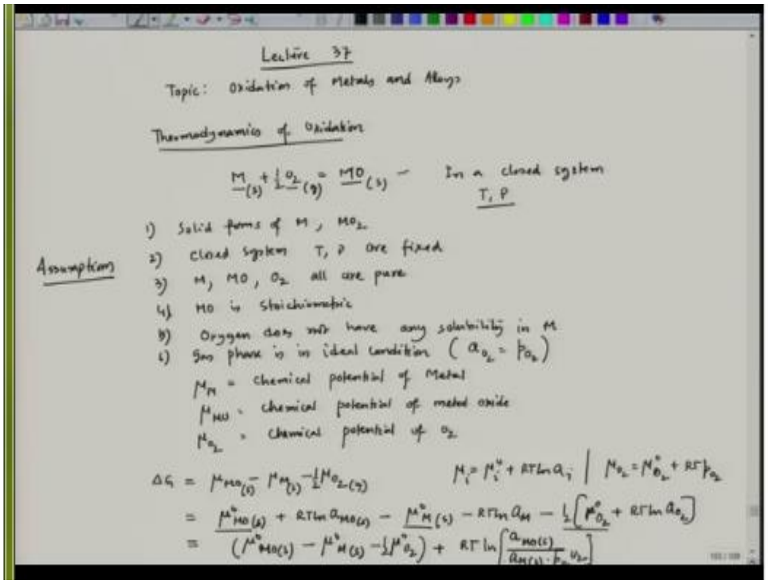

Lecture 37

Topic: Oxidation of Metals and Alloys

Thermodynamics of Oxidation

$$\underline{M}_{(s)} + \tfrac{1}{2}\underline{O_2}_{(g)} = \underline{MO}_{(s)}$$ – In a closed system $\underline{T, P}$

Assumption

1) Solid forms of M, MO_2
2) closed system T, P are fixed
3) M, MO, O_2 all are pure
4) MO is stoichiometric
5) Oxygen does not have any solubility in M
6) Gas phase is in ideal condition ($a_{O_2} = p_{O_2}$)

μ_M = chemical potential of Metal
μ_{MO} = chemical potential of metal oxide
μ_{O_2} = chemical potential of O_2

$\mu_i = \mu_i^\circ + RT\ln a_i$ | $\mu_{O_2} = \mu_{O_2}^\circ + RT p_{O_2}$

$$\Delta G = \mu_{MO_{(s)}} - \mu_{M_{(s)}} - \tfrac{1}{2}\mu_{O_2(g)}$$
$$= \underline{\mu^\circ_{MO(s)}} + RT\ln a_{MO(s)} - \underline{\mu^\circ_{M(s)}} - RT\ln a_M - \underline{\tfrac{1}{2}\left[\mu^\circ_{O_2}\right.} + \left. RT\ln a_{O_2}\right]$$
$$= \left(\mu^\circ_{MO(s)} - \mu^\circ_{M(s)} - \tfrac{1}{2}\mu^\circ_{O_2}\right) + RT\ln\left[\frac{a_{MO(s)}}{a_{M(s)}\cdot p_{O_2}^{1/2}}\right]$$

And we will continue our discussion on this topic oxidation of metals and alloys. Till now we have seen different stages of oxidation as well as we have considered Pilling–Bedworth ratio which gives a kind of or crude estimation or crude idea about oxidation resistance of a metal. But we have seen that there are various issues associated with PBR and now we have to try to understand some of the basics of oxidation.

And when we start talking about basics of oxidation where you consider 2 fundamental aspects, one is thermodynamics of oxidation or thermodynamics of oxide formation and of course the kinetic analysis of oxide growth or oxide formation even. Now when we talk about thermodynamics of oxidation, it is a very detailed subject but we will try to simplify in order to have a quick understanding of metal oxidation or rather feasibility of a metal to get oxidized. Now for that will take some assumption.

Now the

$$2M + O_2 = 2MO$$

metal reacts with oxygen and form metal oxide and now here we are taking metal oxide in the form of metal MO and this is the metal, and this is the oxygen and M is always in solid state, this is also in solid state. In the beginning we will try our analysis on the basis of solid state of metal and metal oxide and oxygen is gas all the time, this is in a closed system and the temperature and pressure is fixed.

So this is 1 condition, so condition 1 is solid forms of metal and metal oxide, second condition it is a closed system where temperature and pressure are fixed, third assumption these are assumption for our treatment. Third assumption is metal, metal oxide as well as oxygen all are pure, fourth metal oxide is stoichiometric, fifth metal oxygen does not have any solubility in metal. So these are the conditions were taking before going for the treatment in order to understand the thermodynamics of oxidation or the formation ability of any oxide.

So now once we have this many assumptions then we can fairly treat this particular oxidation process in the form of equilibrium condition. So now if mu M is the chemical potential of metal, mu MO is the chemical potential of metal oxide, mu O2 is the chemical potential of oxygen. Then we can write this free energy change for this reaction in the form of

$$\Delta G = \mu_{MO} - \mu_M - \frac{1}{2}\mu_{O_2}$$

and now we have to balance it also.

So here half term will come, so this will be half, now we can write this, this is solid state, this is solid state, this is gas state. And later we can see that how the solid liquid transformation that metal oxide can go to the liquid form metal can go to the liquid form and that time what could be the change in the formation of del G will see later. But in the beginning our treatment would be considering only solid state of metal and metal oxide and then oxygen would be in the gaseous form.

Now this we can write it as

$$\Delta G = \mu^o_{MO(s)} + RT\ ln a_{MO(s)} - \mu^o_{M(s)} - RT\ ln a_M - \frac{1}{2}\left[\mu^o_{O_2} + RT\ ln a_{O_2}\right]$$

Now since μ = μₒ + RT ln a for a component, okay, so then and at the same time when it is a gaseous form mu I can write it as μ_o or $\mu_{standard}$ chemical potential of oxygen the gas form + RT instead of the activity I can write pO2.

And here also I am considering the gas phase is in ideal condition, so if it is ideal condition that time activity of O2 would be equal to activity partial pressure of O2. So this would be equal to if I consider these terms then I can write + RT ln half this factor will come.

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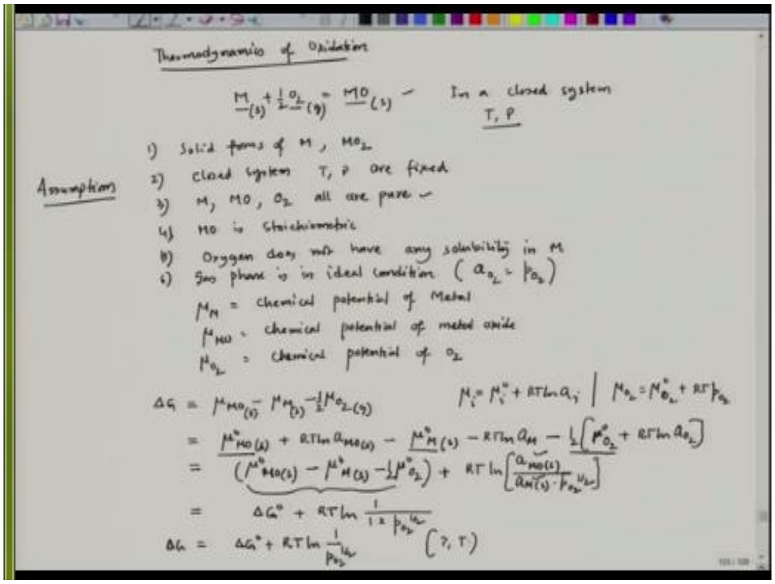

Thermodynamics of Oxidation

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$\mu_i = \mu_i^o + RT\ln a_i$ | $\mu_{O_2} = \mu_{O_2}^o + RT p_{O_2}$

$$\begin{aligned}\Delta G &= \mu_{MO(s)} - \mu_{M(s)} - \tfrac{1}{2}\mu_{O_2(g)} \\ &= \mu^o_{MO(s)} + RT\ln a_{MO(s)} - \mu^o_{M(s)} - RT\ln a_M - \tfrac{1}{2}\left[\mu^o_{O_2} + RT\ln a_{O_2}\right] \\ &= \underbrace{\left(\mu^o_{MO(s)} - \mu^o_{M(s)} - \tfrac{1}{2}\mu^o_{O_2}\right)} + RT\ln\left[\frac{a_{MO(s)}}{a_{M(s)} \cdot p_{O_2}^{1/2}}\right] \\ &= \Delta G^o + RT\ln\frac{1}{1 \times p_{O_2}^{1/2}}\end{aligned}$$

$$\Delta G = \Delta G^o + RT\ln\frac{1}{p_{O_2}^{1/2}} \quad (P, T)$$

So if I see this particular term which is the difference of standard values of MO, standard free energy value of MO M and O2. So these are pure form, so I can say that these are the molar free energy of MO, M and O2 and this I can write it as delta G0 + RT ln. Now since is a pure component, these are all considered as pure, so this I can consider to be 1 and since it is a solid also, so this is 1 this I considered as 1, so pO2 half.

So this becomes

$$\Delta G = \Delta G^o + RT\ ln\ ln\ \frac{1}{P_{O_2}^{\frac{1}{2}}}$$

So this is at a particular temperature and pressure that closed system.

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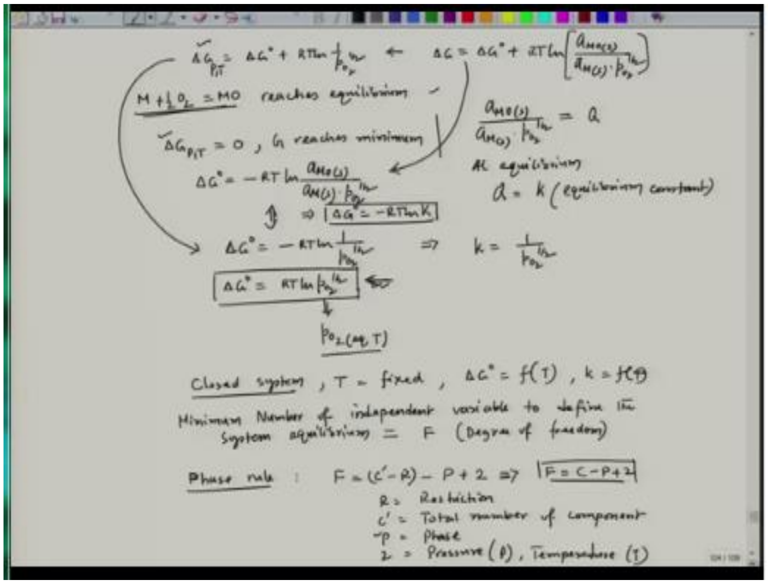

$\Delta G_{P,T} = \Delta G^\circ + RT\ln\frac{1}{p_{O_2}^{1/2}}$ ← $\Delta G = \Delta G^\circ + RT\ln\left[\frac{a_{MO(s)}}{a_{M(s)}\cdot p_{O_2}^{1/2}}\right]$

$M + \frac{1}{2}O_2 = MO$ reaches equilibrium

$\Delta G_{P,T} = 0$, G reaches minimum

$\Delta G^\circ = -RT\ln\frac{a_{MO(s)}}{a_{M(s)}\cdot p_{O_2}^{1/2}}$ ⇒ $\boxed{\Delta G^\circ = -RT\ln K}$

$\frac{a_{MO(s)}}{a_{M(s)}\cdot p_{O_2}^{1/2}} = Q$

At equilibrium

$Q = K$ (equilibrium constant)

$\Delta G^\circ = -RT\ln\frac{1}{p_{O_2}^{1/2}}$ ⇒ $K = \frac{1}{p_{O_2}^{1/2}}$

$\boxed{\Delta G^\circ = RT\ln p_{O_2}^{1/2}}$

$p_{O_2(eq,T)}$

Closed system, T = fixed, $\Delta G^\circ = f(T)$, $K = f(T)$

Minimum Number of independent variable to define the system equilibrium = F (Degree of freedom)

Phase rule : $F = (C' - R) - P + 2$ ⇒ $\boxed{F = C - P + 2}$

R = Restriction
C' = Total number of component
P = Phase
2 = Pressure (P), Temperature (T)

Now if I take O2 it is coming from delta G = + RT ln, so this from this it is coming. Now this particular thing I can consider to be a MO, we can consider it to be Q which is reaction quotient. Now when this

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

This reaches equilibrium then this value should be equal to 0. So I can also put P T this would be 0 that means the system reaches, the G reaches minimum value.

So that time delta

$$\Delta G = -RT\ ln\ ln\ \frac{a_{MO(s)}}{a_{M(s)}\,P_{O_2}^{\frac{1}{2}}}$$

So these term when this reaction reaches equilibrium at equilibrium I can consider Q to be K which is the equilibrium constant. Now this is coming from this equation gives this even this equation can also give

$$\Delta G = -RT\ ln\ ln\ \frac{1}{P_{O_2}^{\frac{1}{2}}}$$

So that means these 2 equations are equivalent equation. So we can write K equal to which is the equilibrium constant 1 by pO2 half and we can also write it to be

$$\Delta G = RT \, ln \, ln \, P_{O_2}^{\frac{1}{2}}$$

So this is an important equation and as well as this can be written as delta G0 = - RT ln K, so these 2 equations are important equations for oxidation and this since it is delta G0 that means we are considering standard free energy change for oxidation. Now we have to understand this equation at is this equation physically what is the meaning of pO2 half at equilibrium. Now when can we write this equation when delta G P T = 0 that means the system reaches equilibrium.

So that means I can write this one to be pO2 equilibrium at that particular temperature. Now this, so we have already fixed the temperature and this system is a closed system**,** temperature is fixed and we know delta G is a function of temperature even K is a function of temperature. So that case we have to first understand that in order to define equilibrium what would be the minimum number of independent variable is to be defined.

So we have to understand the minimum number of independent to define the system equilibrium, we need to find out this is nothing but degree of freedom. Now if I try to see this equation this is a closed system, so I can for a reaction I can write the phase rule I can write it as F = C - R - P + 2. Since here we have a vapor phase that is what we have to write 2, so now in this case R is the restriction which is coming from the equilibrium number.

C is the number of or I can say C prime C is the total number of components, P is the phase and 2 is coming from pressure and temperature. So these pressure this is phase and this is pressure, so let me write the full. So this is pressure P and temperature T and the C by this is equivalent to

$$F = (C - R) - P + 2$$

which is the famous phase rule expression.

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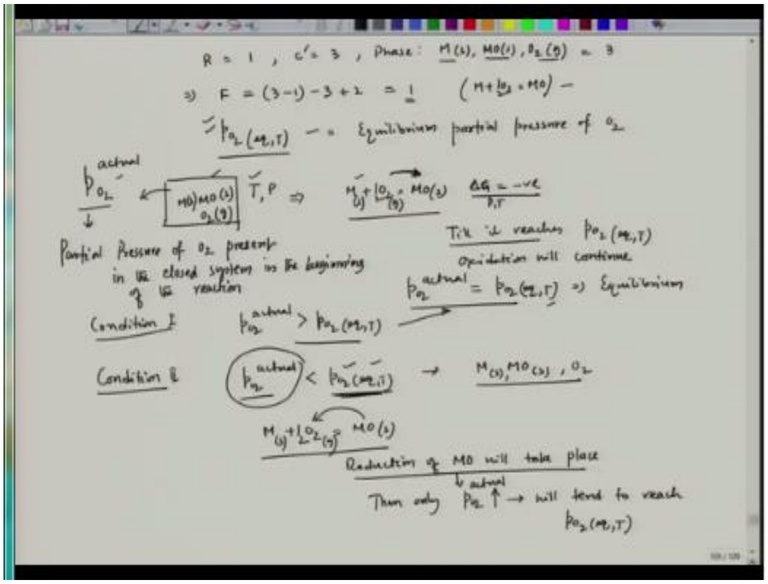

$R = 1$, $C' = 3$, Phase: $M(s)$, $MO(s)$, $O_2(g)$ = 3

$\Rightarrow F = (3-1) - 3 + 2 = 1$ $(M + \frac{1}{2}O_2 = MO)$ —

$\Rightarrow p_{O_2}(eq,T)$ — = Equilibrium partial pressure of O_2

$p_{O_2}^{actual} \leftarrow \boxed{M(s)\ MO(s)\ O_2(g)}$ $T, P \Rightarrow M_{(s)} + \frac{1}{2}O_{2(g)} \xrightarrow{} MO(s)$ $\frac{\Delta G = -ve}{P,T}$

Partial Pressure of O_2 present in the closed system in the beginning of the reaction

Till it reaches $p_{O_2}(eq,T)$ Oxidation will continue

$p_{O_2}^{actual} = p_{O_2}(eq,T) \Rightarrow$ Equilibrium

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

Condition II $p_{O_2}^{actual} < p_{O_2}(eq,T) \rightarrow M_{(s)}, MO_{(s)}, O_2$

$M_{(s)} + \frac{1}{2}O_{2(g)} = MO(s)$

Reduction of MO will take place

Then only $p_{O_2}^{actual} \uparrow \rightarrow$ will tend to reach $p_{O_2}(eq,T)$

Now if I try to see if what is the restriction here since it is the 1 equilibrium restriction is 1, C prime is 3, there are 2 solid phases and 1 gas phase metal, metal oxide and oxygen. So C prime is 3, so then and pressure and temperature of course, so then we can find out F equal to just degree of freedom 3 - 1 - phase how many phase. So phase we see that we have 3 phase metal solid, metal oxide solid, O2 gas.

So these are 3 phases and metal and metal oxide though both are solids but they have a definite boundary and as per the definition of phase a phase is defined as a constituent or the portion of a system with a distinct physical significance and with a chemical identity and it should have a definite boundary separating it from other portion of the system. So that is what these is a separate phase, this is a separate phase, this is a separate phase.

So phase number is 3, so phase 3 + 2, so this becomes 1, so now that means the degree of freedom to define the equilibrium of this reaction

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

is 1. So now this 1 is nothing but pO2 equilibrium at temperature T because the degree of freedom is 1 at the same time delta G0 is only function of temperature. So in order to define this equilibrium at a particular temperature we must have a definite partial pressure of oxygen.

Now this definite partial pressure of oxygen which is nothing but equilibrium partial pressure of oxygen. Now let’s understand the physical significance of it, let’s consider this reaction now in a closed chamber we have metal, we have metal oxide solid, solid and oxygen gas and this is kept at a particular temperature and overall pressure P. Now it will have reaction, now when this reaction is taking place inside if we have oxygen and that partial pressure of oxygen is pO2.

So this is the partial pressure of oxygen that is there in the beginning of the reaction, so that means I can term it is to be this is the partial pressure oxygen present in the closed system in the beginning of the reaction. So now there will be reaction at that temperature, of course provided this forward direction free energy change is negative, interestingly here I am not putting delta 0 because we are not considering standard condition.

We are considering a free energy change if it is negative, so this thing will go this way and as per the equilibrium concept the forward reaction would be faster and once we start forming product phase the product phase would also like to go back at a different rate. But when these 2 rates are equal and those rates will not change with the time, so that means will reach a steady state but at the same time these 2 rates forward as well as backward rates are equal that time will achieve equilibrium.

But in the beginning of it will form oxide, so that means oxygen will be consumed by metal in order to form metal oxide. Now up to how long this oxygen will be consumed this will be consumed till it reaches pO2 equilibrium as if with the function of that particular temperature what where we are doing this oxidation. So till then till it reaches pO2 oxidation will continue, now once pO2 actual.

So that means this is I can say that this is actual oxygen present in the beginning of the reaction till pO2 is equal to pO2 equilibrium temperature then oxidation would cease and the system would reach equilibrium. So that means in this case at least we are considering that pO2 actual is greater than pO2 equilibrium temperature and that is what we have and then it reaches there these are the oxidation, now if a condition is this is condition 1.

If the condition in case of second condition where pO2 actual in the system is less than pO2 equilibrium temperature and let's say that time in this case we have started with M and oxygen only, that time that is what in the beginning oxidation is whatever would be the pO2 oxidation will start and then it will try to reach pO2 equilibrium at the temperature. And if this partial pressure is greater than this then only it will try to reach there.

But if we contain M MO solid as well as oxygen all 3 are present and if this partial pressure in that system at that temperature is less than the partial pressure of oxygen that should be present when this reaction reaches equilibrium. That case the system would always try to achieve this partial pressure of equilibrium, partial pressure of oxygen at that temperature. So in that case we have to increase this pressure actual pressure, how can we increase the pressure.

Because here the system is already closed that means we are not allowing any mass flow with the surrounding. So something has to happen within, so now if I see $2M + O_2 = 2MO$, so now if this is reaching equilibrium then the partial pressure would be this but the actual pressure is oxygen pressure is less than this equilibrium pressure. But the system would try to reach this value, so in order to do that this particular MO should go back to M and O2 that means the reduction will take place.

And then only oxygen partial pressure would increase, actual would increase and then which will tend to reach pO2 equilibrium temperature. So this is the physical significance of this pO2, in a system if we have M MO and O2, if that system contains at a particular temperature contains oxygen which is whose partial pressure is less than the equilibrium partial pressure of oxygen then the metal oxide will reduce and for metal and oxygen that means metal oxide would become unstable till it reaches equilibrium again.

But if there is a system where pO2 is pO2 actual of the system is more than the pO2 equilibrium at that temperature then the metal would definitely get oxidized, in order to reduce the partial pressure and reach pO2 equilibrium at that particular temperature. So this is the physical significance of this pO2 equilibrium temperature, so we can have a small mathematical treatment too.

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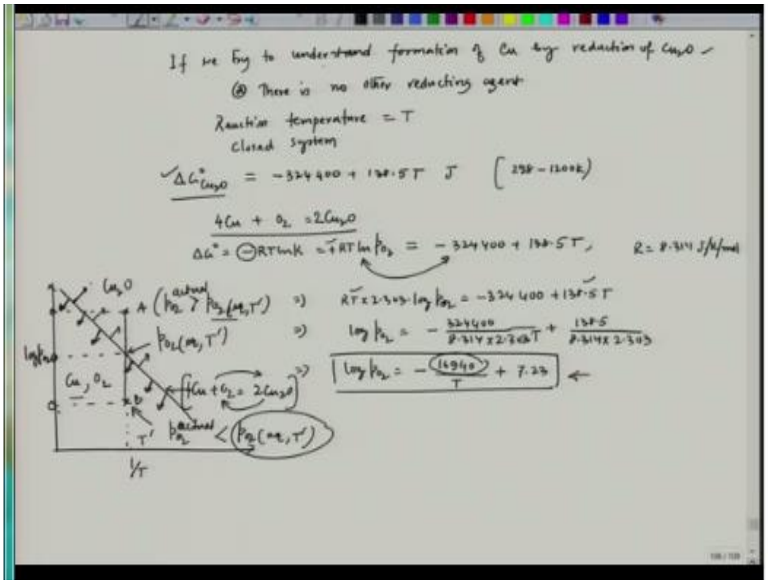

If we try to understand formation of Cu by reduction of Cu_2O ✓

ⓐ There is no other reducing agent

Reaction temperature = T

Closed system

✓ $\Delta G^\circ_{Cu_2O} = -324400 + 138.5T$ J (298 – 1200K)

$4Cu + O_2 = 2Cu_2O$

$\Delta G^\circ = -RT\ln K = +RT\ln p_{O_2} = -324400 + 138.5T$, R = 8.314 J/K/mol

$\Rightarrow RT \times 2.303 \log p_{O_2} = -324400 + 138.5T$

$\Rightarrow \log p_{O_2} = -\frac{324400}{8.314 \times 2.303T} + \frac{138.5}{8.314 \times 2.303}$

$\Rightarrow \boxed{\log p_{O_2} = -\frac{16940}{T} + 7.23}$ ←

So for example if we try to see understand formation of copper by reduction of CuO if we try to this is the, this we want and we do not have any other reducing agent. So the reduction should happen by modulating the partial pressure of oxygen only at a particular reaction temperature see if we try to see let's understand and a condition is there is no other reducing agent, so this is happening at a particular temperature.

So that means it will try to reach equilibrium reaction temperature is let's say T and this is closed system. So that case where you first see standard free energy change for CuO and which can be written as + 138.5 T joule, so this is the expression this is the free energy standard free energy change of CuO varies with temperature like this. And now we know and this is valid within the temperature range of in this range this is valid.

So now I know if we write this equation oxidation reaction, so this is the reaction, so that case I can write

$$\Delta G^o = -RT\,lnK = +RT\,lnp_{O_2}$$

and remember only changes this - sign and there is a positive sign because this was in the denominator. So when you change it that time it becomes positive mark positive sign, so now this can be related to this can be written as 324 T. So I can write if we try to simplify this equation RT * 2.303 log pO_2 = 324 400, R is 8.314 * 2.303 + this T is coming.

So this T will come here and T and this T would get cancelled for this case 8.314 into 2.303 and we know R which is a gas constant is 8.314 joule R Kelvin per mole. So this is the equation we are getting, so in the simplified form, so this is this data is taken from a book written by this book on introduction to the thermodynamics of materials by David R Gaskell this a classic book, so there from we have taken this data.

Now once we know this equation, I can find out relation between log pO2 with 1 by temperature. So you can calculate these values but the plot would be having a negative slope of this one, so this will be the slope. Now any temperature if you consider let's say this is a temperature T prime, so I can draw a line. So this is the equation this line indicating the equilibrium equation bit for this is the for this equation.

Now if I draw a line like this, so at that temperature this point corresponds to pO2 equilibrium T prime. Now if I try to see at this location as well as this location this is let's say A, this is B now A pO2 is actually greater than pO2 equilibrium T prime. So since it is equally greater than, so that means this system will try to go from this to this oxide will form, why because this is a closed system and it will try to reach this pO2 equilibrium T prime, at T prime what is the equilibrium partial pressure of oxygen for this reaction equilibrium.

So the excess oxygen needs to be consumed and if we have enough amount of copper in that closed system this copper will try to consume that excess oxygen and try to read this for the equilibrium attainment. So that means this side will have Cu2O, now if I consider this here the value of pO2 and this value of pO2 is coming like this, this is the value and here this is the value and here this is the value.

So at this point I could see that pO2 actual that means system is A is less than pO2 T prime, fine. So that means the system would always try to reach this pO2 this value but already the partial pressure of oxygen present in the system is lower than that. So in order to increase this partial pressure of oxygen the system would try to go reverse, so that means Cu2O would reduce, so that means this side would have CuO as well as O2.

So that means whenever we try to find a reduction condition from of Cu2O without having any reducing agent at a particular temperature, that case I have to choose a partial pressure of oxygen, so that we always remain left to this. So if we stay this line if you stay lower to this, this direction then only will have reduction of Cu2O. But if by chance if we go the partial pressure of oxygen at a particular reaction temperature, if it goes on the right side of this particular line then of course Cu2O 2O will form.

So that indicates that by controlling the partial pressure of oxygen one can have a reduction condition of that oxide or one can have oxidizing condition of a metal depending on this value and the equation what we are getting after doing little bit of simplification of this equation. So let me stop here, we will continue our discussion and this is the initiation of one interesting diagram which is called Ellingham diagram.

And by looking at Ellingham diagram one can decide at a particular temperature at a particular partial pressure of oxygen whether one metal will oxidize or not whether if we have 2 oxides and 2 metals present in a closed system at a particular temperature which metal would get oxidize and which metal which oxide would reduce those can be told with a quantitative analysis that can be given from this Ellingham diagram. So those we will try to understand Ellingham diagram in our next lecture. Let’s stop here, thank you very much.