Corrosion – Part I
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Lecture - 12
Derivation of Nernst Equation

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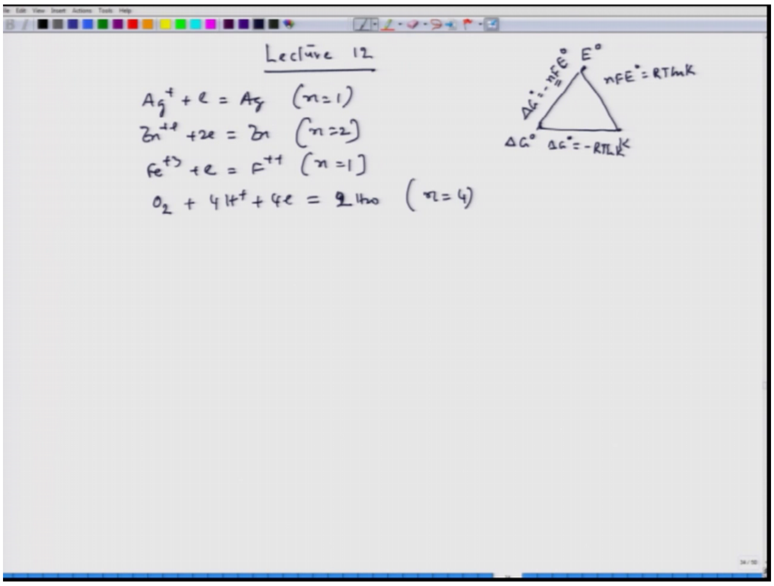

Lecture 12

$Ag^+ + e = Ag$ $(n=1)$

$Zn^{++} + 2e = Zn$ $(n=2)$

$Fe^{+3} + e = F^{++}$ $(n=1]$

$O_2 + 4H^+ + 4e = 2H_2O$ $(n=4)$

Let us start lecture 12. In lecture 11 we have learnt this triangle delta G 0 K and E 0, where this I can write minus n F E 0 delta 0 equal to minus RT ln K and this one would be n F E 0 equal to RT ln K. So, this is the relation between all 3 quantities. Now, we will go ahead with this triangle and try to see if we can have some sort of correlation between potential cell potential or the redox reaction potential with the equilibrium constant.

Now, to start with since we are talking about n we are not fixing what is that value of n, the n could be for example, Ag plus plus E equal to Ag, where n equal to 1, zinc plus plus plus 2 e equal to zinc, where n equal to 2 we can have Fe plus 3 plus e equal to Fe plus plus where n equal to 1 again. Even we can have this relation where n equal to 4.

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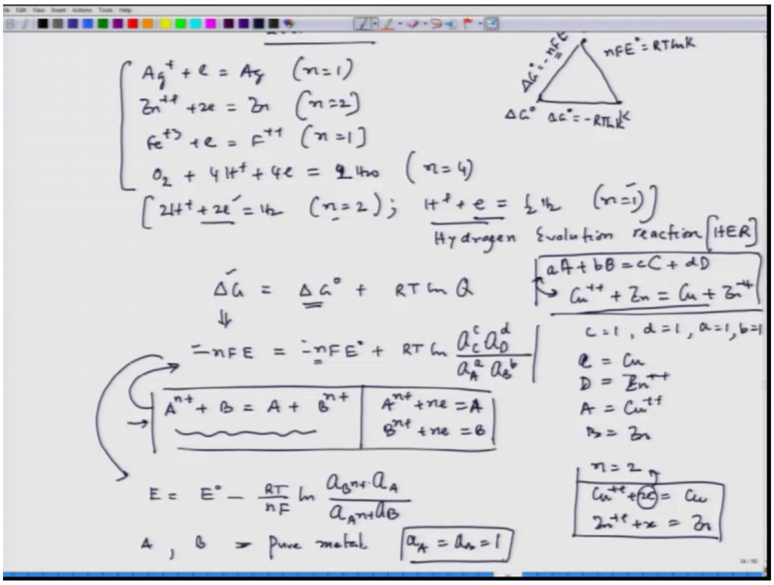

$Ag^{+} + e = Ag \quad (n=1)$

$Zn^{++} + 2e = Zn \quad (n=2)$

$Fe^{+3} + e = F^{++} \quad (n=1)$

$O_2 + 4H^{+} + 4e = 2H_2O \quad (n=4)$

$[2H^{+} + 2e = H_2 \quad (n=2); \quad H^{+} + e = \frac{1}{2}H_2 \quad (n=1)]$

Hydrogen Evolution reaction [HER]

$\Delta G^{\circ} = -nFE^{\circ}$, $nFE^{\circ} = RT\ln K$, ΔG°, $\Delta G^{\circ} = -RT\ln K$

$aA + bB = cC + dD$

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

$c=1, d=1, a=1, b=1$

$C = Cu$

$D = Zn^{++}$

$A = Cu^{++}$

$B = Zn$

$n = 2$

$Cu^{++} + \bigcirc{2e} = Cu$

$Zn^{++} + 2e = Zn$

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

$$\Downarrow$$

$$-nFE = -nFE^{\circ} + RT\ln \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

$A^{n+} + B = A + B^{n+}$ | $A^{n+} + ne = A$, $B^{n+} + ne = B$

$$E = E^{\circ} - \frac{RT}{nF}\ln \frac{a_{B^{n+}} \cdot a_A}{a_{A^{n+}} a_B}$$

$A, B \to$ Pure metal $\boxed{a_A = a_B = 1}$

And we have taken 4 reduction reaction and there is one more reduction reaction which we call it H 2, where n equal to 2 interestingly if I write this way then n equal to 1. We will see later on that whether you take this reaction or that reaction whether you take this reaction or this reaction it does not matter you will get the same potential value. But, from the reaction since we had to electron is involved.

So, that is what n becomes two and here one electron is involved that is what n equal to 1, but both the cases if the concentration of hydrogen ion remains fixed. And if the hydrogen ion hydrogen gas pressure is maintained at one atmosphere pressure, then both the reactions it will lead to same potential of that particular electron. And this reaction is also called hydrogen evolution reaction or it is shortly call at called as HER which is Hydrogen Evolution Reaction. So, this is very important reaction in electrochemistry.

Now, let us start with this, ok since we cannot write K because, we are taking non standard values that is what we write Q reaction quotient. And this will be standard when this goes to equilibrium and that time this K becomes 1, K becomes this Q becomes Q and this becomes my standard change in free energy. Now, we can write it as minus n F E equal to minus n F E 0 plus RT ln activity of C to the power c, activity of D to the power d activity of a b. Now, this is almost similar like now, where c equal to 1, d equal to 1, a equal to 1 and b equal to 1 as well as that time C goes to copper, D goes to zinc plus plus, A copper plus plus, B equal to zinc. So, like this a A plus b B equal to c C plus d D, I am trying to correlate electrochemistry with the chemical reaction.

Now, since we are not specifying here the number of electrons associated with this particular process n equal to 2 why copper plus plus plus 2 e equal to copper since our convention is we will always take reduction reaction and zinc plus plus plus 2 e equal to zinc so, the n becomes 2. And since we are taking n equal to n, so then my reaction pattern would be A n plus plus B equal to A plus B n plus. So, that case so exact this kind of similarity if you see this and this two and then of course, this two they are quite similar only thing is the numbers are changing. So, if we take this then we can write this equation.

Now, from this I can write E equal to E 0 plus RT n F ln. Now, since we are writing with reference to this reaction a B n plus a A, ok so, this becomes like this. So, I have to put minus here because, this minus minus would go and the minus would come here. Now, if we take A and B are pure metal that case a A equal to a B I can write it as this.

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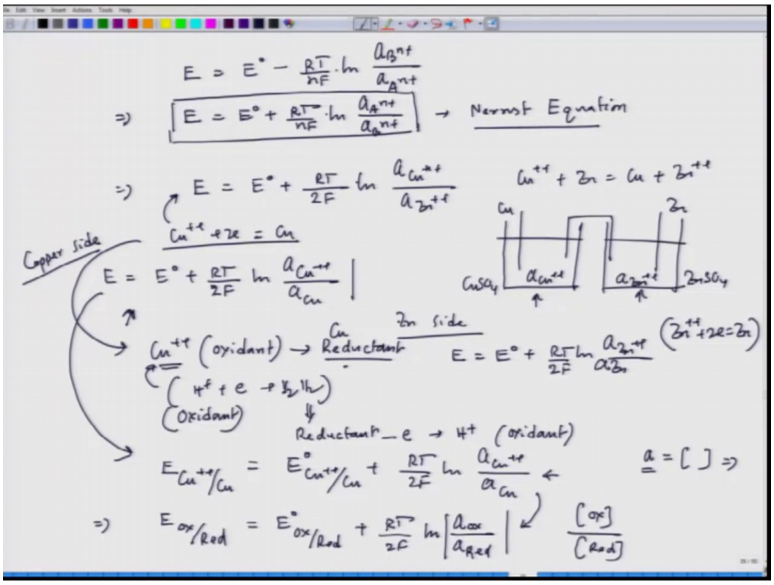

$$E = E^\circ - \frac{RT}{nF} \cdot \ln \frac{a_{B^{n+}}}{a_{A^{n+}}}$$

$$\Rightarrow \boxed{E = E^\circ + \frac{RT}{nF} \cdot \ln \frac{a_{A^{n+}}}{a_{B^{n+}}}} \rightarrow \text{Nernst Equation}$$

$$\Rightarrow E = E^\circ + \frac{RT}{2F} \ln \frac{a_{Cu^{++}}}{a_{Zn^{++}}}$$

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

Copper side

$Cu^{++} + 2e = Cu$

$$E = E^\circ + \frac{RT}{2F} \ln \frac{a_{Cu^{++}}}{a_{Cu}}$$

Zn side

$$E = E^\circ + \frac{RT}{2F} \ln \frac{a_{Zn^{++}}}{a_{Zn}} \quad (Zn^{++} + 2e = Zn)$$

Cu^{++} (oxidant) → $\overset{Cu}{\text{Reductant}}$

$(H^+ + e \rightarrow \tfrac{1}{2} H_2)$

(Oxidant)

Reductant − e → H^+ (oxidant)

$$E_{Cu^{++}/Cu} = E^\circ_{Cu^{++}/Cu} + \frac{RT}{2F} \ln \frac{a_{Cu^{++}}}{a_{Cu}}$$

$a = [\ ] \Rightarrow$

$$\Rightarrow E_{ox/Red} = E^\circ_{ox/Red} + \frac{RT}{2F} \ln \left| \frac{a_{ox}}{a_{Red}} \right| \quad \frac{[ox]}{[Red]}$$

So, my equation becomes E equal to E 0 minus RT n F ln a B n plus n plus. We can write so, we are just changing this positive sign we are changing denominator and numerator and then accordingly we can change it. So, this is a very important relation. Now, from the look of this who have little idea you will say that this is nothing but Nernst equation.

Now, we would look beyond this Nernst equation we would try to see K, this is for the overall reaction. Now, we would try to see what happens on the one beaker and what happens on the other beaker. Now, if we write this thing in terms of copper and zinc reaction, so then we can write E equal to E 0 plus RT 2 F ln a copper plus plus zinc plus plus so, that time n becomes 2 for this reaction.

Now, let me see to cell this is my soil bridge; this is a copper terminal, zinc terminal, copper sulphate, zinc sulphate. So, we have some activity of copper plus plus ion activity of zinc plus plus ion. Now, if I try to look at the reaction copper plus plus plus 2 e equal to copper this is also electrochemical reaction, for that also we can construct equation like this.

So, that would become E equal to E 0 plus RT 2 F ln a activity of copper plus plus activity of copper. Now, this is a relation for copper side and for the zinc side this is copper side and zinc side I can write other relation reaction is zinc.

Now, both this, now look at this let me look at this. So, this relation if I see copper plus plus is nothing but oxidant and then it goes to reductant how do I know that oxidant and reductant because, again go back to hydrogen this relation and where we know that hydrogen gas is a very good reducing agent. That is what in some cases when we try to avoid oxidation of metal during sintering of some metal we do quartz hydrogen gas. So, the hydrogen gas actually reduces the oxides that are forming on the top surface of that metal. So, hydrogen is a very good popular reducing agent so, this becomes my reductant.

So, reductant would always get oxidized so, reduction reductant minus e equal to H plus. So, this becomes my oxidant so, this is oxidant. Similar way if you see that here the iron is accepting electron and forming reductant so, the oxidant can only get reduced. So, our convention is fine. Now, from this can I not write E since I am converting copper plus plus to copper. So, I can write copper equal to E 0 copper plus plus copper plus RT 2 F ln a copper plus plus activity of copper.

In general can I not also write, I can also write this this is a generalized form. Now, instead of this I can also replace this with concentration of ox and concentration of red if I see that the solution is dilute. So, in case of dilute field solution a becomes concentration, activity becomes concentration because that time activity quotient activity coefficient goes to 1 in case of dilute solution. Dilute solution extremely dilute case of course, but in general we can take it as a kind of simplification.

This is valid in case of ideal case, an ideal situation can arise when the system is dilute, because the interaction between the molecules or the spaces could be minimised. And what do you mean by dilute or ideal system? Ideal system is the interactions between the spaces is nil, that means, there is no interactions. So, that is normal that is possible in case of dilute medium.

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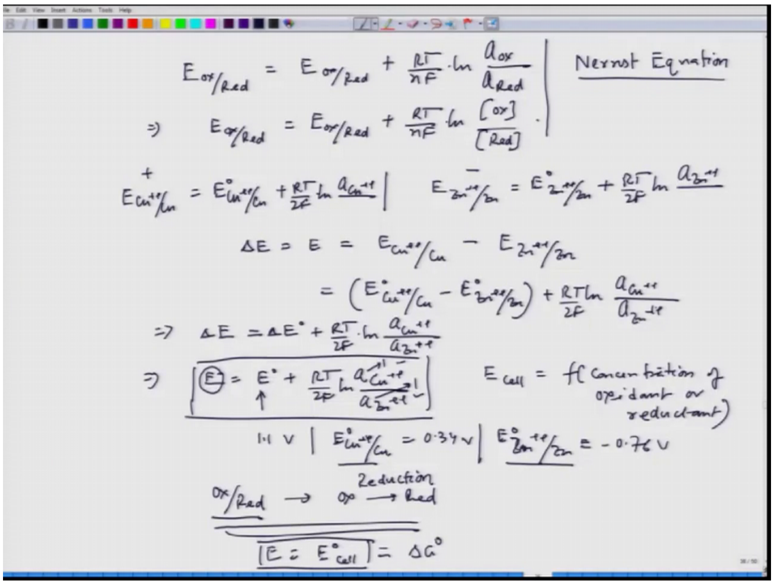

$$E_{ox/Red} = E_{ox/Red} + \frac{RT}{nF} \cdot \ln \frac{a_{ox}}{a_{Red}}$$

Nernst Equation

$$\Rightarrow E_{ox/Red} = E_{ox/Red} + \frac{RT}{nF} \ln \frac{[ox]}{[Red]}.$$

$$\overset{+}{E_{Cu^{++}/Cu}} = E^{\circ}_{Cu^{++}/Cu} + \frac{RT}{2F} \ln a_{Cu^{++}}$$

$$\overset{-}{E_{Zn^{++}/Zn}} = E^{\circ}_{Zn^{++}/Zn} + \frac{RT}{2F} \ln a_{Zn^{++}}$$

$$\Delta E = E = E_{Cu^{++}/Cu} - E_{Zn^{++}/Zn}$$

$$= \left(E^{\circ}_{Cu^{++}/Cu} - E^{\circ}_{Zn^{++}/Zn}\right) + \frac{RT}{2F} \ln \frac{a_{Cu^{++}}}{a_{Zn^{++}}}$$

$$\Rightarrow \Delta E = \Delta E^{\circ} + \frac{RT}{2F} \cdot \ln \frac{a_{Cu^{++}}}{a_{Zn^{++}}}$$

$$\Rightarrow \boxed{\textcircled{E} = \underset{\uparrow}{E^{\circ}} + \frac{RT}{2F} \ln \frac{a_{Cu^{++}} \to 1}{a_{Zn^{++}} \to 1}}$$

$E_{cell} = f$(concentration of oxidant or reductant)

$1.1 \text{ V} \mid E^{\circ}_{Cu^{++}/Cu} = 0.34 \text{ V} \mid E^{\circ}_{Zn^{++}/Zn} = -0.76 \text{ V}$

$$ox/Red \rightarrow ox \xrightarrow{Reduction} Red$$

$$\boxed{E = E^{\circ}_{cell}} = \Delta G^{\circ}$$

So, I can write E equal to ox red equal to E ox red plus RT 2 F. Now, instead of 2 I can generalize n F ln a ox red or I can write. So, these two the generalized statement of Nernst equation, why you are writing ox and red? See this is oxidant this is reductant which is copper and similarly we are writing this and from this we are writing this and these are coming this is when we do not know whether the system is dilute and this is when the system is dilute.

Now, similar pattern we can write in case of zinc side, zinc side we can write E zinc plus zinc equal to E 0 zinc plus zinc plus RT 2 F ln and the copper side is. Since we know that copper is pure and zinc is also pure in the metal part this goes to 1, this goes to 1 so, then we are getting only this term and only this term. Now, this side is positive, this side is negative, as per our observation that the current is flowing from copper side to the zinc side.

So, then the potential difference would be which is nothing but E 0 equal to not E 0, because we are not specifying that whether the system has reached a standard situation because, the activity of copper plus plus and activity of copper zinc plus plus may not be 1. So, then this becomes E which is nothing but or we can write; this is the same one what we have seen here. So, we can also get to the same equation considering the individual cells or the considering individual half cell.

So, this relation will enable me to find out E as a function of concentration of copper plus plus and zinc plus plus this is extremely important statement. The E cell would be function of concentration of oxidant or reductant. Since this is a fixed quantity which is 25 degree Celsius, 1 atmosphere pressure in case of this copper zinc system we have this to be 1.1 Volt. And the half cells are E 0 copper plus plus copper equal to 0.34 and E 0 zinc plus plus plus zinc equal to minus 0.76 Volt.

And as we have already mentioned that we would all the time talk about the reduction process and this entire relations are on the basis of reduction because whenever I am writing ox slash red. That means, ox is going to red it means that ox red it means that ox going to red or we are having reduction this is important.

So, reduction potential on one half cell is this and reduction potential of other half cell is this and also this relation tells me that the what would be the cell potential if we change the concentration. Now, if we make it 1, this goes to 1, this goes to 1 then of course, E becomes my E 0 cell, which is the standard potential difference. This also becomes delta G 0 because, we are considering the standard value. Once we know this now, we have to look at the value the quantification.

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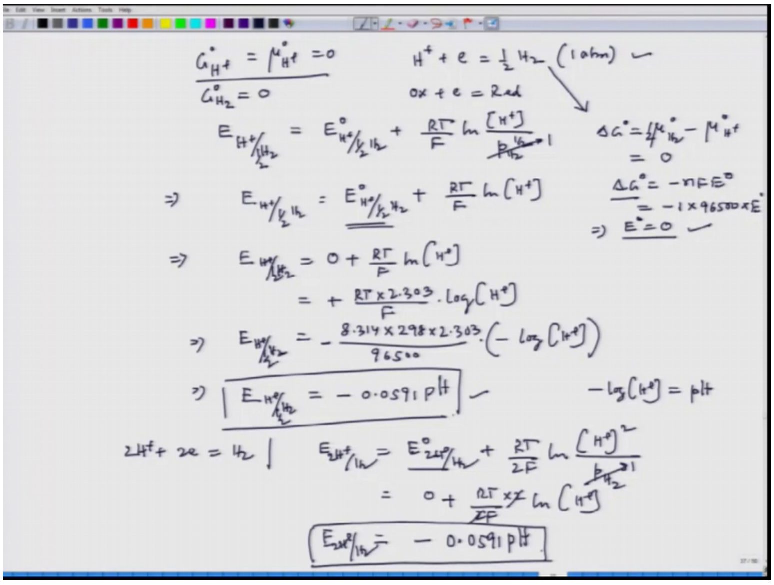

$G^{\circ}_{H^+} = \mu^{\circ}_{H^+} = 0$

$G^{\circ}_{H_2} = 0$

$H^+ + e = \frac{1}{2}H_2 \ (1\,atm)$

$Ox + e = Red$

$E_{H^+/\frac{1}{2}H_2} = E^{\circ}_{H^+/\frac{1}{2}H_2} + \frac{RT}{F}\ln\frac{[H^+]}{\cancel{p_{H_2}^{1/2}} \rightarrow 1}$

$\Delta G^{\circ} = \frac{1}{2}\mu^{\circ}_{H_2} - \mu^{\circ}_{H^+} = 0$

$\Rightarrow E_{H^+/\frac{1}{2}H_2} = \underline{\underline{E^{\circ}_{H^+/\frac{1}{2}H_2}}} + \frac{RT}{F}\ln[H^+]$

$\underline{\Delta G^{\circ}} = -nFE^{\circ} = -1 \times 96500 \times E^{\circ}$

$\Rightarrow \underline{E^{\circ} = 0}$

$\Rightarrow E_{H^+/\frac{1}{2}H_2} = 0 + \frac{RT}{F}\ln[H^+]$

$= + \frac{RT \times 2.303}{F}.\log[H^+]$

$\Rightarrow E_{H^+/\frac{1}{2}H_2} = -\frac{8.314 \times 298 \times 2.303}{96500}.(-\log[H^+])$

$\Rightarrow \boxed{E_{H^+/\frac{1}{2}H_2} = -0.0591\,pH}$

$-\log[H^+] = pH$

$2H^+ + 2e = H_2 \mid E_{2H^+/H_2} = \underline{E^{\circ}_{2H^+/H_2}} + \frac{RT}{2F}\ln\frac{[H^+]^2}{\cancel{p_{H_2}} \rightarrow 1}$

$= 0 + \frac{RT \times \cancel{2}}{\cancel{2}F}\ln[H^+]$

$\boxed{E_{2H^+/H_2} = -0.0591\,pH}$

Now, in order to quantify since we have already told that G 0 H plus or we can tell it as mu 0 H plus equal to 0, 25 degree Celsius one atmosphere pressure. Then let us look at hydrogen evolution reaction. Now, in this case let us say the hydrogen gas which is evolving from this reaction is maintained at 1 atmosphere and this is also following this route, can write E H plus half H 2 dilute and if we considered to be that concentration of H plus ion and pressure of H 2.

Since we have considered this is to be 1, 1 atmosphere, so this turns out to be plus H plus. We have to find out this quantity since we know this another convention is 1 atmosphere pressure 25 degree Celsius. So, if we both the quantities are 0 then for this reaction free energy change delta G 0 would be mu half H 2 minus mu 0 H plus equal to 0.

Now, delta G 0 equal to minus n F E 0, n equal to 1 for this reaction n equal to 1 F is equal to 96500 into E 0. So, this is 0, so, E 0 equal to 0, this is interesting the standard reduction potential of hydrogen evolution reaction is here. So, this goes to E H 2 equal to 0 plus RT F ln H plus. Now, ln H plus I can write in this form minus RT ok, into 2.303 by F log H plus, I can write 8.314, 298 Kelvin 2.303, 96500. So, I am taking minus here in the bracket. So, I am taking another minus so, if you remove the bracket it would become plus.

So, E H plus half H 2 equal to this. So, if I calculate this let me calculate 8.314 into 298 into 2.303 divided by 96500 equal to this becomes this. Now, interestingly minus log H plus is nothing but pH. So, I can remove this term I can have p H this is a crucial relation also we will use this relation. Now, interestingly if we have this reaction would there be any change in this reaction for in this particular equation.

Let us see so, that time E H plus H 2 equal to E 0 2 H plus H 2 plus RT 2 F ln H plus square p H 2 so, this becomes p H 2, this is 1. So, it is becomes this should be also 0 because in this case this half term will go off and then finally, you will see that E 0 becomes 0. So, this is 0 plus RT 2 F and this 2 I can take it out ln H plus. So, this 2 2 gets cancelled finally, we get again if we put those values 0.0591 p H.

So, this reaction and this equation both the equations are same. So, if we go and look at this we said that both the reactions have the same electrochemical potential. So, it is also showing that they are same electrochemical potential and their slopes are also same.So, let us stop here we will continue our discussion on electrochemical nature of corrosion and also the associated thermodynamics of corrosion.

Thank you.