Corrosion – Part I
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Lecture – 31
Electrical Double Layer and Polarization

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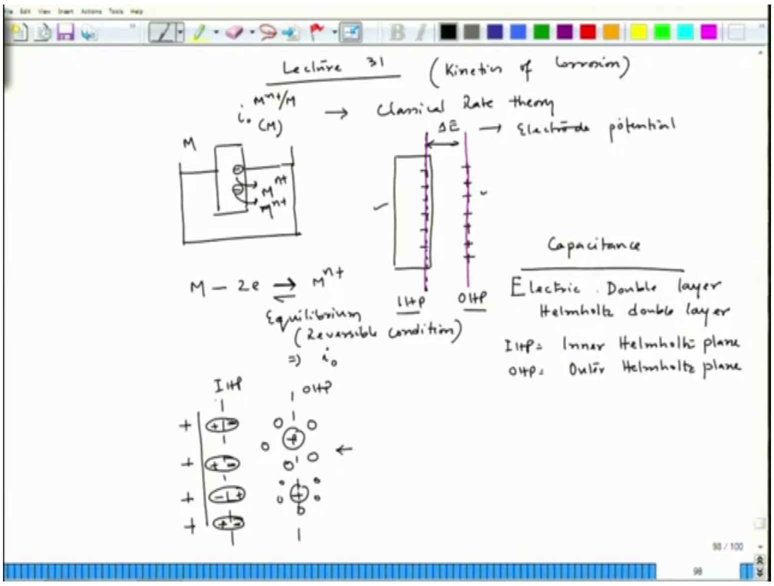

Let us begin lecture – 31 and we will continue on Kinetics of Corrosion. So, we have seen i 0 on metal surface for this. So, like that we have i 0 for everything every reaction and that time we have to mention the metal surface because that reaction is taking place on the metal surface.

Now, let us look at this from this classical rate theory. Since classical rate theory says that there would be jump of metal atom from one surface to another and this is a thermally activated process. So, that is what it has to have a barrier which is called as activation barrier and then, once it crosses that barrier it goes to the other surface. And, this barrier height decides the rate at which this metal would go from one surface to another.

When we dip a metal in a solution aqua solution this is metal the metal ion forms metal ions forms. Now, these metal ions would keep forming, but at the same time when it released to the solution it will leave negative charges on the metal surface. So, you are having a situation this is metal surface metal ions would go to the solution or instead of

M n plus let us put in the form of positive charge. So, we have positive charge formation positive charge formation and then we have to maintain the neutrality. So, the negative charges will be left to the metal surface and these two would try to balance each other. Now, when this forms then of course, the reverse reaction also forms.

Now, after some time they reach equilibrium or reversible or I would say that it establishes i 0 and then because of this electrostatic interactions are positive and negative charges they would form a kind of surface on metal surface as well as on the solution surface very close vicinity to the metal surface and that time we have two boundaries and that boundaries or two surfaces this is one surface and this is another surface these two surfaces will be in close vicinity and they will try to cancel out the charge they would try to balance the charges each other.

And, these two layers are called electric double layer electric double layer and this was the very fast concept of electric double layer and it is termed as Helmholtz double layer. And, the inside part is called IHP and out one outer one is called OHP and then IHP is nothing, but inner double layer inner Helmholtz plane and OHP outer Helmholtz plane and when this double layer forms it is associated with a capacitor capacitance. And since they are charged surfaces, we have a potential difference creation and these potential differences nothing, but the electrode potential or the potential on that metal surface for that reaction.

Now, these two planes this is a very primitive concept of electric double layer and then later on this has been modified and now when this metal ions forms they get solvated because water is a polar molecule and because of that polar molecule presence this positive charge is solvated by water molecule and on the metal surface since there are negative charges the water molecule would get attracted depending on what charges are there on the metal surface. If it is negative charge in the case what we have considered here, the water molecule will be distributed like this. Sorry, this is plus, this is plus and this side would be negative charges.

So, like this rearrangement of water molecules take place takes place. Now, the center of this particular water molecules which are close proximity to the charge metal surface and the center of this positive ion solvated vapors solvated ions positive ions close vicinity to the water molecules which are arranged close to the charged metal surface that becomes my OHP and this is my IHP and because of this situation the double layer this is becoming my double layer and that also leads to a potential difference and also finally, it would lead to electrode potential.

But, this is an advanced level of consideration of the surface we would stay on this preliminary consideration of double layer which is Helmholtz double layer where we do not consider this salvation as well as water molecule polar molecules distributing close to the charged metal surface depending on the charge of the metal surface. And, if it for example, if it is positive charge, then this becomes. So, this water molecule would be like this instead of positive charge is close to the metal surface negative side of the polar molecule would be close vicinity would be directing towards the metal surface.

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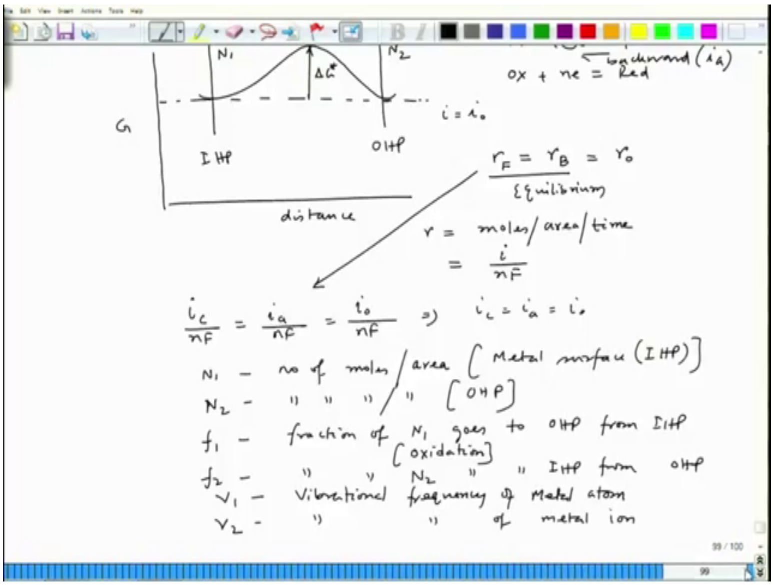

ox + ne = Red

$\underline{r_F = r_B} = r_0$

{Equilibrium}

r = moles/area/time

$= \frac{i}{nF}$

$\frac{i_c}{nF} = \frac{i_a}{nF} = \frac{i_0}{nF} \Rightarrow i_c = i_a = i_0$

N_1 – no of moles / area [Metal surface (IHP)]

N_2 – " " " / " [OHP]

f_1 – fraction of N_1 goes to OHP from IHP [oxidation]

f_2 – " " N_2 " " IHP from OHP

ν_1 – Vibrational frequency of Metal atom

ν_2 – " " of metal ion

So, now, if we consider this particular situation we can constitute like this is IHP and this is OHP and this is metal and this is n plus. Or we can call it as reductant or we can call it as red and this is nothing, but oxidant or ox. So, M n plus n e equal to M or ox plus ne equal to red and when this metal goes to metal ion or metal ion goes to metal they would not go straight way like this.

Since it is a thermally activated process, they will go over a energy barrier and this they are on the same value if we consider G free energy with distance. So, they will be on the same plane when i equal to i 0. Why, because if I consider the rate forward rate and backward rate. So, let us say this is my forward and this is my backward. So, rate r in terms of if we consider rate or we simply say r forward equal to we can consider it to be same as r backward and when this situation arrives it reaches equilibrium or it calls it we can call it as r 0 and rate of if we consider rate in terms of moles per unit area per unit time. So, this would be equal to i divided by n F, we have already seen this particular formula.

So, this turns out to be i forward is nothing, but i c backward is nothing, but i a i c divided by n F equal to i a divided by n F equal to i 0 n F. So, then it terms out to be i c equal to i a equal to i 0. So, that means, the rate at which forward direction reaction happens the similar rate the backward reaction also happens. Now, if this is this barrier is nothing, but delta G star and if we consider n one or n prime or I would say n 1 let us put it as capital N 1 in order to differentiate between this n and this N.

This is N 1, this is N 2; this N 1 and N 2 N 1 is number of moles per unit area on metal surface or rather IHP and N 2 is equal to number of moles per unit area on OHP; that means, the center of the metal ion align in front of the metal surface f 1 is nothing, but or the fraction N 1 goes to OHP from IHP. So, this is nothing, but oxidation, f 2 is the fraction of N 2 goes to IHP from OHP and nu 1 is vibrational frequency of metal atom and nu 2 is vibrational frequency of metal ion.

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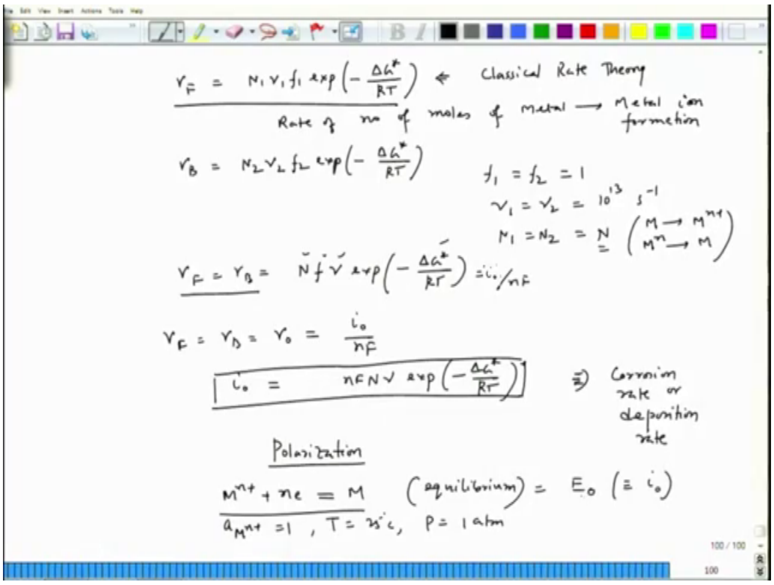

$\underline{r_F = N_1 \nu_1 f_1 \exp\left(-\frac{\Delta G^*}{RT}\right)}$ ← Classical Rate Theory

Rate of no of moles of metal → Metal ion formation

$r_B = N_2 \nu_2 f_2 \exp\left(-\frac{\Delta G^*}{RT}\right)$

$f_1 = f_2 = 1$

$\nu_1 = \nu_2 = 10^{13}\ s^{-1}$

$N_1 = N_2 = \underline{N}$ $\begin{pmatrix} M \rightarrow M^{n+} \\ M^{n} \rightarrow M \end{pmatrix}$

$\underline{r_F = r_B} = \check{N} \check{f} \check{\nu} \exp\left(-\frac{\Delta G^*}{RT}\right) = i_0/nF$

$r_F = r_B = r_0 = \frac{i_0}{nF}$

$\boxed{i_0 = nFN\nu \exp\left(-\frac{\Delta G^*}{RT}\right)}$ ⇒ Corrosion rate or deposition rate

Polarization

$\underline{M^{n+} + ne = M}$ (equilibrium) = E_0 ($\equiv i_0$)

$a_{M^{n+}} = 1$, $T = 25^\circ c$, $P = 1\ atm$

Then we can write this r forward equal to N 1 nu 1 f 1 exponential minus delta G star by RT y. So, this is as per classical rate theory and then multiplication of these quantities this is basically this entire equation indicates the rate of metal number of moles of metal atom; metal going to ion formation and this is basically a thermally activated process. It indicates that metal atom should jump over this barrier and then should go to the OHP. Similar the backward reaction r B would be N 2 nu 2 f 2 exponential minus delta G star by RT.

Now, if I consider that whatever metal atom goes to the metal ion surface everything gets it gets absorbed there or the metal ions which are getting reduced they all will deposit on the metal surface. So, then f 1 equal to f 2 equal to 1; so, since this is a fraction, so, this becomes 1 because whatever metal ions are forming they are going to the OHP or whatever metal ions are reducing they are going onto the IHP.

Now, nu 1 equal to nu 2 is of the order of 10 to the power 13 per second and N 1 and N 2 what we have decided let us say N 1 equal to N 2 equal to N which is number of moles of metal ions or either the metal atom, metal those are converting to either metal or metal ions. So, that means, for both the situation going to M n plus or M n plus going to M both the cases this becomes similar number because we have assumed that whatever metal ions are forming they are getting absorbed on the metal ion surface which is OHP or whatever metal ions are producing they are also becoming part of IHP.

So, then I can write r F equal to r B equal to N f nu exponential minus delta G star RT now we know from the previous discussion as we have seen here we can use this equation. So, we know r F equal to r B equal to r 0 equal to i 0 by n F. Now, since we are considering that they are they are jumping over the same barrier this is same this all factors are same that is what they can be equated. So, this equal to i 0 by n F; so, i 0 equal to i 0 by n F; so, i 0 becomes n F N f nu exponential minus delta G star by RT and here F is considered as 1. So, I can remove this F. So, it becomes N f N nu.

This is an important derivation because this will be used up when we talk about polarization. So, we have an expression of i 0 with reference to the activation barrier which is delta G star. Now, we have already termed and then you see this is also becoming moles, this is current density our current density we can relate it to corrosion rate or deposition rate. So, this is not same as corrosion rate, but it can be related to.

Now, we have used one term called polarization. So, when we talk about polarization it means that it is a shift from the stable value. Now, we see that when M n plus n e M this is reaching equilibrium. So, we have a potential which is of course, giving a situation of i 0 which is exchange current density and if we have maintains standard value it would be E 0 so; that means, activity of M n plus equal to 1, temperature equal to 20 degree Celsius and pressure equal to 1 atmosphere pressure. So, then it becomes E 0 E 0.

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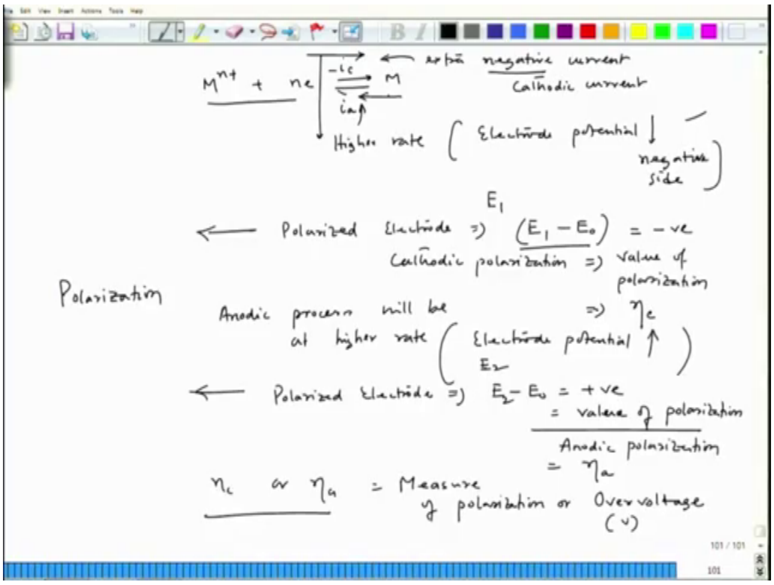

$M^{n+} + ne \underset{i_a}{\overset{-i_c}{\rightleftharpoons}} M$ ← extra negative current
Cathodic current

Higher rate (Electrode potential ↓ negative side)

Polarization

← Polarized Electrode ⇒ $(E_1 - E_0) = -ve$
Cathodic polarization ⇒ Value of polarization ⇒ η_c

Anodic process will be at higher rate (Electrode potential ↑ E_2)

← Polarized Electrode ⇒ $E_2 - E_0 = +ve$
= Value of polarization
Anodic polarization
$= \eta_a$

η_c or η_a = Measure of polarization or Overvoltage (v)

So, if this equilibrium is disturbed and how can we disturb this is i c this is i a with a negative sign. Let us say I supply little extra negative current this negative means we are supplying little extra cathodic current which is opposite to the anodic current. So, then this reaction would happen at higher rate. So, if it happens at a higher rate; that means, this reduction process happens at a higher rate in order to maintain that reduction current density it means that the electrode potential would switch to the negative side.

So, why negative side because when it switches to the negative side this metal surface is becoming more and more negative and that is why the electrons supply of electron to this reduction process would become easy. So, then it potential becomes let us say E 1, now the polarization would be this is called polarized electrode and that time the value of the polarization would be E 0 because now we have switched from E 0 to E 1. This is also negative since the potential goes to the negative side and this is the value of polarization or we call it eta c; c is nothing, but the cathodic.

Similarly, if we supply anodic current then the potential this anodic reduction, anodic process will be at higher rate. The way we have discussed here the electrode potential would increase from the standard value or the equilibrium value and we also call it as polarized electrode. And that time if the potential goes to E 2. So, E 2 minus E 0 is the positive quantity since the potential has moved on the positive side because we are actually taking this oxidation process at a much higher rate.

So, this becomes the value of polarization and when we have seen when we see that the potential increases from the reduction potential at that equilibrium condition, we call it anodic polarization. And when it is termed as eta a and when we have this situation we call it cathodic polarization and potential drops from the equilibrium value and the entire this polarized situation arrives because of polarization and this n c or n a. They are the measure of polarization or or we call it over voltage and this unit is nothing, but in volt.

So, from this particular information or the discussion what we see that the polarization happens because of the supply of extra current either in the positive side or negative side or either extra cathodic current or extra anodic current. And if we send extra cathodic current the potential drops from the equilibrium potential which is E 0 here and when we send extra positive current or we call it anodic current, then the potential increases from the equilibrium potential which is E 0 here also. And the difference in that potential we call it the measure of potential and in this case it is cathodic over polarization in this case it is anodic polarization.

And, now in the next lecture we would get into this polarization part and then try to see the relation between this over voltage and current density. Let us stop here.

Thank you.