Corrosion – Part I
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Lecture – 35
Tafel Plot and Activation Polarization

So, let us start lecture 35.

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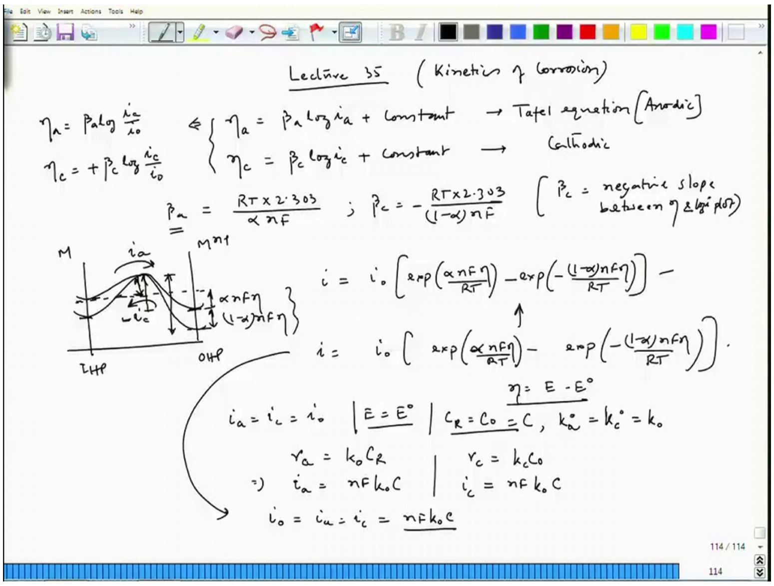

Lecture 35 (Kinetics of Corrosion)

$\eta_a = \beta_a \log \frac{i_a}{i_0}$ $\Leftarrow$ $\eta_a = \beta_a \log i_a + \text{Constant}$ → Tafel equation [Anodic]

$\eta_c = +\beta_c \log \frac{i_c}{i_0}$ $\quad$ $\eta_c = \beta_c \log i_c + \text{constant}$ → Cathodic

$\underline{\underline{\beta_a}} = \frac{RT \times 2.303}{\alpha nF}$; $\beta_c = -\frac{RT \times 2.303}{(1-\alpha) nF}$ [β_c = negative slope between η & $\log i$ plot)

$i = i_0 \left[\exp\left(\frac{\alpha nF\eta}{RT}\right) - \exp\left(-\frac{(1-\alpha)nF\eta}{RT}\right)\right]$ –

$\uparrow$

$i = i_0 \left[\exp\left(\frac{\alpha nF\eta}{RT}\right) - \exp\left(-\frac{(1-\alpha)nF\eta}{RT}\right)\right]$.

$\underline{\eta = E - E^0}$

$i_a = i_c = i_0$ | $\underline{E = E^0}$ | $\underline{C_R = C_O = C}$, $k_a^0 = k_c^0 = k_0$

$r_a = k_0 C_R$ | $r_c = k_c C_O$

$\Rightarrow i_a = nFk_0C$ | $i_c = nFk_0C$

$i_0 = i_a = i_c = \underline{nFk_0C}$

And we will continue our discussion on Kinetics of Corrosion. In fact, we have already reached to the state of state where we can find the relation between current density and over voltage. And that relation we have found in the last lecture which is i a equal to beta a log of i eta a which is anodic over voltage rather high over voltage value positive quantity i a plus constant. This is we termed it as a Tafel equation.

Similarly, for cathodic over voltage it was beta c log ic plus constant and they were you can this constant value also and if we try to write it the complete one which is n a equal to beta a log i a by i 0 and here it is eta c equal to minus beta c log i c by i 0.

So, this we can put it plus because I can take this negative sign minus sign into beta c and where beta a equal to RT into 2.303 divided by alpha n F and beta c equal to RT into 2.303 divided by 1 minus alpha n F. And these two equation these are same as Tafel's for anodic and this is for cathodic Tafel equation and this beta c this main as minuses minus sign is incorporated here.

So, that is what beta c is basically the negative slope between over voltage and i plot and this is definitely a positive slope between over voltage and i plot, which is the current density plot, rather I would say log i plot.

Now, these two equations we have derived from a basic Butler Volmer equation. We have two forms of Butler Volmer equation; one we have found out from consideration of atomic jump from one side to another which is inner Helmholtz plane to the outer Helmholtz plane. And that time we have this particular energy distribution initially it was like this and then we have considered that the anodic current density is higher than the cathodic current density.

So, that is what we have this kind of energy distribution plot which this one is alpha n F eta and this part is 1 minus alpha n F eta and this is M side this is M n plus side. So, this is ia and this side is ic with a negative sign because its flowing negative opposite to ia.

When they were equal when ic equal to ia they are experiencing same activation barrier, but when ia is higher than the ic then the activation barrier for the forward reaction is reducing; this is my activation barrier for the forward reaction and the backward reaction we are getting higher activation barrier.

So, that is what the rate of backward reaction is reducing. So, that time we are getting a equation of this short which is i 0 exponential alpha n F eta by RT minus exponential minus 1 minus alpha n F eta by RT. So, this with this consideration we would get to this particular equation what we have proven in the last lecture. Now, there is one more form which is i equal to n F k 0 concentration of oxidant exponential minus alpha n F.

If we consider the way we have considered here I can write the similar fashion which this one should be C R then; then it would be alpha n F eta by RT minus C O exponential minus 1 minus alpha n F eta by RT, where this eta was taken as E minus E 0. And remember in this case, the previous case what we have seen earlier if we go back to that particular expression go back to that particular expression. If you see this that time we have considered the reducive symmetry factor that alpha was reducive.

But in this current case we are considering oxidative reducing factor that is what this C R part is coming before then C O. Now, that time if we consider condition i a equal to ic equal to i 0 and that time E equal to E 0 and that case r a equal to k a C of R concentration of R and since it is E equal to E 0 that time we have considered it to be k 0.

And then I can convert into i a equal to n F k 0 C R and similarly I can convert r c equal to k c C O which I can write in this form C 0. And in that case we have considered one more consideration which is C R equal to C O equal to C if we consider and then in that situation k a 0 equal to k c 0 if you go back in the last lecture you can find it.

So, this I can consider as k 0. So, I can replace this C with the C R, C R with C as well as C, because I am considering that the concentration for reductant as well as oxidant, both are same. So, then from this equation I can get i 0 equal to ia equal to ic equal to n F k 0 C. Is not it?

So, then I am if I take this C out then I am getting the same expression here because this part is nothing but i 0. Is not it? So, we are getting the same equation considering the both the roots; one was considering the rate equation and then another one is the jumped system jump theory that classical rate theory and where we are considering the jump of atom due to their vibration of the atoms from one plane to the another. Now, coming back to these two equations; these two equations are very important when we try to look at the corrosion part.

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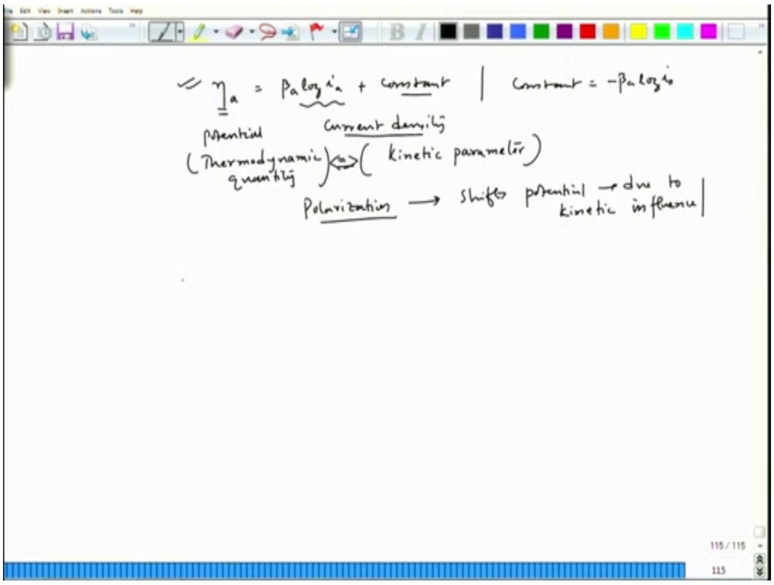

$\eta_a = \beta_a \log i_a + \text{constant}$ | $\text{Constant} = -\beta_a \log i_0$

potential

Current density

(Thermodynamic quantity) ⟺ (kinetic parameter)

Polarization → Shifts potential → due to kinetic influence

Now, before we try to relate this corrosion theory corrosion of metal with these Tafel equations, first see how they can be plotted. In fact, when I consider this over voltage let us say n a equal to beta a log i a plus constant that it means that this is potential and this is that means, thermodynamic quantity. And this part is nothing but current density, this part also involves current density because this part this constant is nothing but beta a of log i with a minus sign log i 0, this is exchange current density.

So, this is current density, this is a kinetic parameter. So, this equation relates thermodynamic quantity with the kinetic parameter that means, whenever we have a current flow; that means, the net current flow we are going to get polarization which shifts the potential due to kinetic influence. And during corrosion you would see that yes we would try to shift the potential of a particular metal from one potential to the another and during that process we can either get higher corrosion, or we can control corrosion.

So, that would be more scientific ways of considering the corrosion control and that is what we have considered. We will see that there are two routes of protection mechanism of metals and alloys from corrosion; one is cathodic protection, another one is anodic protection until unless we know and we until unless we understand this Tafel equation or the relation between current density and polarize potential, till then we will not be able to understand those protection mechanism properly.

Now, let us look at so it is basically relating these two kinetics and thermodynamics of electrode processes electrode reactions or electrode or the corrosion I would say because we have to considering in terms of corrosion, we are not looking at the deposition part. Here we have to look at the anodic current density all the time. So, let us try to see how it can be plotted in a particular diagram.

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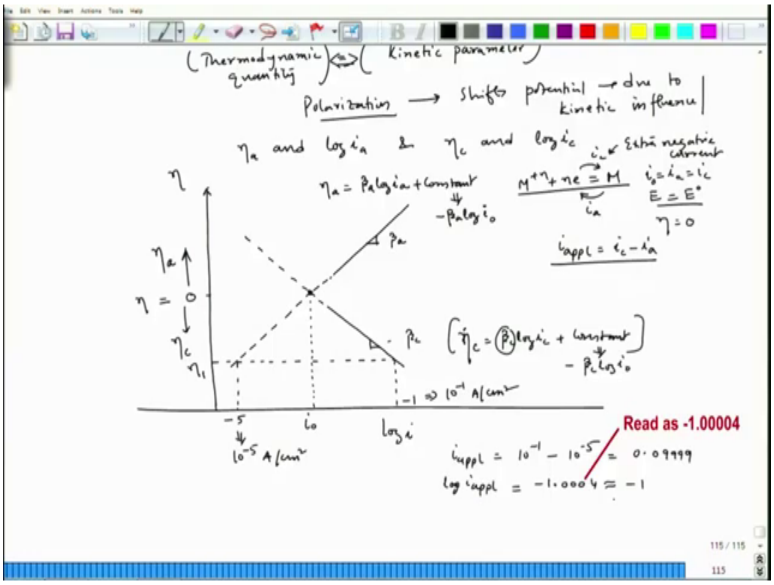

(Thermodynamic quantity) ⇔ (Kinetic parameter)

Polarization → Shifts potential → due to kinetic influence

η_a and $\log i_a$ & η_c and $\log i_c$

$\eta_a = \beta_a \log i_a + \text{Constant}$ ⇓ $-\beta_a \log i_0$

$M^{+n} + ne \rightleftharpoons M$ (i_c ← Extra negative current; i_a)

$i_0 = i_a = i_c$

$E = E^0$

$\eta = 0$

$i_{appl} = i_c - i_a$

$\left[\eta_c = \boxed{\beta_c} \log i_c + \text{Constant}\right]$ ⇓ $-\beta_c \log i_0$

$i_{appl} = 10^{-1} - 10^{-5} = 0.09999$

$\log i_{appl} = -1.0004 \simeq -1$

Read as -1.00004

So, let us try to see the plot between eta a and log i a as well as eta c and log i c. Let us say this side is log i and this direction is this particular axis is eta.

Now, we before we when we when the system reaches equilibrium for example, this particular system we have considered M, when it reaches equilibrium; that means, i equal to i 0 equal to ia equal to ic and E equal to E 0, if it is in standard condition that time this is equal to 0. So, this is 0 value equal to 0 and let us say this is that point we are considering, where this is i 0.

Now, at this I know that over voltage is 0. Now, if I try to plot eta a beta a log ia plus constant, s, that plot would be this and if we extend this it will go through this point. Because at this point eta a goes to 0 also because this term is nothing but beta a log i a and i 0 log i 0 and at this point I do not get any net current rather I would remain at i 0. And the slope is beta a. I can also have a plot between eta c and beta i c.

So, that plot would be this one and if we extend, this would also follow through this particular i 0 point and this slope is beta c which is of negative slope and the relation is eta c equal to beta c log ic plus constant and here the constant is beta c log i 0. Of course, here also it is a minus term and this minus this beta c is the negative slope has a negative slope. Now that means, when I am doing cathodic polarization eta is going down. So, this is eta c and this is anodic polarization eta a.

Now let us see that if we send a preferential current; that means, this is ic, this is ia, and when I send extra negative current then I would get i applied equal to i c minus i a that is the difference. Now, if I go to a very high over voltage let us say this is my over voltage 1, eta 1 that time the current density is log of that current densities let us say that current density part is this is minus 1 and this is minus 5.

So, it corresponds to the current of 10 to the power minus 5 ampere per centimeter square and this corresponds to the current of 10 to the power minus 1 ampere per centimeter square. So, that occasion my i applied would be 10 to the power minus 1 minus 10 to the power minus 5 which is equal to 0.09999. And then if I try to take a log of this it would be close to minus 1 rather minus 1.0004 which is close to minus 1.

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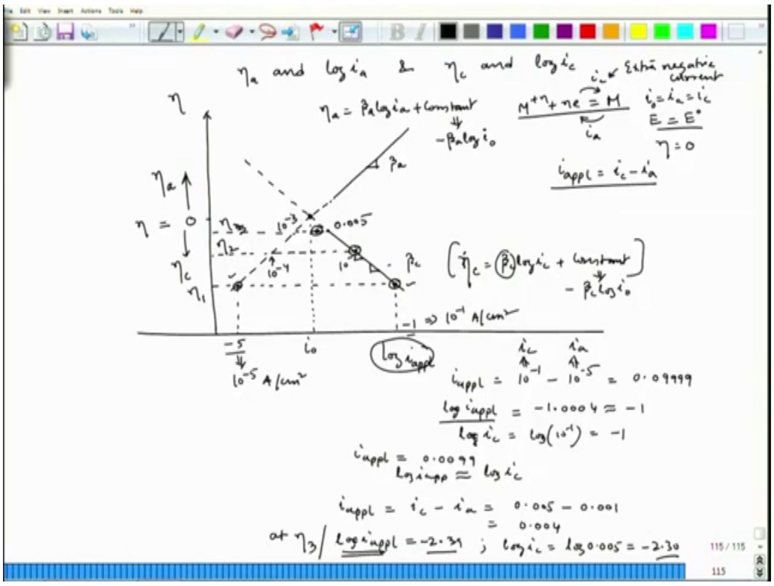

η_a and $\log i_a$ & η_c and $\log i_c$

$\eta_a = \beta_a \log i_a + \text{Constant}$; Constant $= -\beta_a \log i_0$

$M^{+n} + ne \rightleftharpoons M$; i_c ← Extra negative current ; i_a

$i_0 = i_a = i_c$

$E = E^\circ$

$\eta = 0$

$i_{appl} = i_c - i_a$

$\left[\eta_c = \beta_c \log i_c + \text{constant}\right]$; constant $= -\beta_c \log i_0$

$-1 \Rightarrow 10^{-1}\ A/cm^2$

$-5 \Rightarrow 10^{-5}\ A/cm^2$

$i_c \Leftarrow 10^{-1}$; $i_a \Leftarrow 10^{-5}$

$i_{appl} = 10^{-1} - 10^{-5} = 0.09999$

$\log i_{appl} = -1.0004 \simeq -1$

$\log i_c = \log(10^{-1}) = -1$

$i_{appl} = 0.0099$

$\log i_{app} \simeq \log i_c$

$i_{appl} = i_c - i_a = 0.005 - 0.001$

$= 0.004$

at η_3 / $\log i_{appl} = -2.39$; $\log i_c = \log 0.005 = -2.30$

Similarly, log ic equal to log of 10 to the power minus 1 equal to minus 1. So that means, if I try to plot log i applied this would also lie on the same point of ic and remember this corresponds to i a and this corresponds to ic because this particular point which is corresponding to current of 10 to the power minus 5 ampere per centimeter square that time we this particular point is lying on the anodic line, anodic Tafel plot and this particular point is lying on the cathodic Tafel plot.

So, this particular point should indicate i c and this one should indicate ia and here I am putting minus 5 and minus 1 because we are taking log axis. So, we could see that log i applied is also it is falling on the same point of i c.

Now, if we go for a different level of over voltage which is let us say eta 2 that time this value is 10 to the power minus 4 and this is 10 to the power minus 2 that time also I could see that they are coming close approximation. So, i applied would be equal to 0.0999 and then also I could see that log i applied equal to log of i c.

So that means, that time also if I try to plot log i applied which is the excess current that the current that is flowing through the circuit would be falling on the same point. But if I go much lower over voltage let us say this is n eta 2, eta 3 that time this value is let us say 10 to the power minus 3 and 10 to the power this is this is let us say this point is 0.005. Then I will not be able to see that log I applied is equal to log ic.

Because in this case i applied equal to ic minus ia equal to 0.005 minus 0.00 rather 0.001, so then it becomes 0.004. So, log i applied equal to 2 point minus 2.39, whereas, log ic equal to log 0.005 equal to minus 2.30. So, then it is not equal, we cannot say that they are equal. So, that time we see that log i applied this particular point at eta 3 should be lined left to this.

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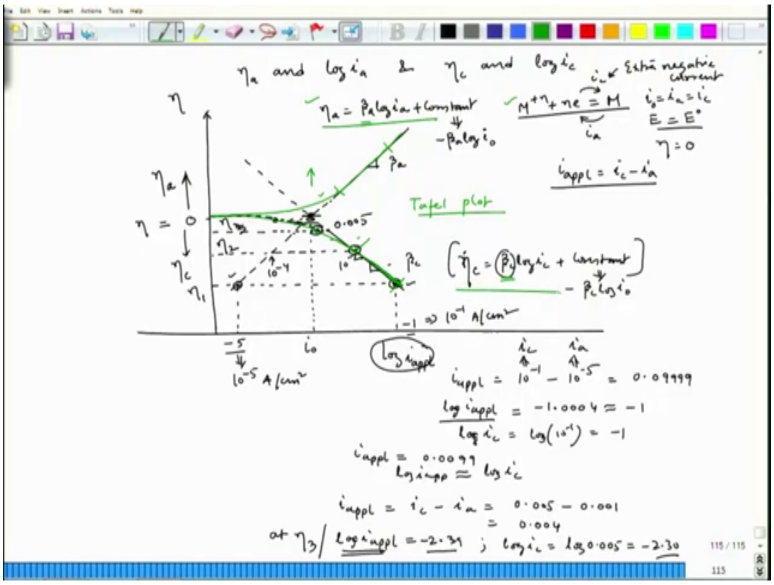

η_a and $\log i_a$ & η_c and $\log i_c$

$\eta_a = \beta_a \log i_a + \text{Constant}$, $\text{Constant} \Rightarrow -\beta_a \log i_0$

$M^{+n} + ne \rightleftharpoons M$; i_c ← Extra negative current; i_a

$i_0 = i_a = i_c$

$E = E^\circ$

$\eta = 0$

$i_{appl} = i_c - i_a$

Tafel plot

$\left[\eta_c = \boxed{\beta_c} \log i_c + \text{Constant}\right]$, $\text{Constant} \Rightarrow -\beta_c \log i_0$

$-1 \Rightarrow 10^{-1}\ A/cm^2$

$-5 \Rightarrow 10^{-5}\ A/cm^2$

$i_{appl} = \underset{i_c}{10^{-1}} - \underset{i_a}{10^{-5}} = 0.09999$

$\log i_{appl} = -1.0004 \approx -1$

$\log i_c = \log(10^{-1}) = -1$

$i_{appl} = 0.0099$

$\log i_{app} \approx \log i_c$

$i_{appl} = i_c - i_a = 0.005 - 0.001 = 0.004$

at η_3 / $\log i_{appl} = -2.39$; $\log i_c = \log 0.005 = -2.30$

Now, as we go let us delete this part. So, that we will be able to understand carefully as we go closer to this particular point I could see that that point also would shift to the left. Because the difference is log of that particular ic minus ia is not falling on the same ic line rather it is switching to the left side.

And now once this as we go much lower over voltage it is falling on this particular point. Now finally, when the over voltage reaches to 0, so; that means, it becomes undefined. So, that point would be meeting somewhere and then if I try to connect those locus of those points i applied point I get a plot like this. Where this portion is a straight line portion which is falling exactly on the beta c line on the eta c versus log ic line.

Similar situation we can think of on the positive side, there also it will be similar way we can construct this particular experimental plot where, this portion which is a straight line portion is falling exactly on the eta a versus log i a plot. And in fact, this green line is basically the polarization plot or the Tafel plot we call it Tafel plot.

So, this Tafel plot actually can be experimentally determined by sending extra current through the system through this particular system. And then try to we just measure the potential as a function of log i applied. And then we get this plot and interestingly you see as the over voltage is very high then we are reaching towards that linearity of that particular Tafel plot for the anodic as well as cathodic sides and that linearity will be enable will enable us to find out beta a or beta c.

So, this beta a which are called Tafel slope, this Tafel slope is important factor to determine the corrosion rate or the corrosion current density, we will see later on. So that means, this is the experimental diagram which is the green line and that green experimental line has been drawn from the concept of polarization which is related to this relation or this relation.

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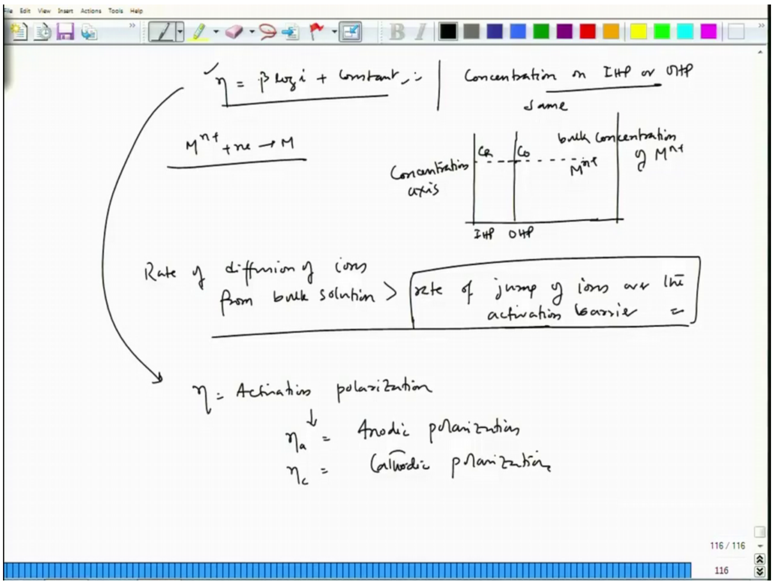

$\eta = \beta \log i + \text{constant}$;

Concentration on IHP or OHP same

$M^{n+} + ne \rightarrow M$

Rate of diffusion of ions from bulk solution > rate of jump of ions over the activation barrier

η = Activation polarization

η_a = Anodic polarization

η_c = Cathodic polarization

Now coming back to this particular general equation eta c is beta log i plus constant. If we see it carefully, here we are considering that the concentration on IHP or OHP they are same, they are not changing during the polarization and when it does not change during its not changing because if I see the actual system, we have a bulk system where this is IHP and this is OHP. And then we have a bulk system where M n plus ions are also present.

Now, if I try to see the concentration if I plot this is concentration, this is concentration axis. So, in this case C R as well as C O they are similar. At the same time C O is also the bulk concentration of M n plus ions so. In fact, we do not get any concentration difference from the bulk to the interface of that electrode and that time this particular situation is arriving.

Now in fact, if I try to see anodic this particular reaction which is cathodic reaction. Now, in that case if we have this continuous cathodic reaction there could be a possibility that metal ion is consumed heavily. So, that there could be a depletion of metal ion at the interface. And so, that depletion is with regard to the bulk concentration of metal ion in the in that particular medium of the aqueous solution.

So, that time we have a concentration difference that concentration difference might lead to some polarization again that polarization is called concentration polarization; we will talk about that part. But if there is enough supply of these ions to the interface that means, OHP, then we would not experience any concentration related polarization.

Now, if we have this condition that the rate of diffusion of ions from the bulk solution is greater than the rate of jump of ions over the activation barrier that time we can say that the slowest step for the overall reaction is this one. And the slowest step actually controls the overall reaction and overall rate of that particular process.

So, then because this is guided this polarization is guided by the rate of the jump of ions over the activation barrier, we call it activation polarization. And this activation polarization it has got two terms na as well as nc which is activation activated activation polarization for anodic polarization and this is cathodic polarization. So that means, we are getting this Tafel equation is basically indicating activation polarization or the rate of the jump of ions or atom from one plane to another. And we will consider concentration polarization in our next lecture. Let us stop here.

Thank you.