# Corrosion – Part I
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## Lecture – 34
## Derivation of Tafel Equation

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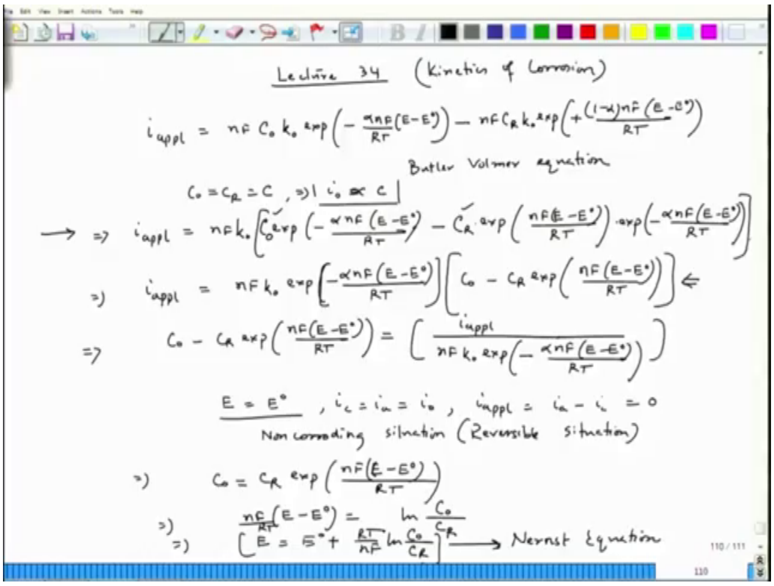

Lecture 34 (Kinetics of Corrosion)

$$i_{appl} = nFC_ok_o\exp\left(-\frac{\alpha nF}{RT}(E-E^0)\right) - nFC_Rk_o\exp\left(+\frac{(1-\alpha)nF(E-E^0)}{RT}\right)$$

Butler Volmer equation

$C_o = C_R = C$, $\Rightarrow \boxed{i_o \propto C}$

$$\rightarrow \Rightarrow i_{appl} = nFk_o\left[C_o\exp\left(-\frac{\alpha nF(E-E^0)}{RT}\right) - C_R\exp\left(\frac{nF(E-E^0)}{RT}\right)\cdot\exp\left(-\frac{\alpha nF(E-E^0)}{RT}\right)\right]$$

$$\Rightarrow i_{appl} = nFk_o\exp\left[-\frac{\alpha nF(E-E^0)}{RT}\right]\left[C_o - C_R\exp\left(\frac{nF(E-E^0)}{RT}\right)\right] \Leftarrow$$

$$\Rightarrow C_o - C_R\exp\left(\frac{nF(E-E^0)}{RT}\right) = \left(\frac{i_{appl}}{nFk_o\exp\left(-\frac{\alpha nF(E-E^0)}{RT}\right)}\right)$$

$\underline{E = E^0}$, $i_c = i_a = i_o$, $i_{appl} = i_a - i_c = 0$

Non corroding situation (Reversible situation)

$$\Rightarrow C_o = C_R\exp\left(\frac{nF(E-E^0)}{RT}\right)$$

$$\Rightarrow \frac{nF}{RT}(E-E^0) = \ln\frac{C_o}{C_R}$$

$$\Rightarrow \left[E = E^0 + \frac{RT}{nF}\ln\frac{C_o}{C_R}\right] \longrightarrow \text{Nernst Equation}$$

So, let us start lecture 34. We will continue our discussion on kinetics Corrosion. And now, actually we are looking into the electrochemistry part and then we will try to relate this electrochemistry to corrosion. Now, we have derived this Butler Volmer equation which is nFCoko exponential minus alpha nF by RT E minus E 0 minus nF CRk0 exponential minus 1 plus 1 minus alpha nF E minus E 0 by RT, this is Butler Volmer equation.

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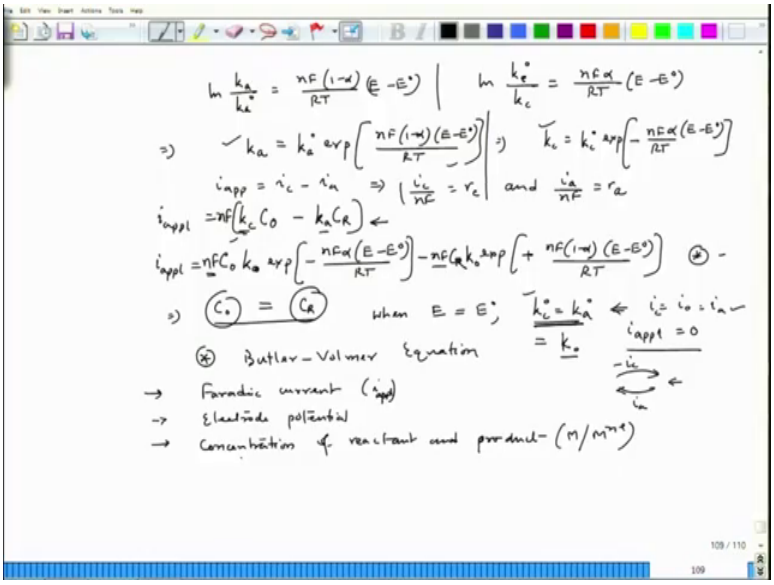

$\ln \frac{k_a}{k_a^0} = \frac{nF(1-\alpha)}{RT}(E-E^0)$ | $\ln \frac{k_c^0}{k_c} = \frac{nF\alpha}{RT}(E-E^0)$

$\Rightarrow k_a = k_a^0 \exp\left[\frac{nF(1-\alpha)(E-E^0)}{RT}\right]$ | $\Rightarrow k_c = k_c^0 \exp\left[-\frac{nF\alpha(E-E^0)}{RT}\right]$

$i_{app} = i_c - i_a \Rightarrow \frac{i_c}{nF} = r_c$ and $\frac{i_a}{nF} = r_a$

$i_{appl} = nF(k_c C_O - k_a C_R) \leftarrow$

$i_{appl} = nFC_O k_0 \exp\left[-\frac{nF\alpha(E-E^0)}{RT}\right] - nFC_R k_0 \exp\left[+\frac{nF(1-\alpha)(E-E^0)}{RT}\right]$ (*)

$\Rightarrow C_O = C_R$ when $E = E^0$; $k_c^0 = k_a^0 = k_0 \leftarrow i_c = i_0 = i_a$

$i_{appl} = 0$

$\xrightarrow{-i_c}$ $\xleftarrow[i_a]{}$ $\leftarrow$

(*) Butler-Volmer Equation

→ Faradic current ($i_{appl}$)

→ Electrode potential

→ Concentration of reactant and product ($M/m^3$)

And if, we see the previous analysis, we see this is my i applied and then I am replacing this kc and ka with these two formulas. And later we have understood that why kc 0 equal to ka 0 and that one we are considering k 0, we are replacing that and we hence, we are getting this Butler Volmer equation. It has relation between faradaic current, electrode potential and concentration of reactant as well as product which are basically, oxidant and reductant.

Now, then we started saying that this particular equation can yield as Nernst equation. Now, we can do little bit of redistribution of this entire formula; i applied equal to n F k 0 exponential minus alpha nF E minus E 0 divided by RT minus this is Co Cr exponential n F E minus E 0 divided by RT into exponential minus alpha nF E minus E 0 divided by RT. Then, we can write equal to nF k 0 exponential minus alpha nF E minus E 0 divided by RT C 0 minus C R exponential nF E minus E 0 by RT equal to it turns out to be then C 0 minus C R exponential nF E minus E 0 by RT equal to i applied divided by n F k 0 exponential minus alpha nF E minus E 0 by RT, so this we are getting.

Now, we see that when, E equal to E 0, ic equal to ia equal to i 0 and i applied equal to ia minus ic equal to 0. So that means, when it is non corroding situation or reversible situation then, this right hand side become 0, so the C 0 minus C R exponential would be equal to exponential nF E minus E 0 by RT equal to nF E minus E 0 equal to ln C 0 C R or E equal to E 0 plus RT nF ln C 0 by C R.

So, this is nothing but Nernst equation. So, we are also getting Nernst equation. So, this particular condition or the equation what we are seeing in this they have two components one is C 0 and C R. Now, if we assume that C 0 and C R are the same values; that means, the physical it means that the concentration at the interface for oxidant and reductant they are not changing and they are having the same value. So, that time, it would turn out to be in this case and then C 0 if we consider C R equal to C then, I could see that, i 0 could have a proportionality with the C, the concentration.

Now, since the concentration and this particular equation in a simplified mode can be found out if we look at this situation these diagram.

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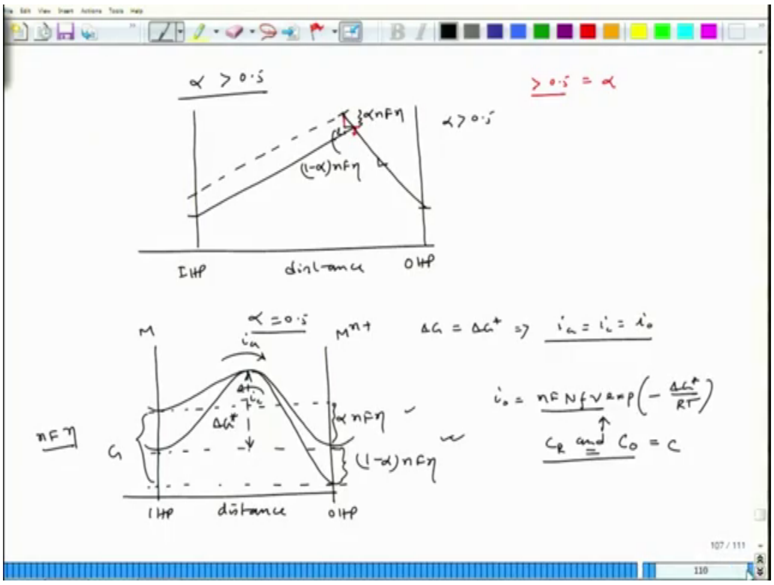

So, these diagram would enable us to get the i applied as a function of over voltage. And that time, this concentration part is already inherited, already included in this particular formula which is i 0 equal to n F N f nu exponential minus delta G star by RT. So, this concentration of R as well as C O they are included here and that time we are saying that there equal and it becomes C. And let us see whether, we can get similar sort of equations by analyzing this particular plot.

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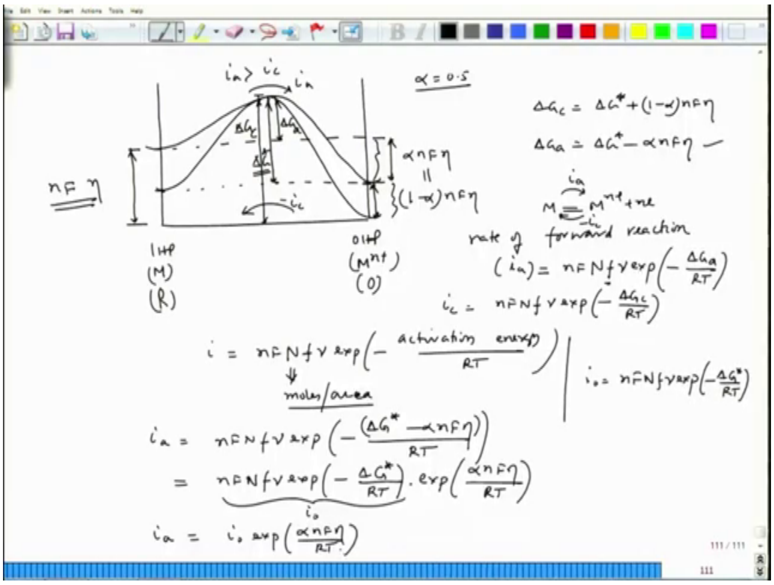

$\underline{\alpha = 0.5}$

$\Delta G_c = \Delta G^* + (1-\alpha)nF\eta$

$\Delta G_a = \Delta G^* - \alpha nF\eta$

$M \underset{-i_c}{\overset{i_a}{\rightleftharpoons}} M^{n+} + ne$

rate of forward reaction

$(i_a) = nFNf\nu \exp\left(-\frac{\Delta G_a}{RT}\right)$

$i_c = nFNf\nu \exp\left(-\frac{\Delta G_c}{RT}\right)$

$i = \underset{\substack{\Downarrow \\ \text{moles/area}}}{nFNf\nu} \exp\left(-\frac{\text{activation energy}}{RT}\right)$

$i_0 = nFNf\nu \exp\left(-\frac{\Delta G^*}{RT}\right)$

$i_a = nFNf\nu \exp\left(-\frac{(\Delta G^* - \alpha nF\eta)}{RT}\right)$

$= \underbrace{nFNf\nu \exp\left(-\frac{\Delta G^*}{RT}\right)}_{i_0} . \exp\left(\frac{\alpha nF\eta}{RT}\right)$

$i_a = i_0 \exp\left(\frac{\alpha nF\eta}{RT}\right)$

This particular plot let me redraw again. This is the over voltage related change in free energy. So, this is become n F eta and the contribution towards the anodic side is alpha n F eta and this part if I consider or (Refer Time: 09:28) alpha prime, alpha prime or simply we put it alpha 1 minus alpha nF eta. This is IHP, this is OHP, this is M or R reductant, this is M n plus or oxidant.

In the beginning, the free energy difference, the activation energy barrier was delta G star and then after redistribution when we are assuming that ia greater than ic, so, this is my ia and this opposite direction flow is ic with a negative sign, this becomes my delta G a.

Change in activation energy for the cathodic side would be this much, this is delta G c and this knows a delta G c equal to delta G star plus 1 minus alpha nF eta; so, this plus this much. Whereas, delta G a equal to this delta G star minus this much. So, delta G star minus alpha nF eta. And we are assuming that alpha is equal to 0.5; that means, the distribution of this total change in free energy towards the activation energy is same quantity; so, these 2 are equal since, if alpha equal to 0.5.

Now, I know that the rate of forward reaction. So, the rate of forward reaction or it is better to say that ia; so that means, M minus equal to M n plus ne, so this is the forward direction ia and this is my ic. We can relate in this form n F N, frequency factor and nu, this fraction of atoms that are going towards the OHP and the fraction of this is the fraction of atom of that goes to the other end and then, exponential minus delta G a by

RT. Similarly, ic can be related as n F N f nu exponential minus delta G c by RT. And this particular general equation for i is equal to nothing but n F N, which is the surface density of moles into f, which is the fraction of atoms or ions that are going from one plane to the other plane and this is the frequency vibrational frequency exponential minus activation energy divided by RT; since, this is considered in terms of moles per unit area.

So, now, ia equal to n F N f nu exponential minus delta G a, I am just replacing this values minus alpha nF eta divided by RT, so this becomes nF N f nu exponential minus delta G a by RT into exponential alpha n F eta divided by RT. This part is nothing but i 0, since, i 0 equal to nF Nf nu exponential minus sorry here we have to put delta G star.

Since, delta G is delta G star minus alpha F n N f eta delta G star by RT. So, this is i 0, so it becomes i a equal to i 0 exponential alpha n F eta by RT.

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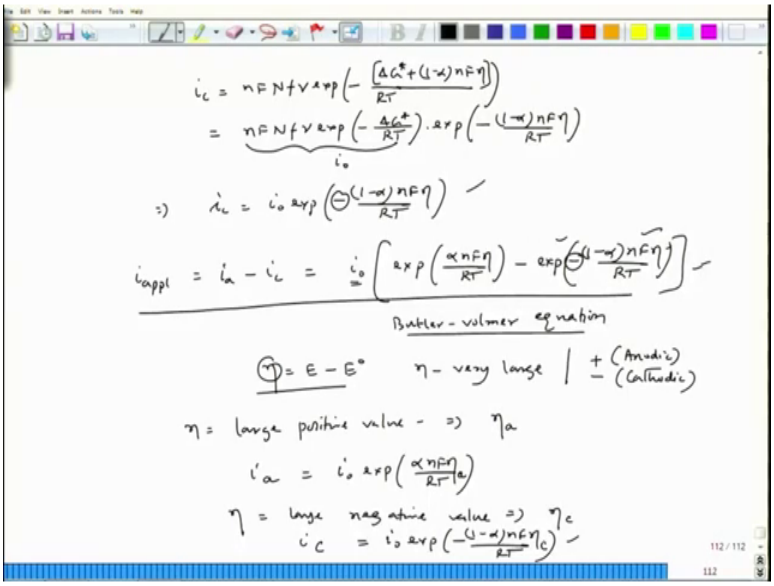

$$i_c = nFNf\nu \exp\left(-\frac{[\Delta G^{*} + (1-\alpha)nF\eta]}{RT}\right)$$

$$= \underbrace{nFNf\nu \exp\left(-\frac{\Delta G^{*}}{RT}\right)}_{i_0} \cdot \exp\left(-\frac{(1-\alpha)nF}{RT}\eta\right)$$

$$\Rightarrow \quad i_c = i_0 \exp\left(\ominus \frac{(1-\alpha)nF}{RT}\eta\right)$$

$$\underline{i_{appl} = i_a - i_c = \underline{i_0}\left[\exp\left(\frac{\alpha nF}{RT}\eta\right) - \exp\left(\ominus \frac{(1-\alpha)nF}{RT}\eta\right)\right]}$$

Butler - volmer equation

$\underline{\eta = E - E^{\circ}}$ $\quad \eta$ - very large $\Big| \begin{matrix} + \text{(Anodic)} \\ - \text{(Cathodic)} \end{matrix}$

$\eta =$ large positive value $\Rightarrow \eta_a$

$$i_a = i_0 \exp\left(\frac{\alpha nF}{RT}\eta_a\right)$$

$\eta =$ large negative value $\Rightarrow \eta_c$

$$i_c = i_0 \exp\left(-\frac{(1-\alpha)nF}{RT}\eta_c\right)$$

And similar way i can see ic equal to n F N f nu exponential minus delta G c by RT, so I replace this G c with delta G star plus 1 minus alpha nF eta by RT. Again nF N f nu exponential minus delta G star by RT into exponential minus 1 minus alpha nF eta by RT.

So, this is again i 0, so ic equal to i 0 exponential minus 1 minus alpha nF eta by RT. So, i applied equal to ia minus ic equal to i 0 exponential alpha nF eta by RT minus exponential 1 minus alpha nF eta by RT. So, here we are considering this quantity, when we are consider this quantity to be this part and the rest part would be 1 minus alpha. So, you can also reverse instead of taking alpha this, you can take 1 minus alpha that time it will be reducive alpha or the reducive symmetry factor. And in this case, we are considering oxidative symmetry factor.

Now, once we have this, now if I compare with this particular Butler Volmer equation here, here we are seeing that there are 2 concentration parts. Now, when we have these concentrations to be same then, we can get the same equations what we are having here ok, so, where in this i 0 that concentration is included. So we are not going into that part, the only we are seeing that this is also a Butler Volmer equation.

Now, these equation has got huge importance on the corrosion of a particular method. We will look into that part, but before that, see this eta is nothing but E minus E 0 and if eta is very large whether, it is positive or negative, when it is positive it is anodic, when it is negative it is called cathodic. Interestingly, if you see that here there is a negative sign and it is there is a negative sign here; so that means, it is actually potential actually goes down from the reversible non corroding potential.

And in the case of anodic case, if I say the anodic case where we have a positive sign in front of it. So that means, it indicates that the potential should not go up from the reversible potential. But, if I try to look at this equation, let us say if it is positive, let us say eta is positive and large positive, let us say eta is large positive value, so that time if we consider this particular part, this part we can omit, we can ignore because, there is a negative sign and this particular value is very high. So, your where I simply say i applied equal to i 0 exponential alpha nF eta by RT.

And since, this i applied would be also equal to ia or the anodic current density because, this part can be ignored because of this is a positive value. Now, in case and that time we can term it as eta a. So, this we can term it as anodic over voltage. Similarly, if has got large negative value, so that time, it will be considered as eta c and this equation will go to i applied equal to i 0 exponential minus 1 minus alpha nF eta by RT. And interestingly, you see this equation is exactly similar to this, so that time we can write it as ic and this would become eta c.

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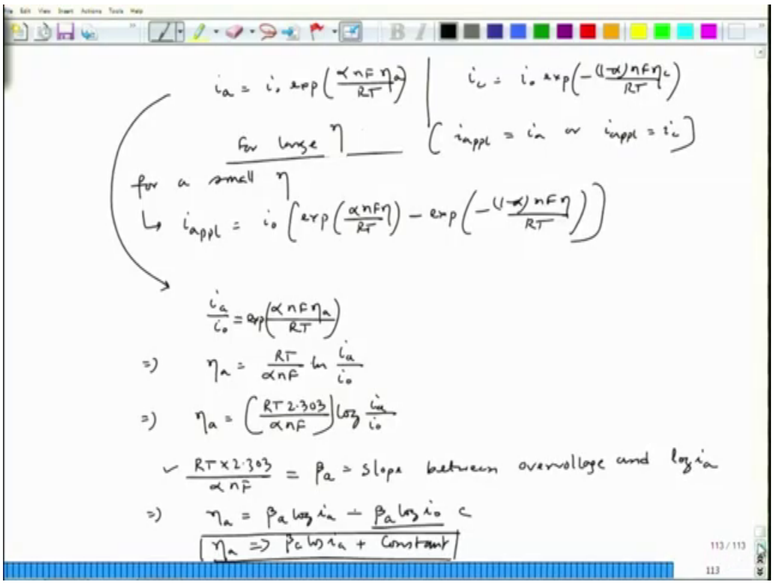

$$i_a = i_0 \exp\left(\frac{\alpha n F \eta_a}{RT}\right) \quad \Big| \quad i_c = i_0 \exp\left(-\frac{(1-\alpha) n F \eta_c}{RT}\right)$$

for large $\eta$ — $[i_{appl} = i_a$ or $i_{appl} = i_c]$

for a small $\eta$

$$\hookrightarrow i_{appl} = i_0 \left[\exp\left(\frac{\alpha n F \eta}{RT}\right) - \exp\left(-\frac{(1-\alpha) n F \eta}{RT}\right)\right]$$

$$\frac{i_a}{i_0} = \exp\left(\frac{\alpha n F \eta_a}{RT}\right)$$

$$\Rightarrow \eta_a = \frac{RT}{\alpha n F} \ln \frac{i_a}{i_0}$$

$$\Rightarrow \eta_a = \left(\frac{RT\, 2.303}{\alpha n F}\right) \log \frac{i_a}{i_0}$$

$\checkmark$ $\frac{RT \times 2.303}{\alpha n F} = \beta_a$ = slope between overvoltage and $\log i_a$

$$\Rightarrow \eta_a = \beta_a \log i_a - \underline{\beta_a \log i_0}\ c$$

$$\boxed{\eta_a \Rightarrow \beta_a \log i_a + \text{Constant}}$$

So, now we have 2 equations, one is i a equal to i 0 exponential minus exponential alpha nF eta by RT, which is a another way ic equal to i 0 exponential minus 1 minus alpha nF eta c by RT. This is valid when there is a large over voltage either, cathodic or anodic.

But when it is not large, then we have to consider this i applied. And that time i applied is not ic or is not ia, small over voltage. So, this is valid, these two equations are valid for large over voltage, but for a small over voltage and that time i applied equal to ia or i applied equal to ic. When a small over voltage, that time I should write combination of this i 0 exponential alpha nF eta by RT minus exponential minus 1 minus alpha nF eta by RT. This is for a small over voltage.

So, let us simplify this particular equation. This equation becomes ia i0 equal to alpha nF eta a divided by RT with exponential equal to. So, then I can write na equal to RT by alpha nF ln i a by i 0 or na equal to RT 2.303 by alpha nF log i a by i 0. Now, this particular factor which is RT into 2.303 by alpha nF is called as beta a or the slope between over voltage and ia or rather sorry this should be log i a. The plot between beta this basically nothing but a slope between over voltage and log ia and this we can relate in a linear equation, a equal to beta a log ia plus minus beta a log i 0.

Now, this is a constant since, RT alpha is 0.5, nF is constant, RT is constant, eta reaction happens at a constant temperature, so this becomes a constant, so this is equivalent to n a beta a log ia plus some constant.

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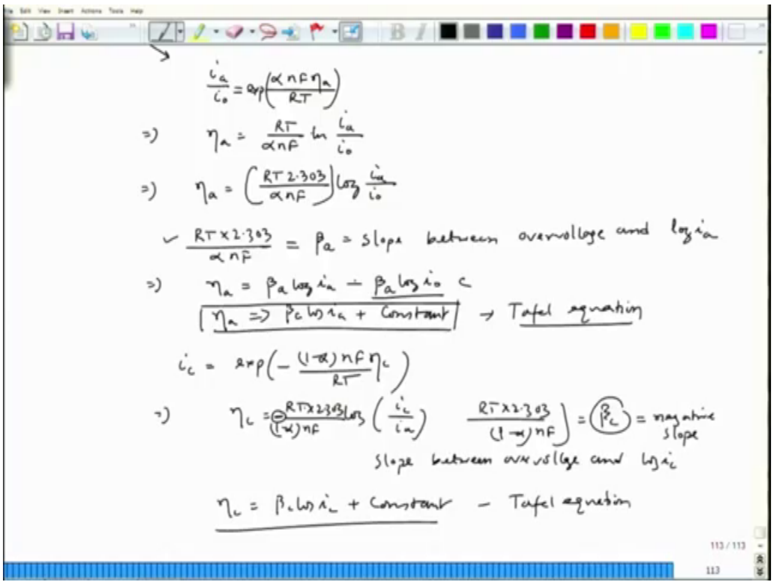

$$\frac{i_a}{i_0} = \exp\left(\frac{\alpha nF\eta_a}{RT}\right)$$

$$\Rightarrow \quad \eta_a = \frac{RT}{\alpha nF} \ln \frac{i_a}{i_0}$$

$$\Rightarrow \quad \eta_a = \left(\frac{RT\, 2.303}{\alpha nF}\right) \log \frac{i_a}{i_0}$$

$$\checkmark \ \frac{RT \times 2.303}{\alpha nF} = \beta_a = \text{slope between overvoltage and } \log i_a$$

$$\Rightarrow \quad \eta_a = \beta_a \log i_a - \underline{\beta_a \log i_0}\ c$$

$$\boxed{\eta_a \Rightarrow \beta_c \log i_a + \text{Constant}} \rightarrow \underline{\text{Tafel equation}}$$

$$i_c = \exp\left(-\frac{(1-\alpha)nF}{RT}\eta_c\right)$$

$$\Rightarrow \quad \eta_c = \ominus\frac{RT \times 2.303}{(1-\alpha)nF}\log\left(\frac{i_c}{i_a}\right) \qquad \left.\frac{RT \times 2.303}{(1-\alpha)nF}\right\} = \textcircled{\beta_c} = \text{negative slope}$$

Slope between overvoltage and $\log i_c$

$$\underline{\eta_c = \beta_c \log i_c + \text{Constant}} \ - \ \text{Tafel equation}$$

Similarly, if I take ic equal to exponential minus 1 minus alpha nF eta c by RT, so then, it will also give us eta c equal to if we do the way we have done, you would get exponential ic by ia and RT by 1 minus alpha nF eta into 2 point sorry here it should be log into 2.303 by this and with a minus sign.

Now, this RT into 2.303 by 1 minus alpha nF, sorry this should not be here, this is called beta c and we consider this negative sign inside this and that is what it is it has a negative slope. So, this is also over voltage slope between over voltage and log ic. So, this is called Tafel equation. This is also called so we can write this one as eta c equal to beta c log ic plus constant, this is also a Tafel equation. So, we would continue our discussion from this Tafel equation, let us stop here.

Thank you.