Corrosion – Part I

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Lecture – 33
Introduction to Butler-Volmer Equation

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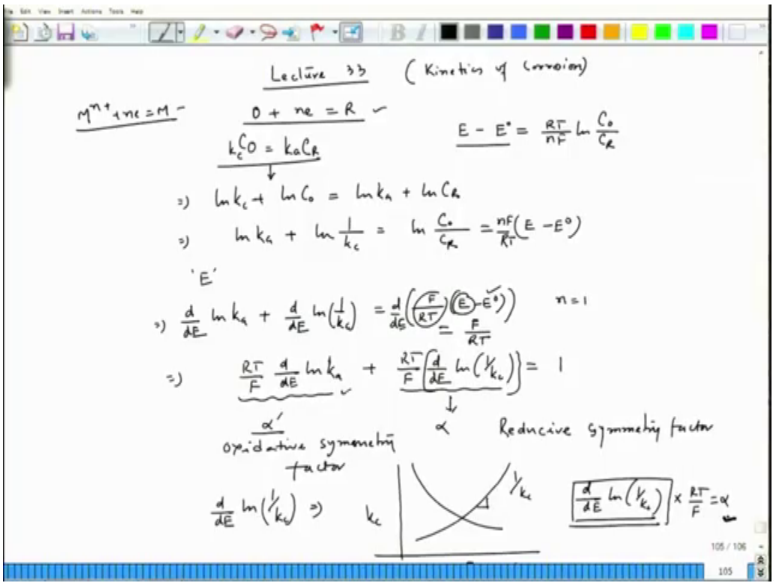

Lecture 33 (Kinetics of Corrosion)

$M^{n+} + ne = M$

$O + ne = R$

$E - E^{\circ} = \frac{RT}{nF} \ln \frac{C_O}{C_R}$

$k_c C_O = k_a C_R$

$\Rightarrow \ln k_c + \ln C_O = \ln k_a + \ln C_R$

$\Rightarrow \ln k_a + \ln \frac{1}{k_c} = \ln \frac{C_O}{C_R} = \frac{nF}{RT}(E - E^{\circ})$

'E'

$\Rightarrow \frac{d}{dE} \ln k_a + \frac{d}{dE} \ln\left(\frac{1}{k_c}\right) = \frac{d}{dE}\left(\frac{F}{RT}(E - E^{\circ})\right) = \frac{F}{RT}$ $n = 1$

$\Rightarrow \underbrace{\frac{RT}{F} \frac{d}{dE} \ln k_a}_{\alpha'} + \underbrace{\frac{RT}{F}\left\{\frac{d}{dE} \ln\left(\frac{1}{k_c}\right)\right\}}_{\alpha} = 1$

α' oxidative symmetry factor

α Reducive symmetry factor

$\frac{d}{dE} \ln\left(\frac{1}{k_c}\right) \Rightarrow$

$\boxed{\frac{d}{dE} \ln\left(\frac{1}{k_c}\right)} \times \frac{RT}{F} = \alpha$

Let us start lecture-33. And we will continue our discussion on kinetics of corrosion. Now in the last lecture at the end we have come to a situation where if we consider a single half cell redox reaction O plus ne equal to R and then we try to see the equilibrium condition which is k c O concentration of O equal to k a concentration of R and then we have taken logarithm on both sides ln k c plus l n C o equal to ln k a plus ln C R. And after distribution we are getting ln k a plus ln 1 by k c equal to ln C 0 by C R and we also know that E minus E 0 equal to RT by nF ln C o C R which is the concentration of ox divided by concentration of R and then we can put this one with reference to potential E minus E 0 nF RT.

Now, if we differentiate both the sides with reference to E potential since k a as well as k c both are potential dependent. So, then we get d and if we consider that n is 1; that means, for this particular reaction the number of electrons participating to reduce 1 oxidant to 1 atom of 1 molar 1 particular ion of oxidant is going to the reductant in case of Mn plus plus ne equal to M is basically 1 on ion of M n plus we are reducing to M which is reductant.

So, then this n goes to 1 we can write RT by F d dE ln k a plus RT by F and this side definitely when we are doing dE then this would become this is constant. So, it will go out since, this is taking place this reaction is taking place a constant temperature and this is one faraday which is constant this is a constant. So, it would become 1. So, this E so del E del E del E of E del del E of E is equal to 1. So, this goes to 1. So, then would be equal to 1.

Now, this quantity and this quantity this is called alpha which is the cathodic or a reducive symmetry factor and this we can term it as alpha prime, which is oxidative symmetry factor. Now if I try to look at this quantity this is nothing, but the slope of 1 by k c for a particular plot of k c and E. So, if we see this quantity only RT I am just considering d dE ln 1 by k c if I try to look at this then we have already noticed that if potential is this and k c is this.

So, this would be like variation would be like this because once k c increases potential drops from the standard equilibrium potential which is cathodic polarization so, 1 by k c would be just opposite to it. So, 1 by k c and the slope of that point which is so d dE ln 1 by k c so, if we take log of this and then try to plot them again and then we have to take the logarithm of that 1 by k c and then we differentiate with reference to with respect to E then this quantity with the multiplication factor RT by F is nothing, but alpha reductive symmetry factor and of course, the other part this is the oxidated symmetry factor which is talking about the talking about oxidation k a value which is the equilibrium the rate constant.

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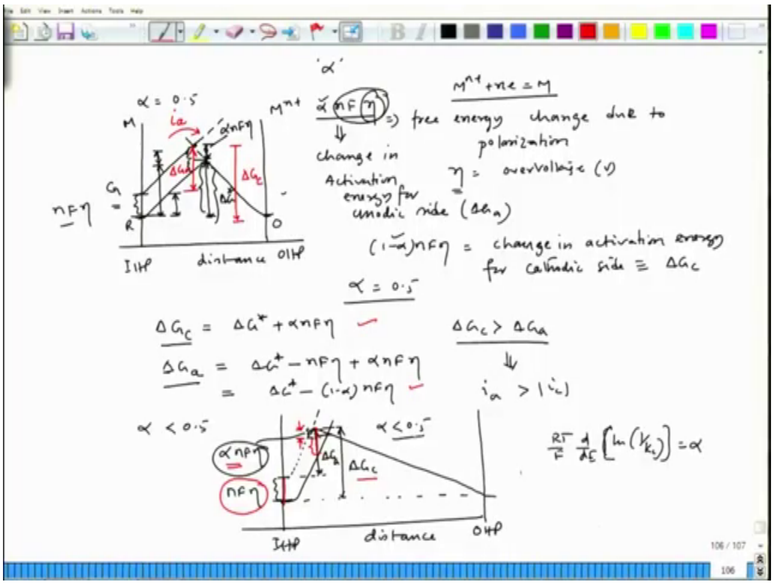

'α'

$M^{n+} + ne = M$

$\alpha nF\eta \Rightarrow$ free energy change due to polarization

$\Downarrow$

change in Activation energy for anodic side (ΔG_a)

η = overvoltage (V)

$(1-\alpha)nF\eta$ = change in activation energy for cathodic side $\equiv \Delta G_c$

$\alpha = 0.5$

$$\Delta G_c = \Delta G^{\neq} + \alpha nF\eta$$

$$\Delta G_a = \Delta G^{\neq} - nF\eta + \alpha nF\eta = \Delta G^{\neq} - (1-\alpha)nF\eta$$

$\Delta G_c > \Delta G_a$

$\Downarrow$

$i_a > |i_c|$

$\alpha < 0.5$

$$\frac{RT}{F}\frac{d}{dE}\left[\ln\left(\frac{1}{k_c}\right)\right] = \alpha$$

Now, we have to have some sort of clear cut picture on this alpha, which is the symmetry factor. which we can explain by drawing some semantics, let us say if alpha equal to 0.5 and if we consider two planes let us say these are the two planes and this is distance. This is G axis this is IHP and this is OHP then initially they are at the same plane because there at equilibrium and then we have the energy axis distribution; energy distribution is like this and here it is R and here it is ox or oxidant metal ion surface and metal surface.

Now, if we see that oxidation process becomes faster then there will be change in the activation energy as we have noticed earlier. So, the new position of the activation barrier would be this one. So, you could see that activation energy is going down for the oxidation process this is oxidation process or ia. So, the ia increases and for the reduction process the activation energy increases from the earlier one this is for this is delta G c and this is delta G a and when it happens symmetrically; that means, maintaining that equal distribution of the total polarization or over voltage if this is my over voltage value eta. So, then in this case M n plus plus ne equal to M for this particular half cell reaction, the free energy change would be nF eta this is my free energy change due to polarization and of course, ne is this the over voltage in volt.

So, out of that alpha this amount will be the amount which will be the change in activation energy for anodic side or delta G a and then the rest of that particular fraction 1 minus alpha nF eta would be the change in activation energy for cathodic side, which will lead to a change in delta G c. Now since alpha is 0.5 so the contribution of this total over voltage and thus the change in free energy towards this activation energy would be equal and in this case if you see this so, this arm and this arm both are equal. That suggests that contribution of the total over voltage or total energy change, which is this one would be this fraction and this fraction and now you need to be need to know that what is that free energy change due to over voltage? This is the amount of free energy change for over voltage, which is equal to n F eta and interestingly if you see this, this was the initial free energy when both i a and i c were equal.

Now, after this distribution when ia is higher than ic in this particular situation you could see that del d G c would be equal to delta G star which is this one this is delta G star plus and if we consider this to be alpha F eta. So, this becomes alpha n F eta and delta G because this height plus this one is basically constituting delta G c and whereas, delta G a would be equal to delta G star.

So this amount plus this amount minus this amount. So, delta G star minus n F eta plus alpha nF eta. So, then it becomes delta G star minus 1 minus alpha nF eta. Now you could see that these value is greater than delta G a, hence it would lead to ia greater than ic. We are taking mod because we have assumed that this is a negative current means the flow is opposite to anodic current. Now this is the situation when alpha is equal to 0.5.

So; that means, the contribution of this over voltage and finally, the contribution of free energy change towards activation energy of cathodic side, anodic side both are equal. Now there could be a situation where alpha is less than 0.5. The situation can be predicted in this fashion, this is also let us say distance. This is OHP and this is IHP. Now I can initially I have a situation like this. This is on the same plane and then if we have a situation, same situation that ia is increasing, now you could see that alpha is less than 0.5. Since this part is alpha nF eta and interestingly if we see the expression for alpha, expression for alpha is this one.

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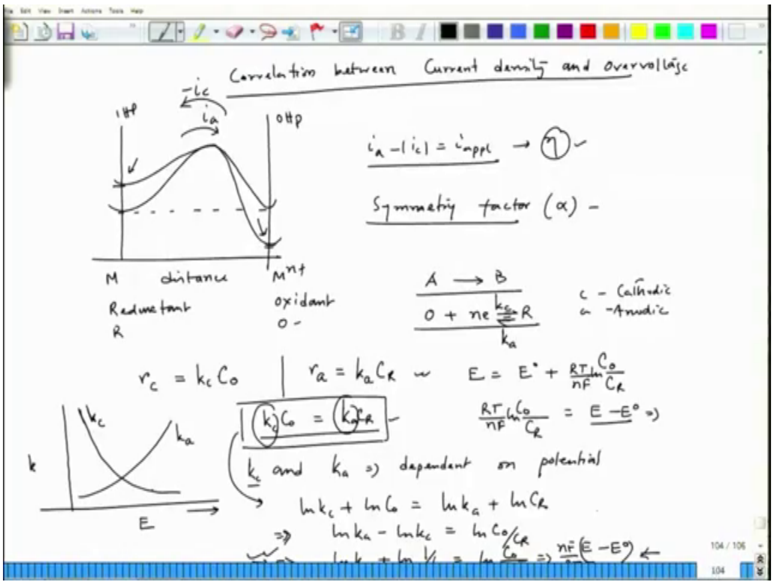

Correlation between Current density and Overvoltage

$i_a - |i_c| = i_{appl} \rightarrow \eta$

Symmetry factor (α) -

$A \rightarrow B$

$O + ne \underset{k_a}{\overset{k_c}{\rightleftharpoons}} R$

c - Cathodic
a - Anodic

$r_c = k_c C_O \quad | \quad r_a = k_a C_R$

$E = E^\circ + \frac{RT}{nF} \ln \frac{C_O}{C_R}$

$\boxed{k_c C_O = k_a C_R}$

$\frac{RT}{nF} \ln \frac{C_O}{C_R} = E - E^\circ \Rightarrow$

k_c and $k_a \Rightarrow$ dependent on potential

$\ln k_c + \ln C_O = \ln k_a + \ln C_R$

$\Rightarrow \ln k_a - \ln k_c = \ln C_O/C_R$

$\Rightarrow \ln k_a + \ln 1/k_c = \ln \frac{C_O}{C_R} \Rightarrow \frac{nF}{RT}(E - E^\circ) \leftarrow$

So, let me write down again which is RT by F d dE ln 1 by k c equal to alpha which is reductive symmetry factor. Now we can have a situation when we have alpha greater than 0.5 that case the plot would look like in this case one more thing see now this is my total free energy change and out of that a small fraction because alpha is less, the small fraction is contributing to the activation energy for delta G c whereas, similar way we can have activation energy change for anodic side. But if we see this arm, these two arms and this arm from this point these arm is smaller than this and this is equal to this total value, because there parallel planes. This is parallel to this.

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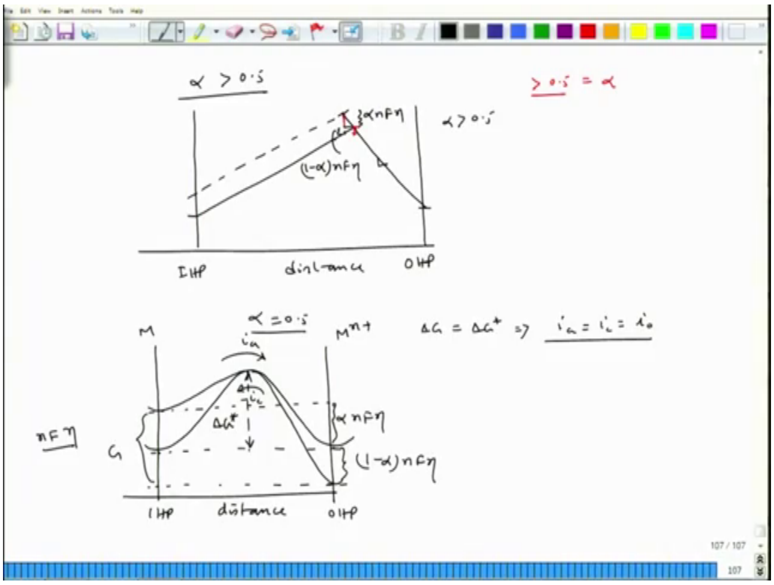

$\alpha > 0.5$

$> 0.5 = \alpha$

$\alpha = 0.5$

$\Delta G = \Delta G^{\ddagger} \Rightarrow i_a = i_c = i_0$

So, that is what the contribution would be this much towards delta G c and the equation would be similar like this and the contribution of this one would give us the same formula which is delta G c minus 1 minus alpha into nF eta this is the situation on alpha is less than 0.5. Now we can have greater than 0.5 this is IHP, OHP distance.

So, the slope of this line would be steeper since alpha is greater than 0.5 and then if we have the similar variation in anodic current density and cathodic current density; that means, the activation energy for the anodic side would decrease then you can see that this becomes my alpha nF eta and this becomes my alpha 1 minus alpha nF eta. And you could see that these two arms these arm and this arm the ratio is greater than 0.5 which is alpha.

So, we could see that how alpha changes the slope of this to free energy lines, one is from the R to the activation energy another one is ox to the activation energy peak. So, these two lines are changing because of this variation in symmetry factor, but in our discussion we would consider alpha to be 0.5.

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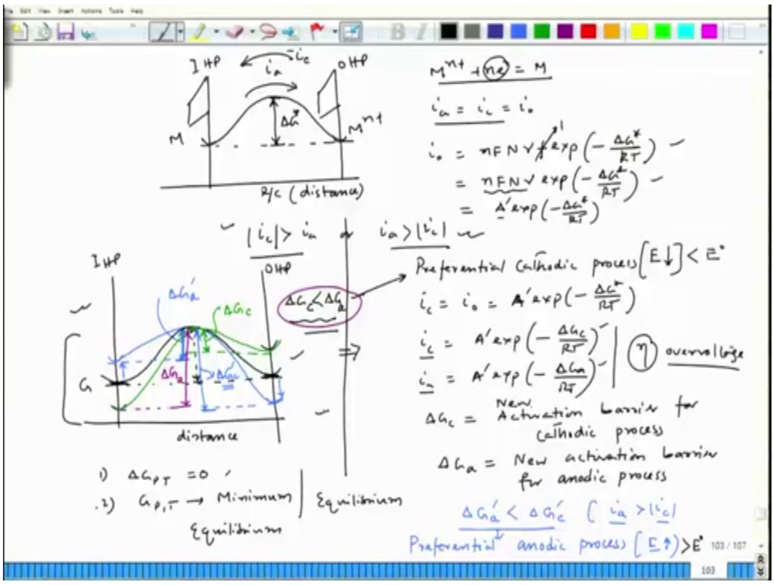

1) $\Delta G_{P,T} = 0$

2) $G_{P,T} \rightarrow$ Minimum | Equilibrium

Equilibrium

$M^{n+} + \boxed{ne} = M$

$i_a = i_c = i_0$

$i_0 = nFNv\cancel{f}^{1}\exp\left(-\frac{\Delta G^*}{RT}\right)$

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

$= A'\exp\left(-\frac{\Delta G^*}{RT}\right)$

Preferential cathodic process $[E\downarrow] < E^\circ$

$i_c = i_0 = A'\exp\left(-\frac{\Delta G^*}{RT}\right)$

$i_c = A'\exp\left(-\frac{\Delta G_c}{RT}\right)$ | η overvoltage

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

ΔG_c = New Activation barrier for cathodic process

ΔG_a = New activation barrier for anodic process

$\Delta G_a' < \Delta G_c'$ ($i_a > |i_c|$

Preferential anodic process $(E\uparrow) > E^\circ$

Now as we have seen before, let us get back to this particular plot, this particular plot. So, if we see that we have seen how the broad pattern changes if we would like to get preferably anodic reaction and preferably cathodic reactions. Let us consider that particular situation now here we are considering alpha to be 0.5 and now we are seeing the change in free energy plot. Now here initially the free energy plot was like this which was on the same line and it was G is same for these two points.

Now, we are having preferably anodic reactions. So, I am having a change in my free energy plots and this is M, this is M n plus this is distance and this part is IHP and this is OHP and you could see that the total change in free energy is after this preferable ia and preferable ic depending on whether in this case in this particular plot we are getting preferably i the anodic reactions. That means, the rate of anodic reaction is increasing as compared to the backward reaction which is rate of cathodic reaction and this is the total over voltage and now the free energy change would be n F eta and out of that if we consider this to be alpha n F eta and this part would be then 1 minus alpha nF eta.

So, then accordingly we can calculate now initially this was my free energy where when delta G equal to delta G star that activation energy that time ia equal to ic equal to i 0. Now interestingly before we analyze this part we need to understand one more issue, the issue is if we try to see same equation, which is r 1 r c equal to k c concentration of ox and r a equal to k a concentration of R.

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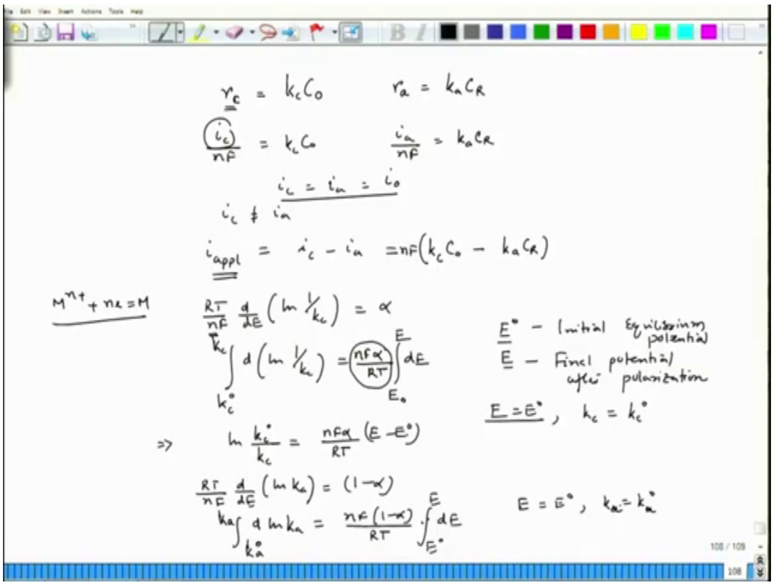

$\underline{\underline{r_c}} = k_c C_o \qquad r_a = k_a C_R$

$\dfrac{\boxed{i_c}}{nF} = k_c C_o \qquad \dfrac{i_a}{nF} = k_a C_R$

$\underline{i_c = i_a = i_o}$

$i_c \neq i_a$

$\underline{\underline{i_{appl}}} = i_c - i_a = nF(k_c C_o - k_a C_R)$

$\underline{M^{n+} + ne = M}$

$\dfrac{RT}{nF}\dfrac{d}{dE}\left(\ln \frac{1}{k_c}\right) = \alpha$

$\int_{k_c^o}^{k_c} d\left(\ln \frac{1}{k_c}\right) = \boxed{\dfrac{nF\alpha}{RT}} \int_{E_o}^{E} dE$

$\underline{\underline{E^o}}$ - Initial Equilibrium potential

$\underline{\underline{E}}$ - Final potential after polarization

$\underline{E = E^o}, \quad k_c = k_c^o$

$\Rightarrow \quad \ln \dfrac{k_c^o}{k_c} = \dfrac{nF\alpha}{RT}(E - E^o)$

$\dfrac{RT}{nF}\dfrac{d}{dE}(\ln k_a) = (1-\alpha)$

$\int_{k_a^o}^{k_a} d \ln k_a = \dfrac{nF(1-\alpha)}{RT} \cdot \int_{E^o}^{E} dE \qquad E = E^o, \quad k_a = k_a^o$

Now, this r can be converted to current density by doing the simple formula which is ic by nF equal to k c c 0 and here it will be i a nF equal to k a C R and when i c equal to ia then we have i 0, but if ic is equal to not equal to ia then there would be a net current flow which I can write in terms of i applied which is ic minus ia equal to to k c C 0 minus k a C R this is the net with multiplication factor nF, because I have to consider ic equal to nF k c 0 as well as ia equal to nF k a C R.

Now, I can also go back to this alpha now I know that RT nF d dE ln 1 by k c equal to alpha and here I have put n because we are considering this reaction. So, the number of electrons is basically n. Now if I integrate this so d ln 1 by k c equal to alpha since these are all constants, this entire part is constants we are taking it out from integration sign. So, this becomes and now we have to see the limit. Now when we have polarization, because of that net current flow either it can go to positive side or negative side.

So, now if E 0 is basically my initial equilibrium potential and E is basically the initial equilibrium potential and this is the final potential after polarization. So, then this should be E 0 E and when E equal to E 0 my k c should be equal to k c 0 and similarly I can put this is k c 0 and this is k c.

So, these are two limits then I would get ln k c 0 by k c equal to nF alpha divided by RT E minus E 0 similarly I can have this relation for the oxidative symmetry factor, we can also find out the limits we can write it in this fashion d ln k equal to n F 1 minus alpha by RT d here also the limit would be same. So, this is this and here it would be k a 0 and k a when E equal to E 0 k c equal to k c 0.

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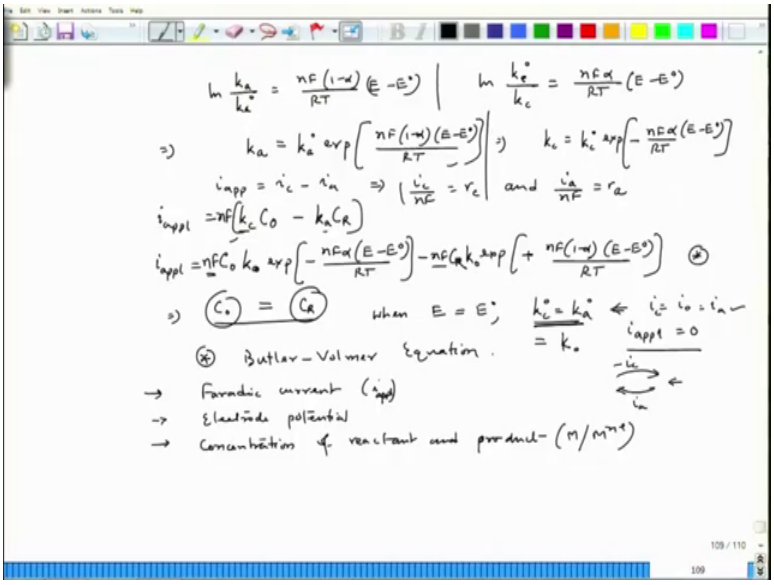

$\ln \frac{k_a}{k_a^\circ} = \frac{nF(1-\alpha)}{RT}(E - E^\circ)$ | $\ln \frac{k_c^\circ}{k_c} = \frac{nF\alpha}{RT}(E - E^\circ)$

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

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

$i_{appl} = nF\left[k_c C_0 - k_a C_R\right]$

$i_{appl} = nF C_0 k_0 \exp\left[-\frac{nF\alpha(E-E^\circ)}{RT}\right] - nF C_R k_0 \exp\left[+\frac{nF(1-\alpha)(E-E^\circ)}{RT}\right]$ ⊛

$\Rightarrow \quad C_0 = C_R$ when $E = E^\circ$; $k_c^\circ = k_a^\circ = k_0$ ← $i_c = i_0 = i_a$

$i_{appl} = 0$

$-i_c$

i_a

⊛ Butlar-Volmer Equation.

→ Faradic current (i_{appl})

→ Electrode potential

→ Concentration of reactant and product (M/M^{n+})

So, I would get ln k c 1 minus alpha RT E minus E 0 this is oxidative and another case ln k 0 k s sorry here it would be if we see this should be k a. So, this would be k a k a 0 and this is k c 0 by k c equal to n F alpha by RT E minus E 0. Now I can write it as ln k a or k a equal to exponential n F 0 minus alpha E minus E 0 divided by RT and here in this side k c 0 or k c would be equal to k c 0 exponential minus nF alpha E 0.

Now, interestingly if we consider that i applied equal to k c C of oxidant minus k a concentration of reductant and if we put those equations. So, I get k c 0 exponential minus nF alpha E minus E 0 by RT minus k a 0 exponential of course, there would be concentration part also this is C R minus nF 1 minus it should be plus E minus E 0 by RT I am just putting this formulas here I am replacing this k c and k 0.

Now, if we assume that C 0 and C R are equal, this concentrations are equal; that means, whatever number of ions are forming on the outermost layer is equal to the number of atoms that are coming out. So, if we have this situation then of course, when E equal to E 0 k c equal to k a 0 this is the condition. So, then I can replace this C part in both the sides it will be simply k 0 this is the new formula I am getting.

Now, this is nothing, but Butler-Volmer equation, this equation is called Butler-Volmer equation and this is coming from the rate of flow of charges those metal ions to the inner surface or the metal from the inner to outer surface or outer Helmholtz layer and we are considering the activation jump of those ions as well as atoms. So, the Butler-Volmer equation actually relates important parameters of electro chemistry one is faradic current which is i applied then it relates to the electrode potential, then it relates to concentration of reactants and product.

So, you can consider either M or M n plus depending on the reaction you are considering whether oxidation or reduction. So, all four are connected, now this condition is subjected to a situation when i equal to i 0 equal to i a and i applied is equal to 0, the net current flow is 0. So, when we have two current density this is ic this is ia there are the same magnitude, but flowing opposite then there will be no net current flow in the circuit.

So, in that situation the concentration of this reactant as well as product or concentration of oxidant and reductant both are same and that time we have got in this particular relation. Now when it actually polarized that time this concentration may change depending on whether it is activation polarization or concentration polarization. So, we would look into that part little later, but for the time being now we see that this Butler-Volmer equation has the correlation has a relation between faraday current electrode potential and concentration of reactant and product and from this reaction we can actually derive Nernst equation too.

Now, before I conclude I would like to say that when we have this particular pro relation I can equate it k 0 and then I can write k 0 here also. So, in lecture 33 we need to have a modification since i applied is equal to i c minus i a then with this we need to multiply nF and here also nF is to be multiplied since, i c by n F equal to R C and i a by n F equal to r a. So, the only small change there should be n F term added to this and that becomes my Butler-Volmer equation.

Thank you.