Corrosion - Part II

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Lecture - 09

Explanation of Corrosion Processes on the basis of Mixed Potential Theory: Part 2 (Cont….)

Hello everyone let's start lecture 9.

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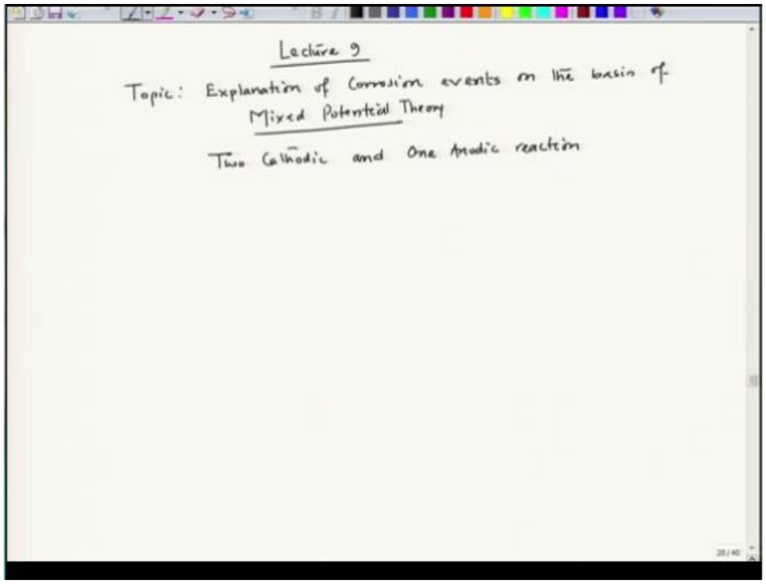

Lecture 9

Topic: Explanation of Corrosion events on the basis of Mixed Potential Theory

Two Cathodic and One Anodic reaction

And topic of course explanation of corrosion event on the basis of mixed potential theory and we have discussed 1 particular situation which is 2 cathodic and 1 anodic reaction. So, we discuss 2 cathodic and 1 anodic reaction that is the situation we have consider.

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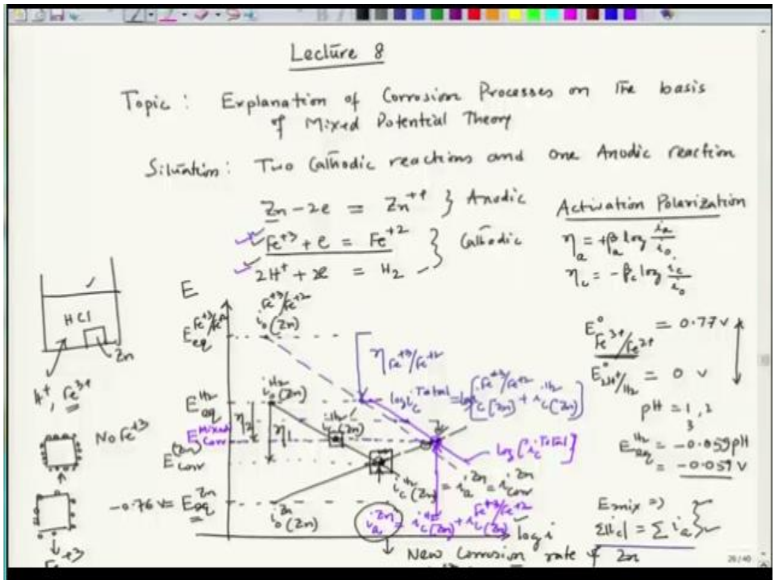

Lecture 8

Topic: Explanation of Corrosion Processes on the basis of Mixed Potential Theory

Situation: Two Cathodic reactions and one Anodic reaction

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

$Fe^{+3} + e = Fe^{+2}$

$2H^{+} + 2e = H_2$ } Cathodic

Activation Polarization

$\eta_a = +\beta_a \log \frac{i_a}{i_0}$

$\eta_c = -\beta_c \log \frac{i_c}{i_0}$

$E^{\circ}_{Fe^{3+}/Fe^{2+}} = 0.77\ V$

$E^{\circ}_{2H^{+}/H_2} = 0\ V$

pH = 1, 2, 3

$E_{eq}^{H_2} = -0.059 pH = -0.059\ V$

$E_{mix} \Rightarrow \Sigma |i_c| = \Sigma i_a$

We have drawn mixed potential plot this was the plot what we have discussed in lecture 8.

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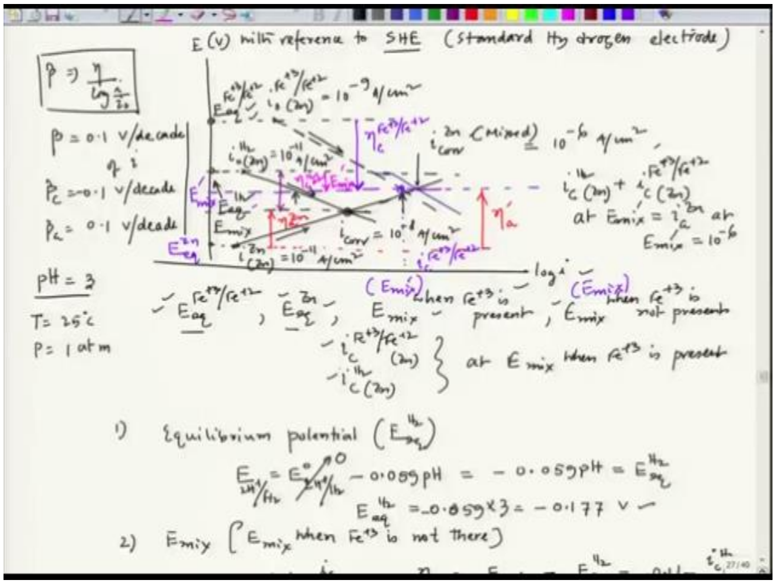

E (V) with reference to SHE (Standard Hydrogen electrode)

$\beta \Rightarrow \frac{\eta}{\log \frac{i}{i_0}}$

$\beta = 0.1$ V/decade

$\beta_c = -0.1$ V/decade

$\beta_a = 0.1$ V/decade

pH = 3

T = 25°C

P = 1 atm

$i_0^{Fe^{+3}/Fe^{+2}}(Zn) = 10^{-9}\ A/cm^2$

i_{corr}^{Zn} (Mixed) $\cong 10^{-6}\ A/cm^2$

$i_0^{H_2}(Zn) = 10^{-11}\ A/cm^2$

$i_{corr} = 10^{-8}\ A/cm^2$

$i_0^{Zn}(Zn) = 10^{-11}\ A/cm^2$

$i_c^{H_2}(Zn) + i_c^{Fe^{+3}/Fe^{+2}}(Zn)$ at $E_{mix} = i_a^{Zn}$ at $E_{mix} = 10^{-6}$

$E_{eq}^{Fe^{+3}/Fe^{+2}}$, E_{eq}^{Zn}, E_{mix} (E'_{mix}) when Fe^{+3} is present, E_{mix} (E_{mix}) when Fe^{+3} is not present

$i_c^{Fe^{+3}/Fe^{+2}}(Zn)$, $i_c^{H_2}(Zn)$ } at E_{mix} when Fe^{+3} is present

1) Equilibrium potential ($E_{eq}^{H_2}$)

$E_{2H^+/H_2} = E^{\circ}_{2H^+/H_2} - 0.059 pH = -0.059 pH = E_{eq}^{H_2}$

$E_{eq}^{H_2} = -0.059 \times 3 = -0.177\ V$

2) E_{mix} [E_{mix} when Fe^{+3} is not there]

And then we started discussing 1 solution numerical problem based on that particular discussion that when we have a strong oxidizer or a strong cathodic reaction in addition to another cathodic reaction. We have seen that the corrosion rate of that active component increases greatly. Why it increases greatly? Because this is log scale. So, that means if we increase it so it will be in orders of magnitude and that is what we could see that the order it was initially 10^{-8} when there was no oxidizer in the form of Fe+3.

Now once we have added oxidizer, so because of the mixed potential theory new dissolution rate which is this has gone into the - 6. So, that means the there is a 2 order of magnitude increase in the corrosion rate of zinc. Now then we wanted to solve this values okay, so let's how do we attack this particular problem, let's go one by one. The first thing we had to find out this equilibrium potentials and as well as I think we missed one more equilibrium potential which was E. Okay.

So, if we consider these many equilibrium, so we have to find out all the equilibrium potentials. Now here how many equilibrium potential which basically the reversible potential that could be present this is one which is E or let me draw it in this colour. So, E zinc equilibrium then this is already I have indicated this one this equilibrium potential which will be decided by the pH of the solution.

And then one more equilibrium potential is this one which is E equilibrium Fe+3 Fe+2, so this is the point and this is the point 3 equilibrium potential. And now we have 2 mixed potentials, 1 mixed potential is this one which is the mixed potential when there is no oxidizer only hydrogen reduction and zinc oxidation are considered. So, this is E mix I simply put it as E mix and this is the potential which is E mix prime.

So, this E mix prime and E mix are nothing but this is nothing but E mix prime and this is nothing but E mix only E mix as per this diagram. Now one by one first let's calculate equilibrium potential E equilibrium for hydrogen reaction, we know that

$$E = E^o - 0.059\,pH$$

so where this value is 0 this will be - 0.059 pH is nothing but E equilibrium H2. And these are the data we have another data weather information what we have is temperature equal to 25 degree Celsius pressure equal to 1 atmosphere.

So, this since we have considered pH to be 3, so E equilibrium H2 = - 0.059 pH equal to and pH = 3. I can change it into 3, is nothing but - 0.177 volt and this is all with reference to a standard hydrogen electrode. The next we have to find out E mix which is nothing but E mix when Fe+3 is not there. Fine.

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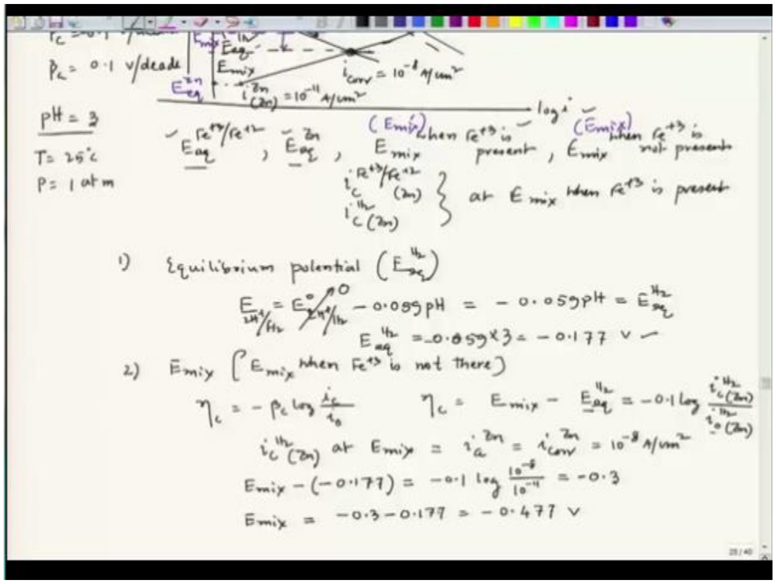

$\beta_c = 0.1$ v/decade

pH = 3

T = 25°C

P = 1 atm

$E_{eq}^{Fe^{+3}/Fe^{+2}}$, E_{eq}^{Zn}, E_{mix} (E_{mix}) when Fe^{+3} is present, E_{mix} (E_{mix}) when Fe^{+3} is not present

$i_{c}^{Fe^{+3}/Fe^{+2}}(Zn)$, $i_{c(Zn)}^{H_2}$ } at E mix when Fe^{+3} is present

1) Equilibrium potential ($E_{eq}^{H_2}$)

$$E_{2H^+/H_2} = \cancel{E^{\circ}_{2H^+/H_2}}^{0} - 0.059\,pH = -0.059\,pH = E_{eq}^{H_2}$$

$$E_{eq}^{H_2} = -0.059 \times 3 = -0.177 \text{ V}$$

2) Emix (E_{mix} when Fe^{+3} is not there)

$$\eta_c = -\beta_c \log \frac{i_c}{i_0} \qquad \eta_c = E_{mix} - E_{eq}^{H_2} = -0.1 \log \frac{i_{c(Zn)}^{H_2}}{i_{0(Zn)}^{H_2}}$$

$$i_{c(Zn)}^{H_2} \text{ at } E_{mix} = i_a^{Zn} = i_{corr}^{Zn} = 10^{-8} \text{ A/cm}^2$$

$$E_{mix} - (-0.177) = -0.1 \log \frac{10^{-8}}{10^{-11}} = -0.3$$

$$E_{mix} = -0.3 - 0.177 = -0.477 \text{ V}$$

So, this potential would be we have to find out applying this equation i zero, so now here neeta c equal to E mix - E equilibrium hydrogen. Now here we are considering the polarization for hydrogen evolution reaction on zinc surface and this is cathodic polarization because the cathodic reaction is nothing but the hydrogen evolution on zinc surface which should be equal to - beta c which is nothing but 0.1 log of ic hydrogen on zinc surface divided by i zero which is the exchange current density of hydrogen on zinc surface.

So, that means we are considering this line, now what would be ic hydrogen on zinc surface at E mix. Since this is the mix potential when Fe+3 is not there, so that means at E mix potential E mix should be ia zinc which is nothing but I corr zinc. So, here i corr zinc is nothing but 10^{-8} ampere per centimeter square, so E mix - and E equilibrium is how much we have already found out - 0.177 = - 0.01 log of 10^{-8}.

And what is i zero for zinc hydrogen of evolution reaction on zinc it is 10^{-11} ampere per second, so, this becomes 0.3 with a - sign. So E mix = 0.3 - 0.177 = - 0.477 volt.

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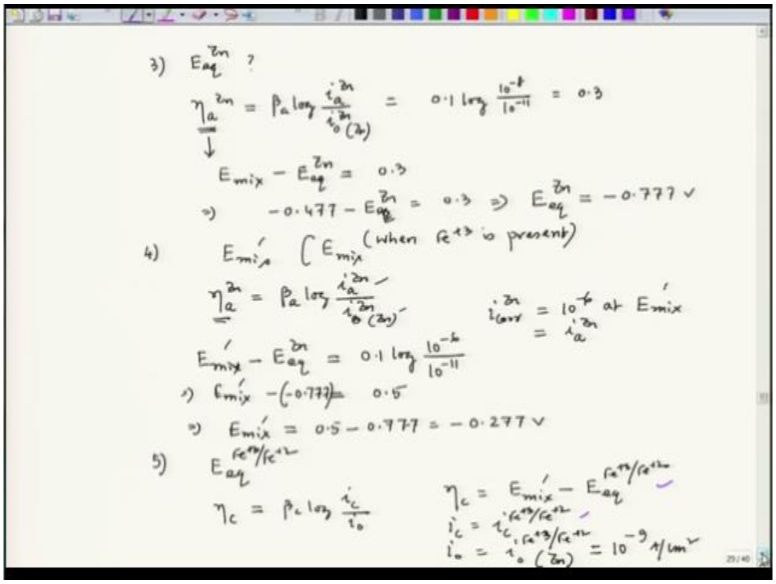

3) E_{eq}^{Zn} ?

$$\eta_a^{Zn} = \beta_a \log \frac{i_a^{Zn}}{i_o^{Zn}(Zn)} = 0.1 \log \frac{10^{-8}}{10^{-11}} = 0.3$$

$$\downarrow$$

$$E_{mix} - E_{eq}^{Zn} = 0.3$$

$$\Rightarrow -0.477 - E_{eq}^{Zn} = 0.3 \Rightarrow E_{eq}^{Zn} = -0.777 \checkmark$$

4) E'_{mix} $\left[E_{mix}^{(\text{when } Fe^{+3} \text{ is present})} \right.$

$$\eta_a^{Zn} = \beta_a \log \frac{i_a^{Zn}}{i_o^{Zn}(Zn)} \qquad i_{corr}^{Zn} = 10^{-6} \text{ at } E'_{mix} = i_a^{Zn}$$

$$E'_{mix} - E_{eq}^{Zn} = 0.1 \log \frac{10^{-6}}{10^{-11}}$$

$$\Rightarrow E'_{mix} - (-0.777) = 0.5$$

$$\Rightarrow E'_{mix} = 0.5 - 0.777 = -0.277 \checkmark$$

5) $E_{eq}^{Fe^{+3}/Fe^{+2}}$

$$\eta_c = \beta_c \log \frac{i_c}{i_o} \qquad \eta_c = E'_{mix} - E_{eq}^{Fe^{+3}/Fe^{+2}}$$

$$i_c = i_c^{Fe^{+3}/Fe^{+2}}$$

$$i_o = i_{o\,(Zn)} = 10^{-9} \text{ A/cm}^2$$

Now we have to find out E equilibrium zinc, so third is E equilibrium zinc. let’s find this, what should be this value. Now if we see this plot again we can consider this line and again we can consider polarization for the anodic reaction that is zinc dissolution. So, this is my E equilibrium zinc parallel line of that, so this should be my over voltage. So, this is

$$\eta_a^{Zn} = \beta_a log \frac{i_a^{Zn}}{i_o^{Zn}}$$

So, let’s see that those points this is the point which is i zero for the zinc dissolution and for the zinc at equilibrium zinc potential and this is the E corr where i corr is 10^{-8} that means ia is nothing but 10^{-8}. So, if we put those values beta a is 0.1 log 10^{-8} divided by 10^{-11}, here is also it is 10^{-11}, so let’s put that, so you will get 0.3.

And this nothing but E mix - E equilibrium zinc = 0.3. So E mix we have already found out - 0.477 - E equilibrium zinc = 0.3, so we are getting E equilibrium zinc = - 0.777, fine, this is the value. Now then let’s find out what should be the E equilibrium 2, so in order to find that if we would like to find this we have to find first we have to find E mix prime which is nothing but let’s so instead of this let’s get to E mix prime which is nothing but E mix when Fe+3 is present.

So, to solve that we can consider na zinc up to the potential of E mix prime, so here we consider, so if we take this extend this values, so we have to consider this polarization which is na prime. So, here

$$\eta_a' = \beta_a log \frac{i_a^{Zn}}{i_{o,Zn}^{Zn}}$$

so here this is E mix prime - E equilibrium zinc = 0.1 log. Now here corrosion rate i corr zinc = 10^{-6} at E mix prime which is nothing but ia zinc.

So, this is 10^{-6} and this value is 10^{-11} so it becomes 0.5 and this is - 0.777 and this is E mix prime, so E mix prime = 0.5 - 0.777= - 0.277 volt. So, once we know E mix prime then we can find out this value we can find out, how, so if we extend this further this particular point. So, if we extend this particular E mix prime and then we have to see the polarization this particular, so this is nc of Fe+3 Fe+2.

So, this polarization if we consider we can find out this particular quantity, how, so now we have this dotted line, this dotted line we have if we consider polarization along this line I can fit this particular equation in this form. So, 5 finding E equilibrium Fe+3 Fe+2 we have to find that, so that case I can consider

$$\eta_c = \beta_c log \frac{i_c}{i_o}$$

equal to E mix prime - E equilibrium Fe+3 Fe+2, ic equal to nothing but ic Fe+3 Fe+2 and i zero equal to i zero Fe+3 Fe+2 over zinc surface equal to 10^{-9} ampere centimeter square.

Now when we try to solve this we have to see this particular data until as I here 1 coordinate is known which is E mix prime that other coordinator is not known which is nothing but this is the value of ic Fe+3 Fe+2 at E mix this value is not known. And here also i zero is known E equilibrium Fe+3 by Fe+2 is not known. So, we have in this equation we have this is unknown as well as this is unknown. So, we need to find at least 1 known parameter, so in order to find that we have to find out ic hydrogen on zinc at E mix prime.

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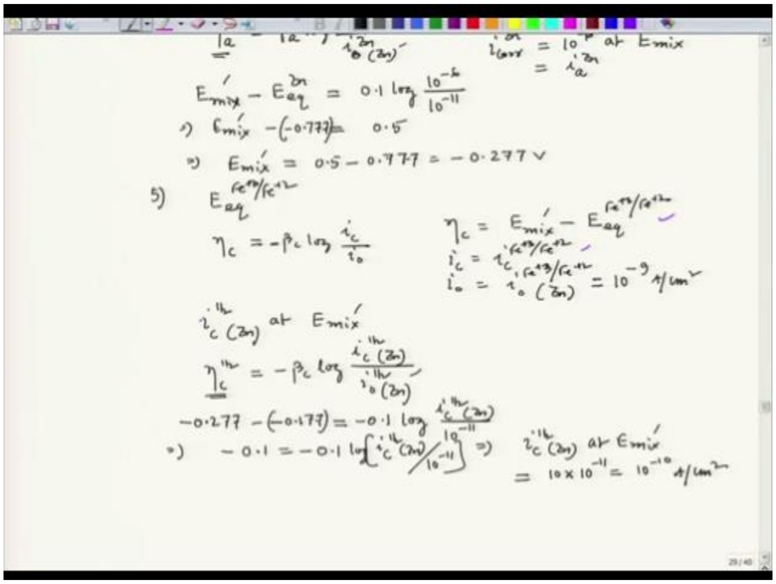

$i_{corr}^{Zn} = 10^{-6}$ at E_{mix}

$= i_a^{Zn}$

$E'_{mix} - E_{eq}^{Zn} = 0.1 \log \frac{10^{-6}}{10^{-11}}$

$\Rightarrow E'_{mix} - (-0.777) = 0.5$

$\Rightarrow E'_{mix} = 0.5 - 0.777 = -0.277$ V

5) $E_{eq}^{Fe^{+3}/Fe^{+2}}$

$\eta_c = -\beta_c \log \frac{i_c}{i_0}$

$\eta_c = E'_{mix} - E_{eq}^{Fe^{+3}/Fe^{+2}}$

$i_c = i_c^{Fe^{+3}/Fe^{+2}}$

$i_0 = i_{0, Fe^{+3}/Fe^{+2}}(Zn) = 10^{-9}$ A/cm²

$i_c^{H_2}(Zn)$ at E'_{mix}

$\eta_c^{H_2} = -\beta_c \log \frac{i_c^{H_2}(Zn)}{i_0^{H_2}(Zn)}$

$-0.277 - (-0.177) = -0.1 \log \frac{i_c^{H_2}(Zn)}{10^{-11}}$

$\Rightarrow -0.1 = -0.1 \log\{i_c^{H_2}(Zn)/10^{-11}\} \Rightarrow i_c^{H_2}(Zn)$ at E'_{mix}

$= 10 \times 10^{-11} = 10^{-10}$ A/cm²

So, we can find that by using this particular equation hydrogen over zinc surface - sorry we missed the - sign here. So, the beta c log of ic hydrogen on zinc surface i zero of hydrogen on zinc surface. So, here we know this particular voltage because we know E mix prime, so here this is the polarization, so let me put it in a different colour, so let me put it this colour, so this is the polarization we are considering, this is the polarization.

So, this is neeta c hydrogen at E mix prime, so E mix prime - E equilibrium hydrogen equal to 0.1 log ic hydrogen on zinc surface and this is known 10^{-11}. And this is also known I can replace it with - 0.177. So this is also known I can replace it with - 0.277. So, this value becomes - 100 - 0.1 = - 0.1 log of 10 to the power sorry, so this is ic hydrogen over zinc surface divided by 10^{-11}.

So, then ic hydrogen over zinc surface at E mix prime equal to 10 to the power into 10^{-11} this becomes 10^{-10} ampere centimeter square. So, once we know this current that means this current if we know then I will be able to know the current corresponding to this. Why? Because ic hydrogen over zinc surface + ic Fe+3 Fe+2 over zinc surface at E mix prime equal to ia zinc at E mix prime which is nothing but 10^{-6}.

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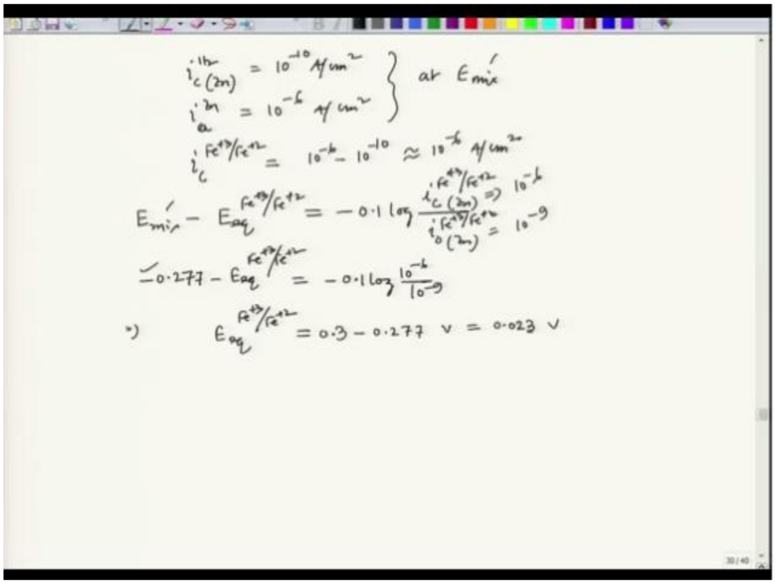

$$\left.\begin{array}{l} i_{c(Zn)}^{H_2} = 10^{-10}\ A/cm^2 \\ i_a^{Zn} = 10^{-6}\ A/cm^2 \end{array}\right\}\ \text{at } E'_{mix}$$

$$i_c^{Fe^{+3}/Fe^{+2}} = 10^{-6} - 10^{-10} \approx 10^{-6}\ A/cm^2$$

$$E'_{mix} - E_{eq}^{Fe^{+3}/Fe^{+2}} = -0.1\log\frac{i_{c(Zn)}^{Fe^{+3}/Fe^{+2}} \Rightarrow 10^{-6}}{i_{o(Zn)}^{Fe^{+3}/Fe^{+2}} = 10^{-9}}$$

$$\simeq -0.277 - E_{eq}^{Fe^{+3}/Fe^{+2}} = -0.1\log\frac{10^{-6}}{10^{-9}}$$

$$\Rightarrow E_{eq}^{Fe^{+3}/Fe^{+2}} = 0.3 - 0.277\ V = 0.023\ V$$

So, if that is true, so then ic hydrogen over zinc surface equal to 10^{-10} ampere per centimeter square and ic ia zinc equal to 10^{-6} ampere per centimeter square at E mix prime. So, ic Fe+3 Fe+2 would be equal to 10^{-6} - 10^{-10} which is nearly 10^{-6} ampere per centimeter square. So, once we know that then

$$E'_{mix} - E_{eq}^{Fe^{3+}/Fe^{2+}} = -0.1\ log\frac{i_c^{Fe^{3+}/Fe^{2+}}}{i_{o,Zn}^{Fe^{3+}/Fe^{2+}}}$$

So, now this value is known now which is 10^{-6} this value is 10^{-9}, so this becomes 0.1 log of 10^{-6} by 10^{-9} and this is - 0.277 - equilibrium Fe+3 Fe+2. So, E equilibrium Fe+3 Fe+2 equal to this is this becomes 0.3 and this should be added up 0.3 - 0.277, so this volt equal to so, 0.023 volt. So, now we got all the things what we wanted to have this value is obtained, this is also obtained, this is obtained, this is obtained, this is obtained.

Now even we have found out these 2 okay, so this is the entire solution of this particular numerical please go through this we will have other problems given to you on the basis of this during your tutorial section. So, let’s stop here we will continue our discussion in our next lecture, thank you.