Corrosion - Part II
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Lecture - 03
Electrochemical Polarization: Activation and Concentration Polarization, Tafel Equation

Hello everyone, let's start lecture 3.

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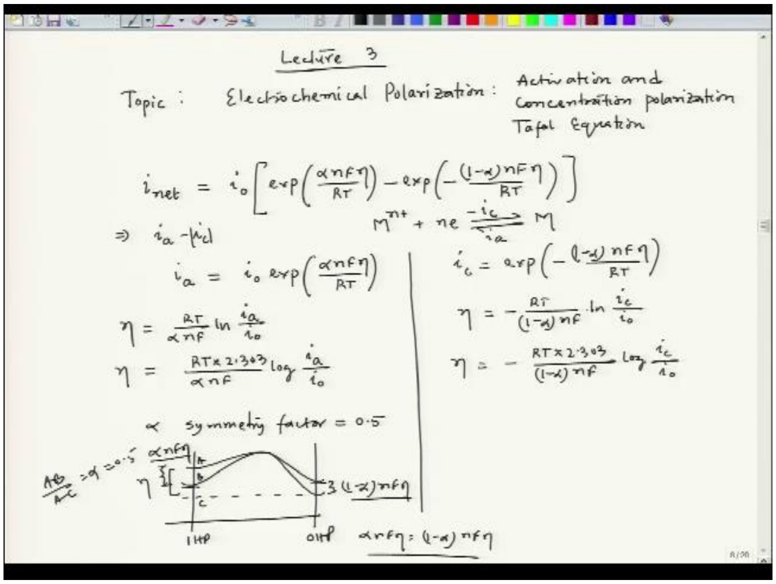

Lecture 3

Topic : Electrochemical Polarization : Activation and Concentration polarization Tafel Equation

$$i_{net} = i_o\left[\exp\left(\frac{\alpha nF}{RT}\eta\right) - \exp\left(-\frac{(1-\alpha)nF\eta}{RT}\right)\right]$$

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

$$\Rightarrow i_a - |i_c|$$

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

$$\eta = \frac{RT}{\alpha nF}\ln\frac{i_a}{i_o}$$

$$\eta = \frac{RT \times 2.303}{\alpha nF}\log\frac{i_a}{i_o}$$

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

$$\eta = -\frac{RT}{(1-\alpha)nF}\ln\frac{i_c}{i_o}$$

$$\eta = -\frac{RT \times 2.303}{(1-\alpha)nF}\log\frac{i_c}{i_o}$$

α symmetry factor = 0.5

$\frac{AB}{AC} = \alpha = 0.5$

$\alpha nF\eta$

η

A

B

C

$(1-\alpha)nF\eta$

IHP

OHP

$\alpha nF\eta = (1-\alpha)nF\eta$

And topic, will continue our discussion on electrochemical polarization and where we will consider activation and concentration polarization and gradually will get into today at least Tafel equation. At the end of lecture 2 we come across 1 equation which is

$$i_{applied} = i_{net} = i_o\left[exp\ exp\left(\frac{\alpha nF\eta}{RT}\right) - exp\ exp\left(-\frac{(1-\alpha)nF\eta}{RT}\right)\right]$$

and then this is nothing but ia - ic, so separately we can write

$$i_c = i_o\left[exp\ exp\left(-\frac{(1-\alpha)nF\eta}{RT}\right)\right]$$

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

and in this case we are considering a generalized equation this ic this is ia. Now if we start operating on this 2 equations I can write overvoltage in the form of

$$\eta = \frac{RT}{\alpha nF}\left[ln\ ln\ \left(\frac{i_a}{i_o}\right)\right]$$

Similarly,

$$\eta = \frac{RT}{(1-\alpha)nF}\left[ln\ ln\ \left(\frac{i_a}{i_o}\right)\right]$$

So if I convert into log with base 10 I can write it as into

$$\eta = \frac{RT * 2.303}{\alpha nF}\left[log\ log\ \left(\frac{i_a}{i_o}\right)\right]$$

Similarly here

$$\eta = -\frac{RT * 2.303}{(1-\alpha)nF}\left[log\ log\ \left(\frac{i_a}{i_o}\right)\right]$$

Interestingly in our case this alpha which is symmetry factor which is considered to be 0.5 it means that the contribution of this over potential towards anodic as well as cathodic side or let us say IHP and OHP is similar or same.

That means the distribution if I go back to that slide if I see this particular condition this is IHP OHP, this is a situation where i zero is setup, now if ia is more than ic so this will be the situation that time this becomes my total η and ABC, so (AB)/(AC) = α which is 0.5. Now this part is αnFη and this part (1- αnFη). So these 2 are equal. So I can say that

$$\alpha nf\eta = (1 - \alpha nf\eta)$$

So that is the situation we are considering.

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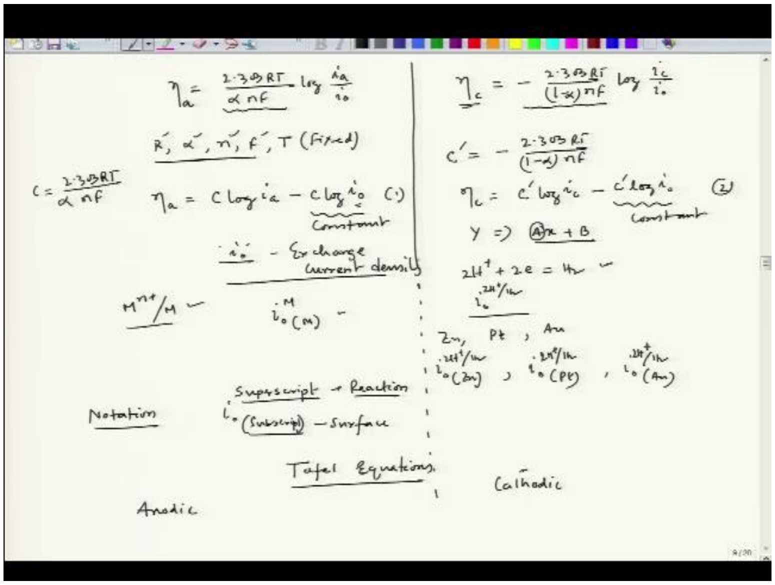

$\eta_a = \frac{2.303 RT}{\alpha nF} \log \frac{i_a}{i_0}$

R, α, n, F, T (Fixed)

$C = \frac{2.303 RT}{\alpha nF}$

$\eta_a = C \log i_a - \underbrace{C \log i_0}_{\text{Constant}}$ (1)

i_0 - Exchange current density

M^{n+}/M — $i_0^{M}(M)$ —

Notation

i_0 Superscript → Reaction
(Subscript) – Surface

Tafel Equations

Anodic

$\eta_c = -\frac{2.303 RT}{(1-\alpha) nF} \log \frac{i_c}{i_0}$

$C' = -\frac{2.303 RT}{(1-\alpha) nF}$

$\eta_c = C' \log i_c - \underbrace{C' \log i_0}_{\text{Constant}}$ ②

$Y \Rightarrow \boxed{A}x + B$

$2H^+ + 2e = H_2$ —

$i_0^{2H^+/H_2}$

Zn, Pt, Au

$i_0^{2H^+/H_2}(Zn)$, $i_0^{2H^+/H_2}(Pt)$, $i_0^{2H^+/H_2}(Au)$

Cathodic

Now once we get this, so we can write

$$\eta = \frac{2.303\ RT}{\alpha nF}\left[log\ log\ \left(\frac{i_a}{i_o}\right)\right]$$

Now interestingly since it is ia with reference to anodic current density I can write it as overvoltage to be anodic overvoltage. Now similarly I can write

$$\eta = -\frac{2.303\ RT}{(1-\alpha)nF}\left[log\ log\ \left(\frac{i_a}{i_o}\right)\right]$$

Since we are considering the cathodic current density we can write it as cathodic overvoltage. Now R alpha nF all are constant quantities because here n is constant for a particular reversible electrochemical reaction.

F is constant, R is thus constant which is constant, also alpha have considered we have considered 0.5, now if I fix temperature this is fixed, so these quantity in both the cases they are fixed. So I can write in a straight line equation. So I can write C log ia - C log i zero. Similarly, that means here

$$C = 2.303\ RT\alpha nF$$

and whereas

$$C' = -2.303\ RT(1-\alpha)nF$$

If that is the situation then I can write it as C' log i_c - C' log i_0.

Now little bit more on i zero, so i zero is exchange current density, now this exchange current density for a particular reversible reaction in this case it is M n+ M, this is a reversible reaction we are considering. Now any electrochemical reaction happens on a particular surface, Now this i zero will see later that i zero is a strong function of the surface on which that reversible reaction is taking place ok. So in this case the reaction these particular reversible reaction is taking place on the metal surface.

So I can write i zero for metal on metal surface, so this is the notation we will use, now these situation will be critical while we consider a gaseous reaction. For example hydrogen evolution reaction let us say we consider this reaction that time i zero when it is non corroding situation that means a reversible situation. So i zero of hydrogen evolution I can write this one as

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

These particular i zero we fix all other parameters like all other factors like solution concentration, temperature.

Al those things are constant, then depending on the surface this i zero of hydrogen evolution reaction can change. Now in an acid solution we fix the pH also, but in the acid solution in the same pH we can have hydrogen evolution reaction on zinc surface, we can have hydrogen evolution on platinum surface, we can have hydrogen evolution on gold surface ok. So like that all the surface for example if zinc with dip in HCL we will see that hydrogen bubble on the zinc surface.

So that means this particular reaction is taking place on zinc surface. Now even similarly if I put a platinum in an acid will see that hydrogen evolution takes place on the platinum surface. So that case this value will change greatly even if we fix the pH value and temperature summation all those things. Now that case we have to indicate that this is on what surface. So it is better to write i zero zinc hydrogen H2 or i zero 2H+ H2 on platinum or i zero H2 on gold surface.

So like that we have to write, so i zero bracket and then subscript superscript and this is subscript. So this is the surface on which that electrochemical reaction is taking place and this is the reaction electrochemical reaction. So this is the notation will use, this is the notation. So now in this case i zero for an electrochemical reaction which has achieved reversibility that means equilibrium, this is a fixed value.

So that means this entire quantity is a constant, similarly here also this is a constant. So now I can indicate this one as a kind of straight line equation x+ B like this I can write Y = AX+ B which is the straight line equation, that the slope is nothing but A is a slope. So now if I try to plot this 2 equations. These 2 equations I can write. So this is another equation, equation 1, this is equation 2. These 2 equations are nothing but Tafel equations.

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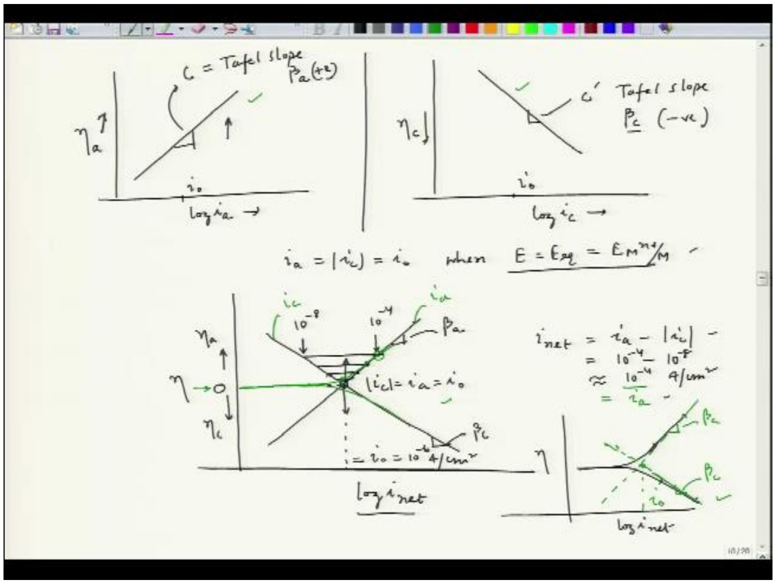

And this Tafel equitation is one case this is this side it is anodic this side is cathode, now if try to plot then let us plot them, one case I will plot with reference to log ia and here overvoltage and here I have to put η_a similarly on the other side I will plot log of ic η_c. Now interestingly this slope C, if you see this, this is a positive slope and here C prime is a negative slope. Fine. So if I try to see that one side the plot would be like this another side the plot would be like this with a negative slope.

So this is the slope which is called C and this is the slope which is C prime and these slope in electrochemistry we write it as a tafel slope, this is also a Tafel slope and these are popularly termed it as beta c and hear it is beta a, why this is the Tafel slope for anodic reaction anodic side, this is the tafel slope for cathodic side and this is a negative and this is positive. And this is also matching with our concept that whenever we send positive current.

That means ia increases with reference to with respect to ic, the potential goes positive side and here also it is C that that means more and more ia ic that overvoltage increasing and overvoltage is nothing but the measure of polarization. And similarly on the other side if beta C has the slope negative slope. So that means with increase in the magnitude of ic I would always fine that η_c is decreasing.

And here it is increasing, so that means this is also perfectly fine as per our convention, now what happens when ia = i zero. Let us say this i zero and here also this is i zero. So i zero when it is achieved when ia = ic = i zero when E = E equilibrium or we considered it as has M n+ M. Fine, so this is the condition that an i zero is similar to same as ia as well as ic. So that means if we combine this 2 curves we can get a curve like this.

So this is η, so this plot is like this and another plot would be like this, so this is nothing but beta c slope and this slope is beta a and what is this value and that time this will be log i, now at this point is nothing but i zero because I see that at this point ic = ia = i zero and that time what is the over voltage because this is at equilibrium potential over voltage should be zero and as we go upward then overvoltage goes up.

And as we are going down overvoltage goes down from the equilibrium potential, so this is going down. Now we have to see that what is the net current because our actual equation is this one. So we have actually going to get the net current this is the difference between these 2 current. Now net current if you see let us say this particular value you assume some value 10^{-6} ampere per centimeter square.

So now if I go to this potential, then this value is let’s say 10^{-4}, these value goes to 10^{-8}. So then what is

$$i_{net} = i_a - |i_c| = 10^{-4} - 10^{-8} \sim 10^{-4}$$

So now if I would like to plot i net what will be the point the that locus point in this particular diagram, that time that point would be lying here. Because it is exactly same as nothing but ia.

Because this current is ia and this current is ic. Now as we go down if we keep going down I could see the difference between ic and ia that is decreasing. So that time at some point of time that means that are very low overvoltage, I will not get this approximation. that time this difference will be some finite difference and then once we get that finite difference then we have to take the log. Ok.

Because we are taking log of i net, so then that time this gradually these points will keep shifting, so here it is this, now I am finding that the difference is coming up we go down further, I could see the difference is here**.** Now as you are coming closer to this overvoltage zero that place at this point I could see that this difference is going to be zero. So once we have zero then these point will go asymptotically towards this point.

So then the plot nature would be like this. Similar, thing happens on the bottom side, on the cathodic side this should be this. So what would be my experimental plot, experimental plot would be and then from this experimental plot because experiment wise I will only get the i net which is the experimental current density I will measure. So then the straight line part I could see the straight line part is happening at the higher overvoltage.

Here also higher over voltage from that I will draw a straight line and similarly here also I draw a straight line. Fine. These are crossing point which is nothing but i zero ok and this straight line slope is nothing but beta c, this line is beta a and this is the polarization line which is nothing but this and this is the polarization line nothing but this. Though these are invisibly present, but we can have an idea that where are those lines from the polarization line polarization diagram.

So the experimental polarization plots, so this green line here and the black line here, this in this case black line, in this case the green line, these are the polarization plots, these plots we can have.
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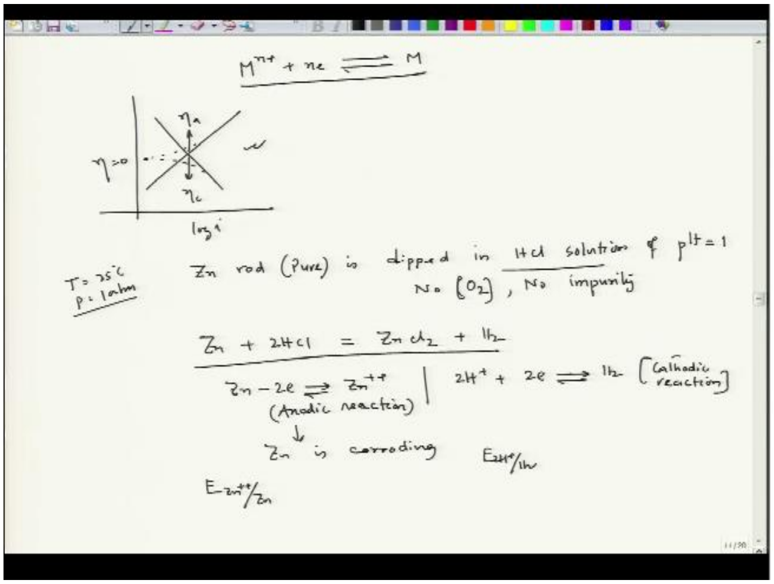

$$M^{n+} + ne \rightleftharpoons M$$

T = 25°C
P = 1atm

Zn rod (Pure) is dipped in HCl solution of pH = 1
No $[O_2]$, No impurity

$$Zn + 2HCl = ZnCl_2 + H_2$$

$Zn - 2e \rightleftharpoons Zn^{++}$ (Anodic reaction) ↓ Zn is corroding | $2H^+ + 2e \rightleftharpoons H_2$ [Cathodic reaction]

$E_{Zn^{++}/Zn}$ E_{2H^+/H_2}

Now coming to this is for a single electrode system, for example here what we are getting for a single system

$$Mn^+ + ne = M$$

in this case we are getting a plot like this. So we are having a situation like this but the plot would be definitely like this. Fine. No issues. So this is over voltage equal to zero, this goes up, this goes down, this is η_a, this is η_c and this is log scale log i and interesting this is a straight line of course this is a straight line we have already explain because this is a straight line equation.

Now coming to a situation where we have 2 such reactions taking place where we can experience such reactions. Let us say we have a situation like zinc rod let us say pure is dipped in HCl solution of pH 1, lets say. Ok. Now the solution has a condition what are those condition, this is dipped, there is no oxygen dissolve oxygen, no oxygen. Fine, no impurity, these condition only we are considering.

And the temperature is let us say room temperature which is 25 degree Celsius, pressure is 1 atmosphere. Fine. Now in this case will have 2 reactions 2 half cell reactions, one reaction would be taking place on zinc plate, so the zinc plate will see what are the observation, observation would be we will see that on the zinc surface will get little bit of bubbling formation and those bubbles and nothing but hydrogen bubbles.

And reaction would be

$$Zn + 2HCl = ZnCl_2 + H_2$$

This is the balance reaction. Now if we break them and then try to see whether they are electrochemical in nature we can easily see that, we see that zinc if it releases 2 electron it goes to zinc++ whereas 2 hydrogen+ it access 2 electron and goes to hydrogen. Now immediately it is very easy to understand that this is the cathodic reaction and this is the anodic reaction.

And since we are considering our context to be only corrosion so though we can easily see that zinc is corroding. Fine, now if we allow them this particularly take them separately let us say I put zinc in a zinc ion zinc ion present, then I can have an equilibrium reaction like this. Similarly, if we have a hydrogen cell where I can have an equilibrium like this. So the both this equilibrium would have some E equilibrium reaction.

And both these cases would have a separate like this diagram. Similarly, here also E, I will get an equilibrium potential like this, if we allow them to equilibrate in a separately if we are not mixing them.

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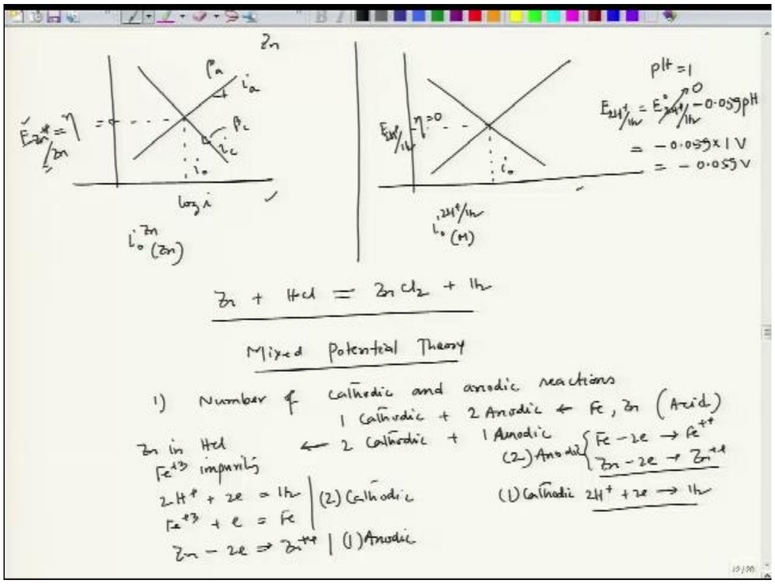

pH = 1

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

$= -0.059 \times 1$ V

$= -0.059$ V

Zn + HCl = $ZnCl_2$ + H_2

Mixed Potential Theory

1) Number of cathodic and anodic reactions

1 Cathodic + 2 Anodic ← Fe, Zn (Acid)

Zn in HCl ← 2 Cathodic + 1 Anodic

Fe^{+3} impurity

(2) Anodic $\left\{ \begin{array}{l} Fe - 2e \rightarrow Fe^{++} \\ Zn - 2e \rightarrow Zn^{++} \end{array} \right.$

(1) Cathodic $2H^+ + 2e \rightarrow H_2$

$2H^+ + 2e = H_2$ | (2) Cathodic

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

$Zn - 2e \Rightarrow Zn^{++}$ | (1) Anodic

Now that case both the cases will have separate diagrams, so that means in this case I will have a diagram like this log i, I have a diagram like this and this is nothing but i zero and these i zero is nothing but zinc on zinc surface. Similarly, and this is ia, this is ic, this is the slope beta a, this is the slope beta c for the zinc case, this is the zinc site and these corresponds to zero which is nothing but E zinc++ zinc.

On the hydrogen side if I see so it will be again like this, and now here it is happening on some this is i zero on some surface. So I will say that metal surface it must be happening a metal surface, hydrogen H2 this is i zero and correspondingly its potential would be E H+ H2 which is nothing but zero overvoltage zero. Now here we are considering 1 pH = 1. So then what will be this equilibrium potential

$$E = E_{H_2}^{o} - 0.059\, pH$$

And we know that this value is zero is nothing but 0.059 and pH = 1 volt = -0.0594. Now here depending on the zinc concentration I can change this particular value. Now when you add when you mix them immediately there will be some finite zinc concentration in that. Now before the reaction starts it will have some finite values. Now what happens if we mix then, now we have to understand this, this reaction from this diagrams

$$Zn + 2HCl = ZnCl_2 + H_2$$

These reaction we have to understand with the help of these 2 diagrams. How do we do that? In order to understand these particular reactions with the reference of these 2 reactions these 2 plots we need to get to the mix potential theory. This mix potential theory we have already discussed in lecture 1 that is in corrosion one will not go detail of those discussions you can go back to those lectures and then follow up.

We will just put forward a brief of it. Ok. So now this mix potential theory what are those 2 major postulates, 1 postulate says that there could be number of cathodic and anodic reactions. There could be number of cathodic and anodic reactions it could be 1 cathodic+ 2 anodic or 2 cathodic+ 1 anodic. Fine. So like that there could be multiple cathodic multiple anodic reactions. For example this example you can easily site that iron and zinc.

They are coupled, and if they are put up in acid, so that case cathode reaction would be hydrogen evolution if it is deaerated that means there is no dissolve oxygen or impurity are there. So that case is 1 cathode reaction which is hydrogen gas evolution and 2 anodic reactions that means iron in this case I can say that iron releases 2 electrons and then form 2 iron++ ion and zinc releases 2 electron and forms zinc++. Fine.

So now these are the 2 anodic reactions and what are the cathode reaction is H+ H2. So this is cathodic reaction. Now I can have example of 2 cathodic 1 anodic where let say zinc in HCl where we have Fe+3 impurity. So that case what are the 2 cathodic reactions

$$2H^+ + 2e = H_2$$

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

These are the 2 cathodic reaction, this is in this case 2 anodic, 1 cathodic and in this case 2 cathodic and 1 anodic.

What is that anodic reaction zinc releases 2 electron and form zinc++. So this is 1 anodic, in this case 2 anodic 1 cathodic and this is 2 cathodic 1 anodic. Fine. So we can have several such examples. So this is the simplest example that could be multiple of cathodic and anodic reactions and the second postulate says that the charge balance.

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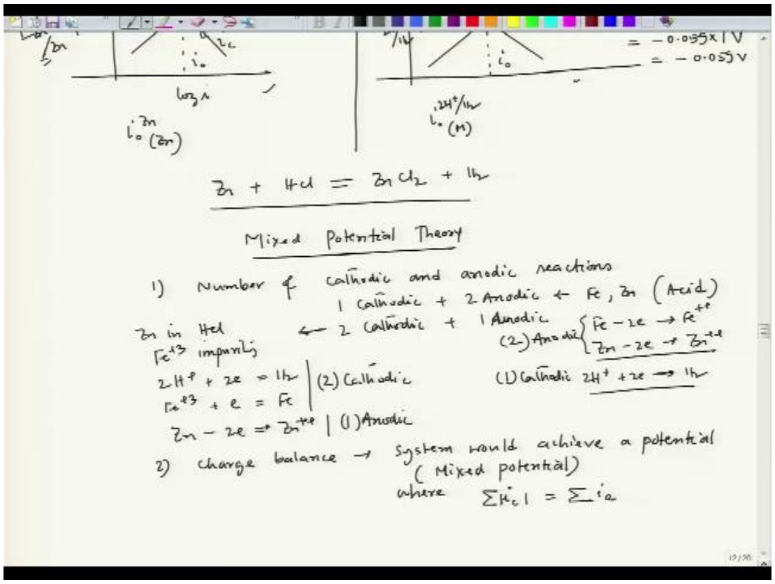

$Zn + HCl = ZnCl_2 + H_2$

Mixed Potential Theory

1) Number of cathodic and anodic reactions

1 Cathodic + 2 Anodic ← Fe, Zn (Acid)

Zn in HCl Fe+3 impurity ← 2 Cathodic + 1 Anodic

(2) Anodic $\left\{ \begin{array}{l} Fe - 2e \rightarrow Fe^{++} \\ Zn - 2e \rightarrow Zn^{++} \end{array} \right.$

(1) Cathodic $2H^+ + 2e \rightarrow H_2$

$2H^+ + 2e = H_2$, $Fe^{+3} + e = Fe$ | (2) Cathodic

$Zn - 2e \rightarrow Zn^{++}$ | (1) Anodic

2) charge balance → System would achieve a potential (Mixed potential) where $\Sigma |i_c| = \Sigma i_a$

There could be global charge balance and for that the system would achieve a potential which is call mixed potential where summation of ic = summation of ia.

So that means the total current density due to anodic reactions and total current density due to cathodic reaction, cathodic reactions will be same. So on the basis of these 2 postulates we can have a mixed potential theory and then we will see that this 2 separate plots can be combined and we will get to mix potential which is nothing but the corrosion potential as well as we can get to the corrosion current density. Let us stop here will continue our discussion in our next lecture, Thank you.