Aqueous Corrosion and its Control
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Lecture - 04
Can we calculate the rate of corrosion: Electrochemical kinetics-Tafel relation?

Welcome to the lecture-4. And today we will continue our discussion on how to determine the corrosion rate of a metal so to say what are the governing equations that can be used to compute the corrosion rate. Before we proceed on this a brief recapitulation of what we discussed in the previous class will be in order.

And towards the you know the end of the class; we saw that how to predict if a metal will undergo corrosion in a given environment that we saw that right. And we also saw that if the metal is under equilibrium, it is not going to corrode; it will corrode only when it is deviating from the equilibrium condition.

Suppose I immerse let say Fe in HCl, you know what the reactions are right. The corrosion will occur by the oxidation of Fe into a ferrous chloride ($FeCl_2$), and the H^+ in the solution will get reduced to H_2 (Refer Time: 02:06). These two equations you know one is an oxidation, other is reduction process.

So, before we looking at the governing equation for the oxidation of Fe and the oxidation of a Fe or similar metals and the reduction of the reducing species like H^+ or metal ions anything can happen, we were trying to discuss what an electrochemical equilibrium is.

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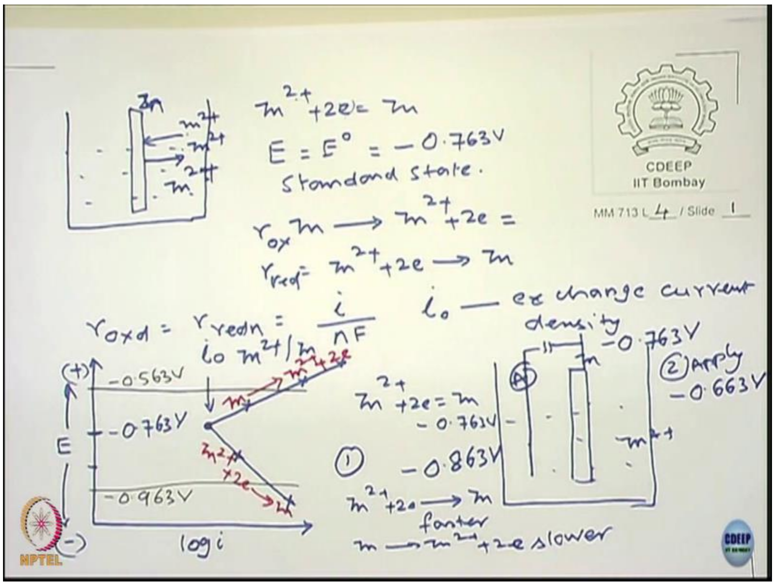

$Zn^{2+} + 2e = Zn$

$E = E^{\circ} = -0.763V$

Standard state.

$r_{ox}\ Zn \rightarrow Zn^{2+} + 2e =$

$r_{red} = Zn^{2+} + 2e \rightarrow Zn$

$r_{oxd} = r_{redn} = \frac{i}{nF}$

i_0 — exchange current density

$i_0\ Zn^{2+}/Zn$

$Zn^{2+} + 2e = Zn$
$-0.763V$

① $-0.863V$

$Zn^{2+} + 2e \rightarrow Zn$ faster

$Zn \rightarrow Zn^{2+} + 2e$ slower

② Apply $-0.663V$

If you recollect, we said that if I am going to construct an electrochemical equilibrium let say if I am going to dip Zn in Zn^{2+}, ok we said that there is going to be an equilibrium between the Zn^{2+} in the solution and the metal that is immersed in the solution right. So, you define this equilibrium as $Zn^{2+} + 2e^- = Zn$ here.

You define this equilibrium by one parameter, all of you know, what is the parameter? Which is E. E depending on what? E depends upon the activity of Zn ions in the solution, you can determine using a Nernst equation. What is more happening here? What is happening here is constantly Zn ions are getting formed in the solution by oxidation, and this Zn ions again go back and get deposited on to the mɳl surface. And we saw this is under equilibrium condition.

For simplicity, we consider that Zn ions are in the standard state right. Then what happens to E? $E = E_0$ right and is this is going to be equal to - 0.763 volts in the standard state right, you know this.

Now, we also said that the rate of $Zn \longrightarrow Zn^{2+} + 2e^- = Zn^{2+} + 2e^- \longrightarrow Zn$ right. This I would say ok, this is the rate of this reaction, this is the oxidation, and this is going to be the reduction reaction.

So, we say that rate of oxidation is equal to rate of?

Student: Reduction.

Reduction right, and you can convert this into current right. How to convert in to current, any of you can recollect?

Student: Yes.

r equals to?

Student: (Refer Time: 06:08).

R=i /nF and right. Since the rate of forward = rate of backward or whatever, and this current i_0 is termed as exchange current density. Am I right? We saw this in the previous class. What are the unit of current density? Its amperes per?

Student: Per unit.

Unit area right ok, so that you know that. Let me go further into this ok. Let me represent this graphically right. I am going to make little simpler. I am please look at I am plotting current density versus the potentials; it is relatively positive; this is relatively negative here. Why? This equilibrium, it has got two characters one is a potential define; second, I defined by the current density. Am I right?

Now, for a standard state the potential is - 0.76. So, this probably let say it is coming somewhere here, it is - 0.763 volt right, this axis now right. It also has a current density. Am I right or not? A forward reaction and backward reactions, they go equally. So, can I represent in this diagram? So, I represent in the diagram somewhere here. What is this current called? This current density = i_0 current density between Z^{2+} / Zn here. It is correct or not?

Student: Correct sir.

Right, agreed?

I am going to now disturb this equilibrium; I disturb this equilibrium. Now, let us look at the equilibrium again. What is the potential of this? The potential of this measured is equal to 0.763 volt with respect to standard hydrogen electrode. Now, what I am going to do, ok, I am writing this equilibrium here again Zn^{2+} + 2e- gives you Zn is equal to - 0.763 volt.

I am going to take the case 1. I am going to make this potential here - 0.863 volt. I am going to make this potential - 0.863 volt. How I make it? I to make it, I need one more electrode here, and I need a dc source right. I just make like that. Now, what will happen this is now made negative by using another electrode. To make it negative what will happen? The e^- will start flowing towards this, the e- flowing through this they make it negative e^- flow through this. Yes.

Student: We can change the potential by (Refer Time: 10:52).

You can change the potentials.

Student: Yes sir.

But the equilibrium will remain the same that will be a new equilibrium potential right.

Student: But there will be no equilibrium on it (Refer Time: 11:05).

Assume that the concentration of the electrolyte Zn ions from 1 molar it has become let say 10^{-2} molar right, you calculate the potential. What is the potential called? Still it is called an equilibrium potential right, is it or not, correct or not?

Student: Yes sir.

And use Nernst equation ok. So, even there the metal is in an equilibrium with Zn ions, but at a different potential is not it? Rate of forward reaction = rate of backward reaction, the exchange current density may not be the same is not it? The rate of reaction depends upon the activity of the species.

So, exchange current density may not be the same, but even at lower concentration when you change the potential right, if I you do not change the potential the potential automatically get adjusted that is a new equilibrium potentials. I put other way around for simplicity.

I take a beaker, I take Zn ions of 1 molar concentration, I put Zn there, I measure the potential using a standard hydrogen electrode its - 0.63 volt. I pour some water into that ok. So, what will happen now? The concentration of Zn ion will?

Student: Decrease.

Decrease. It will establish a new potential. Zn ions still will have in equilibrium with the Zn metal. The new potential is different you can calculate using the Nernst equation. So, that is not a deviation from equilibrium. It is a new equilibrium, not same equilibrium, am I right or not?

Student: Yes.

This is different ok, but it is also an equilibrium potential. So, standard that is why I said what is the difference between a equilibrium potential under standard potential, standard potential is a special case of equilibrium potentials the standard state, it is not different at all, they are in equilibrium conditions.

That is why I always say that when you are predicting corrosion, you please do a simple calculation of equilibrium potential using Nernst equation, please do not go into shortcuts right. Then use that to determine whether corrosion occurs or not otherwise you jump into conclusion that - 0.6, it has become - 0.7.

So, mɳl is going to corrode, it is not going to corrode at all that is thing you should understand. Equilibrium potential is independent of the concentration of ions, independent of even the activity of metal ion, metal on the metal, because the pure metal we consider the activity of Zn is or metal is unity ok. So, I think it is a good point that you raised then you should understand that.

So, let us put the come back to this. I apply a potential here -, what happens? Now, what will happen now please look at this reaction if you do this what will happen Zn^{2+} + $2e^-$, this becomes faster. And what will happen to this, $Zn \longrightarrow Zn^{2+}$ + 2e- becomes slower, agreed or not agreed?

Let us look at this one right. Let us look at this equation right. If I provide more e^-, what will happen to this reaction the forward reaction will be?

Student: Increasing.

Increasing. The backward reaction will be.

Student: (Refer Time: 15:03).

Simple you know some normal chemistry concepts only nothing different right. So, by doing this, that means, now the net current is going to flow am I right or not? So, if I am going to have an ammeter here, if I am going to have an ammeter here, I can measure the current when the current is going to flow, on this surface earlier the rate of oxidation equal to rate of reduction here rate of reduction is more.

So, there is going to be a net flow of e- in this direction like this, it goes like that only. So, the ammeter will start showing some values. So, there is going to be net currents in do you agree or not? No, I think some of you have problems ok. So, the current is going to increase. So, I am going to move from that to this to this value the current is now is increasing now. Agree?

Now, I am going to make it even more negative, what will happen? I make it let say - 0.963, what will happen?

Student: (Refer Time: 16:07).

The forward reaction will be faster, the reverse reaction becomes?

Student: Slow.

Slower. So, the current will start increasing like that. Agreed? So, you find that you are going to follow like this. It is a good question, I come to that later actually ok, is a good is very important question is a straight line is slope is fixed variation right, a good question is a straight line not.

Student: No sir not.

Of course, we are I put a log scale here, I come back to that answer, it is a good answer, I mean it is a good question right. So, you will also have a question why not the slope be like this ok, they are right, I am going to answer all these, because it is a mathematical equation we are going to derive from this ok. So, it happens like that.

Now, on the other hand, I am going to now apply ok, now I am going to apply, now what I am going to do now second, I am going to apply let say - 0.663 volts. Please see here I am applying - 0.663 volt, I am not applying + 0.663 ok. Now, what will happen now? Now, this reaction will start moving faster this become slower.

Student: Slower.

That means, now I am going to get a current given by this by increased voltage further, further like this.

You follow or not? Please do not worry right now why am I writing like that, but at least conceptually do you agree that when I move the potential relatively positive anodic reaction occurs relatively negative cathodic reaction occurs that is what I want. Do not worry about this slope and all these things, all I want to say that how things really changing.

Now, I am going to write this here as $Zn \longrightarrow Zn^{2+} + 2e^-$ represent this. And this is what is $Zn^{2+} + 2e^- \longrightarrow Zn$ here, conceptually you understand right. I have some value of potential I move relatively positive, that means, I am going to remove e- from metal surface right is not it? When I am going to make it - 0.63 V, what does it mean?

I mean the e- are going to leave out of system right because it is moving out system that means there is going to be oxidation. When I make it relatively negative, the e- will move in, so there is going to be reduction process, so depending upon that the things are start moving up and down like this.

Please understand, this is if you understand this, you understood corrosion full, you will have no problems in anywhere in understanding the electro chemical corrosion process at all this is basic things.

Please see here why I am saying it is important. I have started with the potential of - 0. 763, I moved to a value which is let say I have moved to a value I give some value let say - 0.563 ok. I moved to a value here let say - 0.963 volt, I am just giving some arbitrary value do not worry about it ok.

At 0.63, I am sorry 0.763 no oxidation no reduction, because same move up its oxidation. Please look at the sign here, the sign is negative here, the sign is negative here. I can have a sign negative, and I can still have oxidation, I can still have reduction.

So, you do not have to change the sign in order to call it a oxidation reaction or reduction reaction; otherwise the old convention European convention used to say E is negative, is reduction E is positive oxidation incorrect.

I can have a negative thing here and still I can have oxidation. I can have a negative over here and still I can have reduction. If I put a equilibrium potentials, there is no oxidation no reduction takes place. So, it is positive negative as no meaning at all in this case.

To illustrate further if I take copper, suppose I take copper, what will be the value here, what will be the value here for a copper + 0.377 point?

Student: 337.

0.337, right? If you move out move, sorry if you move up, it is positive; slightly move down, still positive; I can have oxidation and I can have reduction.

Student: Reduction.

This is a important thing. So, do not get carried away with the sign and tell that its oxidation that is reduction process, no, that is totally incorrect to attribute the sign for oxidation and reduction process. E is independent of convention; it is value that you determine from the equations that you get from here.

And please notice we said last time it is measurable just not only calculable I can measure it only thing is I have to measure with respect to another reference electrode that is all it is ok. You understood this actually any of you have any questions here, please.

Student: Sir. For changing current does equilibrium stabilize again, stabilized again?

No,

Student: No (Refer Time: 22:25).

No, that we call steady state. What is the different between a steady state and equilibrium? Steady state means there will be a drift slowly, and then it becomes constant.

Student: Constant.

So, we so when you change the potential I understand the reaction rate will not jump immediately, it will take some time, but after some time it reaches a value a steady state value.

Student: Current will be flowing around this.

Yeah, when you say equilibrium no oxidation no reduction. Steady state, no, it can be oxidation it can be reduction, but does not change with respect to time. Steady state means it is not changing with respect to time. So, do not confuse between equilibrium state and the steady state. They are totally different at all ok; they are not the same.

Let us continue this. This is an important one, you should continue, we will we continue this spending some time on this ok. Now, come back to this discussion now.

Student: What happen if we consider transient or unsteady state?

See I will tell you right now you do not bother because now we are trying to stand, walk, run, then we going to take up faster ok, people do calculate transients when you do research for examples. These transients have meaning around actually that probably we have time we will talk about it.

Transients do have meaning they are used in understanding the electrochemical interface, but right now we are not going to talk about transients. We are talking about steady state because that is only a state where you can define very well right you can define about it right; otherwise transients have a meaning we do it electro chemical impedance spectroscopy, all these we do that where the transients are being used ok; right now we will not talk about that particular one.

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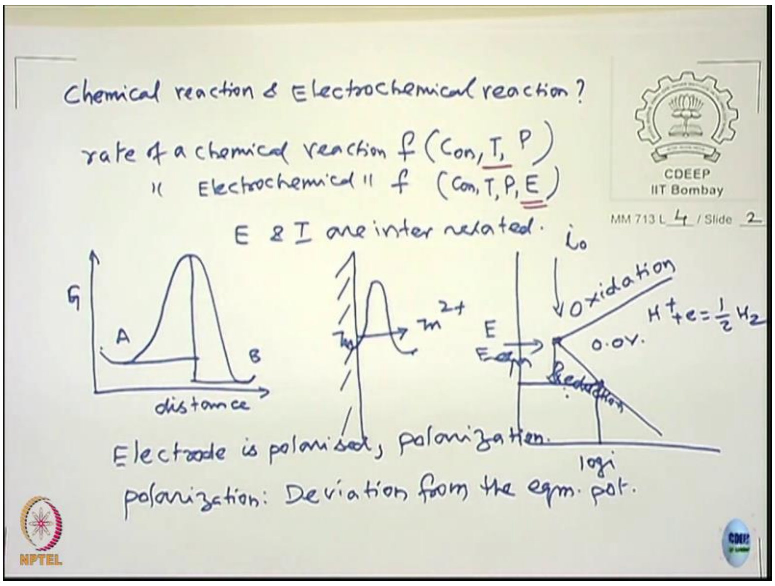

Chemical reaction & Electrochemical reaction?

rate of a chemical reaction $f(\text{Con}, \underline{T}, P)$

" Electrochemical " $f(\text{Con}, T, P, \underline{\underline{E}})$

E & I are inter related.

Electrode is polarised, polarization.

polarization: Deviation from the eqm. pot.

Let us talk about the difference between chemical reaction and electrochemical reaction. What are the difference between these two? Metallurgists should tell, chemistry guy should tell, every should say actually right ok. Let me give a lead rate of chemical reaction ok. Now, what are the factors that affect the rate of a chemical reaction? Concentration, temperatures.

Student: Pressure.

Ah.

Pressure ok, pressure is I can talk about temperature, pressure activity.

Student: Order of reaction order.

Order of reaction of course, we talk about ok. So, the rate of a chemical reaction, it is a function of what function of concentration, temperature, pressure rate equation right this is what happens right the rate equation is what you get to use it right. Let us look at rate of electrochemical reaction. What is this function of what, can somebody guess now? We are reasonably now we have seen.

It depends on what?

Student: (Refer Time: 26:12).

So, it depends upon the concentration, temperature, pressure and what and

Student: (Refer Time: 26:23).

Potential. I can alter the rate of reaction by altering the potentials. So, when you are talking about reaction kinetics rate of corrosion, for example, we talk about what is the concentration of species, what is the temperatures what is the pressure you are going to add one more dimension what is the potential is going to be there. And potential and current are interrelated. Is not it?

We have seen in the previous in the previous thing right. I will show you here, please, the potential and current are interrelated. I have not completed the story here, but I just wanted to tell you that rate of reaction depends upon potential and potential and current are interrelate to each other ok. You talked about what happened to the change of concentration that will change ok. So, that is a difference between a chemical reaction and electro chemical reaction

Let us look at other things what difference between these two we have. Suppose, I have hydrogen and oxygen, I put them together. Do you think the water will form very easily? Why does not form? I put take oxygen, I put some combination of will be explosion, but otherwise you just take hydrogen, oxygen put in a cylinder the free energy change is negative that is why we have water right; otherwise water will not be will not be there.

So, the free energy change for hydrogen combining with water I am sorry hydrogen combining with an oxygen giving rise to water is negative right. But put oxygen and hydrogen together and it does not form water easily.

Why, why, people can ask question differently you know (Refer Time: 28:44) why? You heard the concept called?

Student: Activation.

Activation energy right? There is activation energy barrier unless you cross the activation energy barrier, you cannot see. So, how do you cross the activation energy barrier in chemical reaction?

Student: (Refer Time: 29:01).

Rise its temperatures. So, temperature is a catalyst kind of thing right or we add a catalyst and do that. So, in the case of chemical reaction ok, we use temperature as a factor to control the reaction.

In electrochemical reaction we use potential to work on the barrier. Corrosion does not occur just like that you apply more potential then only corrosion occurs, otherwise the free energy change is negative only it does not happen. So, we need to understand what an equivalent of activation energy barrier in electro chemical reaction is ok.

So, I am going to now talk about what they are ok. So, let us go into that concept of what it is. Now, we all know this is I call it a how do you use the term G, E is a potential right I use this term, G maybe, I do not know may be distance. A turning into B, there is a barrier for that, and B coming to A, you have bigger barrier for that. So, is these all you guys know about it right. In electrochemical reaction also there is a barrier ok.

What is happening in the electro chemical reaction? Let say Zn here goes in the solution as Zn^{2+} ions, it cannot simply come out, it is a lattice, it has to break the bonds right. So, there is a barrier of activation from this to come over here, this not exactly correct ok. So, there is a barrier, it has to overcome ok, unless you have these barriers overcome, the lattice Zn will not come to solution ok. And for that to overcome we use what is called as the potentials.

I come back to this concept here ok. Let us see what it is E versus log i like this. This is true for most of the electro chemical reaction be it H^+/H and Zn^{2+}/Zn, Cu^{2+}/Cu whatever, and this is your oxidation. And this is reduction. And what is this? This is your i_0. What is this? This is your equilibrium branches, am I right?

Now, please notice if let say the reaction is let say the reaction I given here, and I will just change the reaction here and what is we can use any reaction here we want right I use this is the equilibrium. What is the reaction here, can you tell me?

Student: (Refer Time: 32:51).

Quick. What reaction for this is the equilibrium that I am representing, what is the reaction here?

Student: (Refer Time: 32:58).

Hydrogen evolution reaction I want you to speak. What is this one?

Student: (Refer Time: 33:06).

This is, is this is hydrogen.

Student: (Refer Time: 33:07).

Oxidation reaction takes place?

Now, if I have to increase the rate of reaction, suppose you know rate of you know suppose I want increase the rate of reaction to this, I need to move the potential from this point to this point. Am I right? I have to move this potential here. What is the equilibrium state? I call it is a 0.0, you want it ok, if the standard state, you call it 0.0.

Now, please look at I moved from this one to this one, in order that the reaction takes place of my own rate I want it. You want to increase it, I move further, I moved further, I moved further. I want to oxidize it, I move up, move up move up ok. Please look at as I move down, down like that, what happens, the reaction becomes either oxidation or it becomes reduction. And the electrode is now set as now the electrode is polarized.

What is mean polarization?

Student: (Refer Time: 34:24).

Yeah, net, now earlier it was just it is not (Refer Time: 34:28) or all, it is simply both are forward, same. Now, it is polarized if I what means if I move down, it becomes a cathode; to move up it becomes an anode.

Student: Anode.

So, it is now polarized, so that means the electrode is now polarized ok. So, and this is called as polarization. A deviation from the equilibrium condition is called as polarization that is polarization means that means you want to say the concept polarization means deviation from the equilibrium potentials is called as polarization. Anybody has a problem? Let me move further into this diagram the concept now, let me move further into this.

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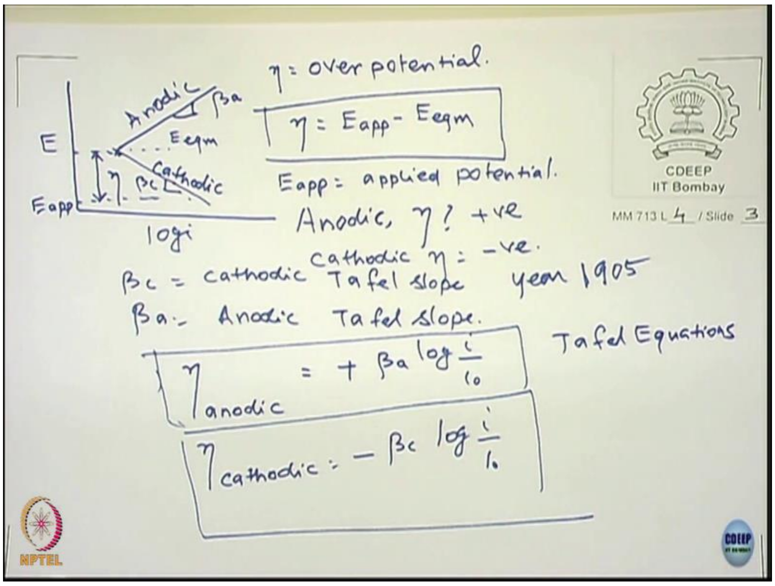

η = over potential.

$$\boxed{\eta = E_{app} - E_{eqm}}$$

E_{app} = applied potential.

Anodic, η ? +ve

cathodic η = −ve.

β_c = cathodic Tafel slope   year 1905

β_a = Anodic Tafel slope.

$$\boxed{\eta_{anodic} = +\beta_a \log \frac{i}{i_0}}$$ Tafel Equations

$$\boxed{\eta_{cathodic} = -\beta_c \log \frac{i}{i_0}}$$

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Let us draw this diagram fresh again ok. I moved to this value, and this is called as ɳ, ok, ok. So, ɳ= over potentials, ɳ is over potential right is a term is called over potentials. And what is this one, which is called as E applied.

And what is this potential called? It is E equilibrium potentials ok. So, ɳ = $E_{applied}$ - $E_{equilibrium}$ potentials. Please remember this equation. If you are confused with equation, you will have a problem ok.

Let me see here. Now, for an anodic reaction, when anodic, what will be the ɳ, will it be positive or negative?

Student: Positive.

Positive right, great. For cathodic is equal to negative, understood?

Student: Yes sir.

Because this is the cathodic side, this is your anodic, this is the cathodic ok. Now, you will ask question, you have been asking question before what is this. This is a slope I call them as β_a, this is a slope I call them as β_c. So, β_c will be cathodic slope, but I am going to use cathodic, please use a term Tafel slope. β_a is equal to anodic Tafel slope.

It you use I use at T here capital here, name of the person right. He, found this relationship in the year 1905, he got this relationship actually. He did an experiment ok.

He did an experiment; he got this similar trend he measured the slope that time he called a slope to recognize his contribution he called that we called that slope as the Tafel slopes.

So, the Tafel slope now defines the rate at which the reaction occurs, am I right or not ok.

Student: Yes sir.

The slope is equally important right. Now, you can now use this he has also derived a equation $\eta_{\text{anodic}} = +\beta_a \log(i/i_0)$; $\eta_{\text{cathodic}} = -\beta_c \log(i/i_0)$. See you guys are all now good in mathematics right you should be able to see how this can be derived. It is a simple linear equation right nothing more right, because you know this is your i_0 right.

Student: Yes sir.

The Tafel slope you know that right, now this is the difference that you have here. So, define this your η.

So, i at any given η, i at any given η can be given by i_0 if I know the Tafel slope this, these are called as Tafel equations. Because see here β is what β is a negative slope right that is why they put here slope is negative so you have $\eta = -\beta \log(i/i_0)$. Now, what is β? Can I take it out?

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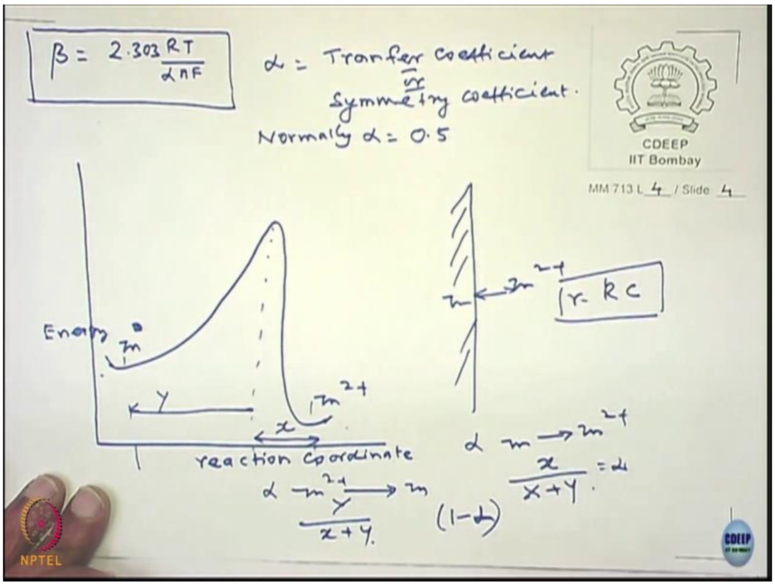

$$\boxed{\beta = 2.303\frac{RT}{\alpha nF}}$$

α = Tranfer coefficient or Symmetry coefficient.

Normally $\alpha = 0.5$

$\alpha \quad Zn \rightarrow Zn^{2+} \quad \frac{x}{x+Y} = \alpha$

$\alpha \quad Zn^{2+} \xrightarrow{Y} Zn \quad \frac{Y}{x+Y} \quad (1-\alpha)$

What is β? $\beta = 2.303RT/\alpha nF$ ok. Now, what is α = transfer coefficient or also called as symmetry coefficient. Generally, normally $\alpha = 0.5$, I will spend a minute on this ok.

Let us take this not a good diagram ok, but I just made it ok. This is energy right versus the reaction coordinate right. It is called reaction coordinate or distances reaction coordinate. This is let say; this is let say Zn to Zn^{2+} say it is Zn^{2+}. Please look at this one. If the guy has to move from Zn has to move from here to this, see I am describing this [FL], I am describing this like right, what is this? It is a Zn^{2+}, this guy goes back and forth like that right.

Zn has to move from here to this is much easier it is because the slope is less, but for the Zn^{2+} to come up here, it is going to be more difficult, that means, what is here α is given as this is let say x, this is y. Now, alpha, alpha for what α for Zn to go as Zn^{2+} it is given as $x / x + y = \alpha$.

Now, for Zn to come out what happens, for Zn to come out this is similarly unless say some other α for Zn^{2+} to move towards Zn, it is going to be what it is going to be $y / x + y$. And you guys would have seen before ok, that means, this is much easier now α is smaller here right, α is smaller this is going to be bigger. So, or I would say this is equal to $(1 – \alpha)$.

Can I say this? If this is α, this is equal to $(1 – \alpha)$. You can able to get this. $\alpha + 1 – \alpha$ is equal to 1 ok, 1 will be there. This is you guys would have studied in many chemical equations and all actually. So, alpha and is what is really means.

Please notice please notice very clearly here, ok, if alpha is going to be small bɳ is if alpha is going to be small, bɳ is going to be is larger actually ok. So, you relate these to much more easier in this case actually ok. Can I move or you have any questions in this case?

Student: Is β a characteristics property?

It is, ok, let us look at what is alpha. Alpha depends upon the hill that moves here

$\beta = 2.303 RT /\alpha nF$. What is n? The number of e$^-$ involved 2 3 whatever, F is a Faraday; T is the temperature, R is the gas constant. So, β is the characteristic property.

Student: So, is i_0?

Ah?

Student: And so is the i_0.

i_0 also characteristic property right, because the guy move going to move a right, alpha means the guy goes you know left and right, right. So, i_0 is characteristics of a given system ok. It is very important. In fact, you will see later i_0 is going to decide what is the rate of corrosion more or less.

If i_0 is small corrosion is small; if i_0 is more corrosion is going to more. We will see later ok. Right now, I want you to get a clarity in terms of the electro chemical equations that is dictating the kinetics of that actually that is that is what you should be really knowing ok. So, this is so far, we understood excuse me the equations.

Now, can somebody you know able to tell whatever we have discussed so far you know? what do you understood actually what are you understood in the discussion we had so far? Anybody?

See in order that in electrochemical reaction to occur either oxidation or reduction, there has to be an over voltage, an over potentials, you have to deviate from the equilibrium potentials, and that is also called as a polarization.

If we increase the over voltage, if we increase the η, what will happen to rate of reaction will automatically increase. If you look at the Tafel equation there, ok, if η is more, i is going to be more; if η is less, i is going to be less. So, higher the η, higher is the polarization, the higher is going to be the rate of reaction taking place. So, this is the most important aspect of the electro chemical reaction, electro chemical kinetics ok.

And you have any questions so far? We can clarify this and then move further. No questions?

Student: Sir, when concentration is changed, then equilibrium potential also changes. So, does i_0 changes with changing concentration of ion corresponding to new equilibrium potential?

You need to have, you need to have these values, either you should theoretically calculate or you should experimentally measure the i_0 values. They are required. Very much the same that equilibrium potential change with change in concentration the i_0 also will change because let us look at this know. See the chemical reaction, the electro chemical reactions there are lot of commonalities that you have ok.

Suppose, go back to this, suppose if these are going back and forth right, how do you determine rate of this reaction? r = k * concentration, it is a first order reaction

Student: Yes.

Am I right? If r is changing, I mean it has to change, if the k is changing and c is changing. If r is changing, then i is going to change.

Student: Yes.

So, exchange current density will change automatically, but only thing it will happen is the exchange current density over a forward reaction is equal to backward reaction that is not going to change.

The difference between i and i_0 is i_0 there is no net oxidation or reduction, but when it is i it is either oxidation or reduction process yeah i_0 will change, if we change the concentration of species if we change even temperature things will change ok. So, but all it means it is an equilibrium, and no oxidation, no reduction, takes place ok.

See I am not going to details actually some of you who are more interested please go through the book Bockris and Reddy, Modern Electro Chemistry, all these are given in details, but since it is not electrochemistry course I am not talking. So, I am discussing electro chemistry to the extent that you can understand corrosion better, it is no way a comprehensive treatment of electro chemistry ok, it is not at all ok.

But those who are interested you please read that book or you can read the book Buckhannon right that is also good book I referred in the in the beginning of my first class.

And I said what are the books I am referring you can refer that book as well, but Bockris and Reddy I would call it is like a Bible or Geeta whatever you can call it the ultimate in terms of in my view in understanding clarifying your concepts or you can also read by Bod, Bod is another you know big guy in the field of electrochemistry ok.

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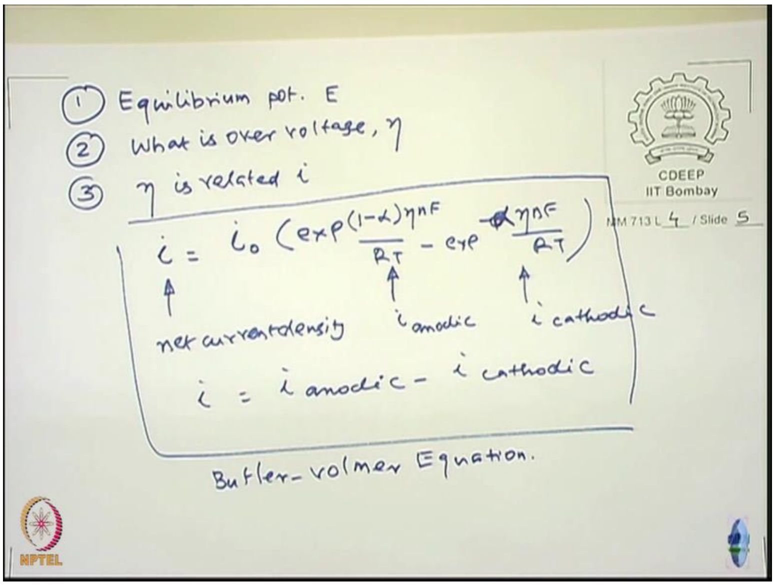

① Equilibrium pot. E

② What is over voltage, η

③ η is related i

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

net current density

i_{anodic}

$i_{cathodic}$

$$i = i_{anodic} - i_{cathodic}$$

Butler-volmer Equation.

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Now, so let us now look at these things and now what I am going to look at here is now what ok. So, what you should know, you should know 1 the equilibrium potential calculations, you should know what is over voltage, you should know that is E, voltage, now you should know how η is related to i. We have not done much so far we are just only you know made only three concepts clear to us actually, hopefully they are clear.

Actually, there is one more if you are a really more keen, I will write the equation here and those of you want to understand better. A better equation to represent this electro chemical kinetics is $i = i_0 [\exp(1 - \alpha)\eta nF /RT - \exp(-\alpha\eta nF/RT)]$.

What is this? Please look at i, what is i here? i is the net current density ok. And this corresponds to i_{anodic} current this corresponds to $i_{cathodic}$ ok, that means $i = i_{anodic} - i_{cathodic}$. These are the equations we have.

And this is called as Butler-Volmer equation, and I am not going to discuss this in detail. But those of you who are interested can read the book and understand it. Or if time permits, we will discuss this during the somewhere in the middle of the course we will discuss this ok.

Let me, just before I proceed, let me just clarify this. So, you should be in a position to calculates the current density right. Can you solve the numerical see if I give you some values based on the Tafel equations; would you be able to do that?

Student: Yes sir.

So, you will have some numerical to understand this concept ok, and probably we in the coming week will give you these numerical actually no ok.

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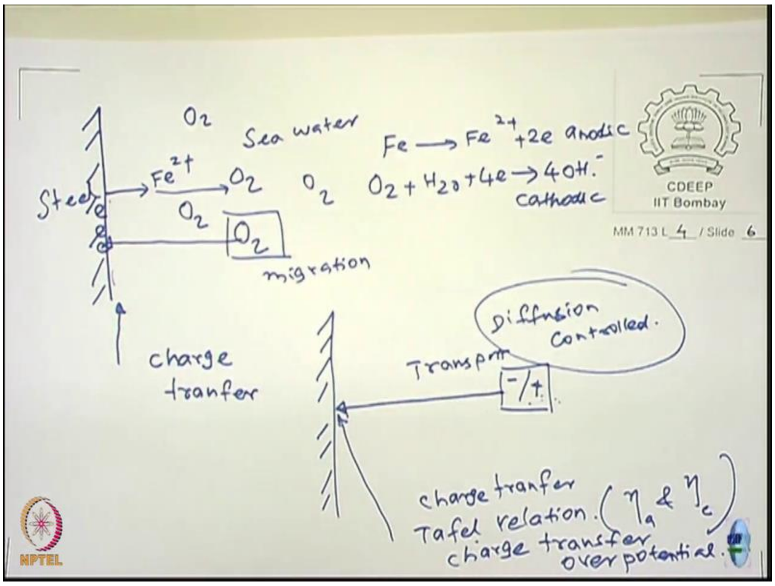

Let us go to the electrochemical reaction more in details. Let me take say steel say in seawater ok, steel in sea water. What is the corrosion? Now, you will have Fe is going as Fe^{2+}, now you also have oxygen, water, metal ions right. Is it clear, is it right, you guys are aware of this equation?

Let us write pictorially here. The sea water it has some oxygen there, dissolved oxygen somewhere, all the places. Fe corrodes; the e^- are liberated here. What will be the cathodic reaction? This is the cathodic reaction, this is cathodic, and this is the anodic reaction. The anodic reaction occurred, the cathodic reaction to occur the oxygen has to migrate from here to this place right or not? Similarly, the Fe has to migrate from here outside it has migrated from here, you cannot just accumulate it there right.

So, what are the reaction here? What is the process involved here? The process involved here are at the interface there is, it charges transfer. What does it mean charge transfer?

Fe becomes Fe^{2+}, trips 2 e^- out; the oxygen moves here and change the e^- it becomes OH^- . So, charge transfer occurs at the interface. But for that to occur, we have to have the migration of this right.

So, to put it simply some species ok, maybe it is a negative, a negative charge or a positive charge, they move here. And what happens then, what happens here charge transfer. And this charge transfer, you see in the relationship now, what is the relationship here it is the Tafel relationship. What you have seen before is a charge transfer is a relationship. And what is this? This is your diffusion controlled.

So, the over voltage we have talked about so far it is η_a and η_c, they are all called as charge transfer over voltage, they are called as charge transfer over voltage ok. They are called as charge transfer over voltage or over potential whatever you call it over potential. This that is the potential required for metal to get oxidized or reduced what happens.

Now, we have one more thing, so we need to know how these are happening at all. If you do this, then you have a complete understanding of electro chemical corrosion process right. You already seen how the relation between the potential and the current exist at the interface. Now, we also know that if the ions have to take charge, they have to move from the bulk to the interface.

So, we need to know the governing equation for that. So, what is the governing equation for that? So that you can completely define in electrochemical corrosion reaction, understood ok? So, we are going to look at this now, and see how we can understand that.

Student: What about the cemented present in the steel?

Well, it is a good question ok. Right now we are not talking in terms of microscopic processes on the surface; we are looking at a macroscopic. I gave steel as an example here, so that you get an idea about how the steel corrodes in the seawater ok.

Student: (Refer Time: 63:53).

You could take an Fe you want ok, you can take nickel you want actually ok, the idea of giving here is that the oxygen you know I gave oxygen here, I did not put sulfuric acid ok. I had given to your problem; I think I am not given yet I think TAs have not given that actually ok. So, the difference between an acid, sea water containing or exposed to air is that the solubility of oxygen here is what is about 6 ppm to 7 ppm, maybe 8 ppm something like that. So, they are not going to be easily available on the surface, they have to migrate from here.

The corrosion now depends upon what, depends on not this, it depends upon how quickly the oxygen ion, oxygen molecule migrates to the interface. If they do not migrate, then the reaction does not occur these equations of no use. So, I am talking in reference to why you should care this one. Please look at this, this is in series. Please look at this is in series right; this moves like this. If this is faster, and this is slower, the rate determining reaction is going to be this right.

If this is the slowest, the fastest, now this is not going to control this is going to control, I mean I do not know I am jumping at all ok. And this would be easier for you it is a series process right. You assume that transfer is much slower, I apply more over voltage right I apply more over voltage. Let us go to this, let us go to this reaction ok.

I apply more over voltage the current is increasing right increasing, but current will increase only when if the species are available for reaction. If they are not available, what happens you only increase the voltage nothing happens right. So, this current will increase only when your species to accept the e^- or release e^- if they are not there. So, that means, you have a transport process and then it is getting accepted here right. So, it is a coupled reaction.

The transport is an integral part of electro chemical process for any chemical processes also you know there is a transport they are happening at all. So, I did not use sulfuric acid, because sulfuric acid the concentration of H^+ ions are huge H^+ move very fast, you never have diffusion control process. But oxygen is less soluble and so in this case the transport becomes very important.

We will see this later when you talk about corrosion of steel in seawater how important these equations are. These equations are very important when you talk about corrosion of steel in sea water, corrosion of stainless steel in seawater, they are very important. Why, because that is governed by this transfer process, that is why we are now trying to understand the equation, governing the transport of ions in the solution at all ok. Am I making the point clear to you?

So, we look at this now. Transport there are two laws governing your transport. What are the laws? I am talking diffusion. What are the governing laws of diffusion?

Student: Fick’s law.

Fick’s law, you cannot forget that. They are the great guys so, they are Fick’s law, one is called Fick’s First Law; second is the Fick’s Second Law.

What is the difference between a first law and second law? First law is steady state and second is a non-steady state. So, we are not getting into non-steady state, it is very complex ok. Though they are useful, when you are going to do research electro chemical, you solve that also, but I am not going to use this in the class.

So, the diffusion processes start with the Fick’s law you cannot start from that.

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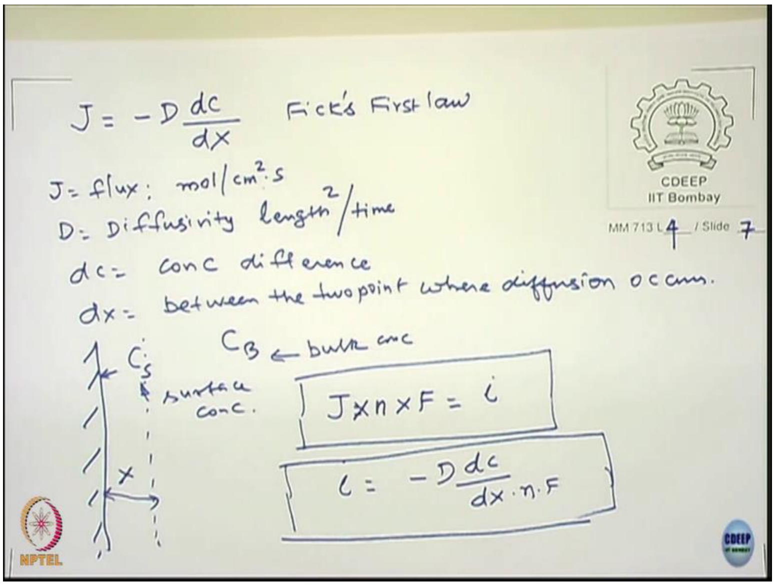

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$J = -D\frac{dc}{dx}$ Fick's First law

J = flux : mol/cm^2·s

D = Diffusivity length^2/time

dc = conc difference

dx = between the two point where diffusion occurs.

$$\boxed{J \times n \times F = i}$$

$$\boxed{i = -D\frac{dc}{dx} \cdot n \cdot F}$$

What is the Fick’s law is says Fick’s law says J = - D (dc/dx) right. What is J is a flux, the reaction rate is given in terms of mol/cm^{2}sec. Am I right? Reaction rate, all of you guys will be knowing. What is D? Diffusivity. What is a unit of this? Length^2 /time is not it? What is dc? Concentration difference in dx, is what is the between two points right ok, between the two points where diffusion occurs.

Let us define the electrochemical system ok. Now, you have the bulk a concentration ok. And what is this concentration here? It is a C_s=surface concentration right. So, this is a C_B=bulk concentration; this is the surface concentration. And assume that the diffusion distance is this is the ok, assume this is your x for example ok.

So, what do you have here? Now, can you convert flux into current? Can you, not? What is the unit of flux? Mol.Cm/ sec How do you convert this? Now, J is equal to, how to convert this? J multiplied by, can you, or can you not?

Student: Yes.

Is it right or not? No? Go back.

Student: Yes.

So, what happens? $i = - D (dc/dx /nF)$. Is it, it is a difficult equation or easy equation? See if you know the number of moles can you not convert that into, see this is number of mol/Cm^2 /sec is a rate know, it is a rate right, it is a rate of reaction. So, you how do you convert that into current? Is equation correct or incorrect? Can somebody find out?

Student: Correct sir.

Correct, how do you get this? Please look at your notes ok. See that is why you see we are now making a slow progress ok. And they are not difficult. But if you are not you know following up completely, you might find it very difficult to understand what it is, it is simply very simple equations only ok.

So, it is possible for us to relate the flux to this. So, you we will find out what is called as the governing equation for what is called as a diffusion process, and how the diffusion is related to the current see what for example, I take H^+ ions. I start moving from here to this, what does it mean? Is it only mass is moving or something else is moving?

Charge moving. When charge is moving, what does it mean?

Student: Current.

Current is moving right. You try to try to understand, they are not neutral molecules right. So, if these ions are moving, they are carrying the charges, and so the current is going to flow accordingly depends upon what direction the ions are moving and which ions are moving positive or negative right. So, the flux is related to current ok.

So far flux was related to what in terms of moles and all these, now we are going to relate a flux to current. Why I am interested? Because I need to know what the diffusion rate of oxygen is to find out the corrosion rate; otherwise I do not know ok.

How do I calculate this? So, I need, so I am really worried or I am bothered I would say that I need to know what happened to the corrosion of steel in water having 5 ppm oxygen there, or 100 ppm for example. If the diffusion coefficient of species changed what happens, corrosion rate is going to change what is the basic equation for that, so these are the basic equations ok.

So, when I say I can calculate corrosion rate, I can able to calculate corrosion rate by knowing all these things, they are not difficult I think you guys have done it in earlier subjects at all actually ok. But please brush up your things when you come back, and we will see this in the next class ok.

Please understand we are now slowly complicating the subject. Why? I talked about so far Zn oxidation, Zn reduction by 1 Tafel equation, may be 2 Tafel equations right. In the actual corrosion process what are happening, Zn is getting oxidized, H^+ is getting reduced. So, there are going to be 4 Tafel governing equations. Am I right or not?

So, please understand ok, they are very simple. But there are two equilibria we are talking about in corrosion, one is Zn is in equilibrium with Zn ions, H^+ is in equilibrium with the H. So, we talked about only one equilibrium of Zn having 2 Tafel equations. Now, there I am going to talk about 4 Tafel relationship because one equilibrium for H^+ H, other one for Zn and H^+.

So, solving that equation becomes more difficult unless you understand it ok. You please do understand it ok, get that things clear to your mind. It is not difficult. Again, I repeat, but please look at the equations and then try to understand what these equations are actually ok.

So, I mean like solving any mathematical problem, but you should know the physics behind these governing equations and all ok. So, please come prepared for the next class.

Next class I can assure you it is going to be more complex, more complex and more, more complex ok, but they have a very common simpler understanding of the electro chemical concepts that I can say ok.

So, that is not difficult, but complex ok. So, please come prepared for the next class, I will really appreciate that. So, we will close todays discussion just introducing the relation between diffusion and the current ok.

Thank you.