Aqueous Corrosion and its Control

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Lecture - 05

Can we calculate the rate of corrosion: Electrochemical kinetics- diffusion & mixed potential theory?

Today we will continue our discussion on Electrochemical kinetics. Yesterday we looked at two concepts.

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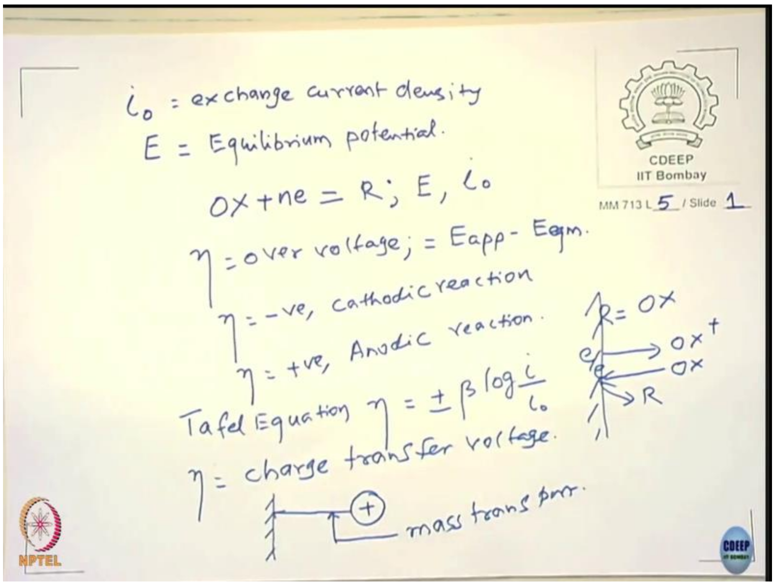

i_0 = exchange current density

E = Equilibrium potential.

$Ox + ne = R$; E, i_0

η = over voltage; = $E_{app} - E_{eqm}$.

η = −ve, cathodic reaction

η = +ve, Anodic reaction.

Tafel Equation $\eta = \pm \beta \log \frac{i}{i_0}$

η = charge transfer voltage.

mass trans fr.

What are the concepts, one concept was on the exchange current density right this talks about the equilibrium condition at which the rate of the forward reaction equal to rate of the backward reaction and the potential exhibited by the electrochemical system we define as the equilibrium potentials at this case you have a potential called as the equilibrium potentials.

Now, we looked at the deviation from the equilibrium, say any equilibria that you can take you can take as let us say the oxidant combines with the e-s and giving rise to R it is an equilibrium here: $Ox + ne^- = R$

They establish an equilibrium potential they establish let us say in current density when you apply a voltage a potential on the surface what happens either there is an oxidation or there is going to be reduction, they said by what, where they will undergo oxidation or reduction depend on what? What is that parameter called? That is called as over voltage and we defined what the over voltage means is equal to what is equal to?

Student: E applied.

η=overvoltage= E applied - E equilibrium condition and when η is going to be equals to negative you get a cathodic reaction and η is going to be positive then you get an anodic reaction. This reaction rates are given by what law what is the law called the reaction rates or the current

Student: (Refer Time: 03:45).

That relates the over voltage is going to be what equation?

Student: Tafel.

The Tafel equation right, the Tafel talks about equation which relates $\eta = \pm \beta \log (i/ i_0)$, you saw that right. So, this is a general equation for anodic and cathodic one and η would change whether it is a cathodic reaction or anodic reaction and what is happening here, what is happening here, what is happening? The e-s are getting transferred to the oxidized species and gets reduced R, R gets oxidized to an oxidized species it releases e-s right. So, it is called as this voltage is called as charge transfer voltage.

You saw that in the in last class ok. So, it is essentially where does it charge getting transferred, the charge is getting transferred at the interface it is this is interface ok, you have an oxidant and reductant are under equilibrium conditions right.

So, they are at this place the charge is getting transferred either this is oxidized species and you have e-s here or with the oxidized species will come over here and accept the e-s and give rise to reducing species and the kinetics of that is given by the Tafel kinetics.

We also saw one more that the electrochemical reaction if it has to occur at the interface if it has to occur the interface the species let us say a positive species it has to get transported to the interface and accept the e-s and this is what do you have you call this as what is called as mass transport.

So, it has been transported from the bulk to the interface it has go from the bulk to the interface so that is the step right. We discussed this in the last class ok, what are the governing equation for that if it is total diffusion it is not convection what is that equation.

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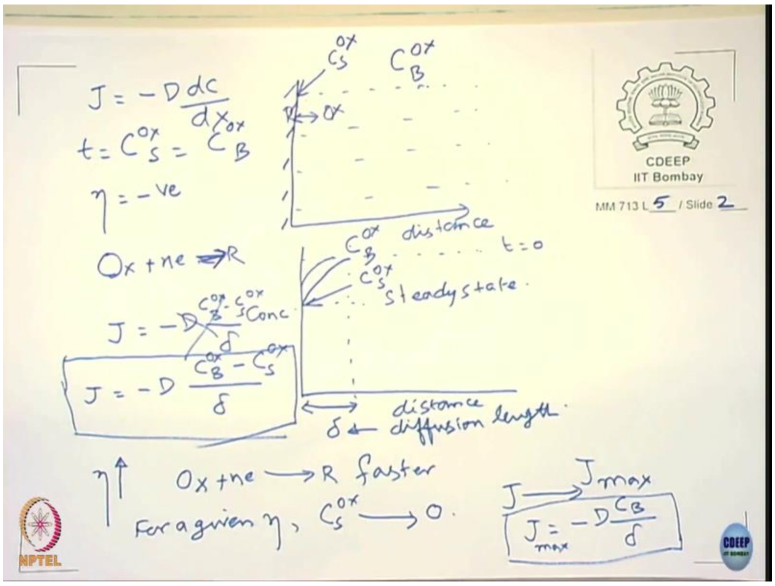

$J = -D\frac{dc}{dx_{ox}}$

$t = C_S^{ox} = C_B$

$\eta = -ve$

$Ox + ne \Rightarrow R$

$J = -D\frac{C_B^{ox} - C_S^{ox}}{\delta}$ Conc

$$\boxed{J = -D\frac{C_B^{ox} - C_S^{ox}}{\delta}}$$

$\eta\uparrow$ $Ox + ne \longrightarrow R$ faster

For a given η, $C_S^{ox} \longrightarrow 0$.

$J \longrightarrow J_{max}$

$$\boxed{J_{max} = -D\frac{C_B}{\delta}}$$

Student: (Refer Time: 07:16).

It is the Fick’s law we discussed that J =-D(dc/dx)

Student: Yes.

D equal to diffusivity or diffusion coefficient and dc is the change in concentration over a distance dx that is what you saw in the last class.

Now let us define this more details right, if I have an electrode to start with the electrolyte these are the electrolytes let us say this is the distance right this is the distance right. Now at this stage it is in the equilibrium condition the oxidized species reduced species whatever that we talk about they are under equilibrium condition they are under equilibrium condition.

The composition of these species let us take; let us take only the oxide species here let us take only the species oxide species the concentration of the oxide species at the bulk. Here at the interface it will be same right when there is no reaction taking place the concentration of the species at the bulk under the surface. This is the surface C_S species right, now at time t = 0 what happens now the concentration of the oxide species at the surface is equal to the concentration of the oxide species at the bulk($C_S = C_B$), understood now.

Now, what is happening now? As the reaction suppose I apply a voltage suppose I apply a overvoltage here apply negative voltage suppose η = -ve, what happens now what will happen see that oxide species will get reduced and form this reaction occurs. So, what will happen to concentration of the species that interface what will happen to that? Decreases right.

Student: Decreases.

So, it decreases the concentration of the oxidized species at the interface decreases with respect to time ok. So, if I plot again distance versus now I am plotting the concentration if I plot it now at time t = 0 it is a concentration right.

Now as a reaction proceeds what happens the concentration would drop and then it may drop further and it could reach a steady state am I right, after some time it reaches steady state and there is going to be diffusion between these point and this is what and this is called as δ or called as diffusion length.

Is not it the diffusion is only between these two beyond this point the concentration is equal so, nothing happens? And as you move from here there is a concentration gradient, C_B^{OX} =concentration of the oxidant at the bulk and what is this and C_S^{OX} =concentration of the oxidants at the surface

So, how do you write the equation? Equation $J = - D (C_B^{OX} - C_S^{OX})/ \delta$ am I right and $C_B^{OX} - C_S^{OX}$ or I think I will just write here; $J = - D\, C_B^{OX} - C_S^{OX} / \delta$

Now this you are right I can change this into this one you are right happening now earlier I just made that is equilibrium now reaction is now turning into this. If I keep increasing the over voltage here assume that I increase the over voltage what is going to happen, this reaction rate is faster, is it not. Now what will happen to the concentration here what will happen to the concentration of the surface?

Student: Reduces.

Reduces right and at one point for a given over voltage $C_S^{OX} = 0$ can you say that.

Student: (Refer Time: 14:14).

Now J what happens then J becomes

Student: J max.

The J max ,$J=J_{max}$. you cannot go beyond that can you go beyond this, why?

Student: (Refer Time: 14:38).

Now, the J is equal to what? $J= - D. C_B /\delta$ that is your J max cannot go beyond this. Let us extend this argument.

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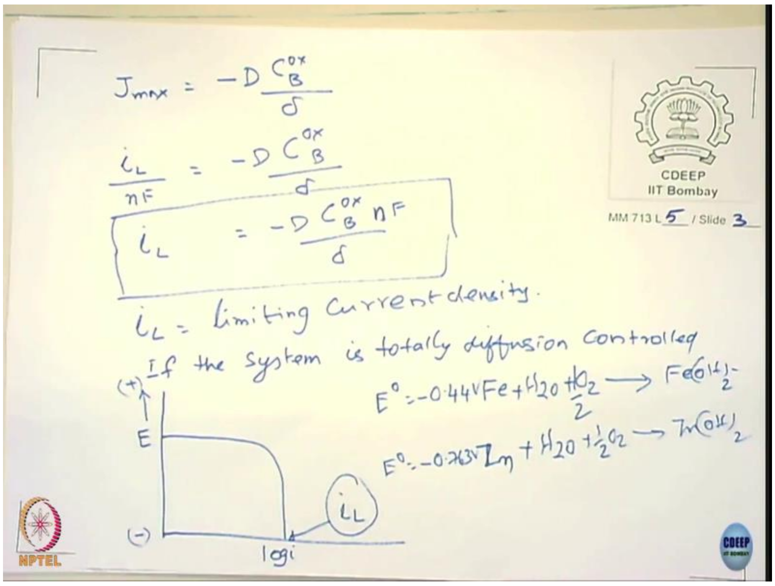

$$J_{max} = -D\frac{C_B^{ox}}{\delta}$$

$$\frac{i_L}{nF} = -D\frac{C_B^{ox}}{\delta}$$

$$\boxed{i_L = -D\frac{C_B^{ox}\, nF}{\delta}}$$

i_L = limiting current density.

If the system is totally diffusion controlled

$E^0 = -0.44V$ $Fe + H_2O + \frac{O_2}{2} \rightarrow Fe(OH)_2$

$E^0 = -0.763V$ $Zn + H_2O + \frac{1}{2}O_2 \rightarrow Zn(OH)_2$

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Now J max I rewrite again here $J_{max}=- D C_B^{OX} /\delta$. So, you know the relationship between i and J right what is the relation between that. So, this can be equal to i.

Student: -.

So, $J= i/nF = - D C_B^{OX/} \delta$, now I call it i_L here $i_L = - DC_B^{OX}$ n F/δ, the i_L is called as limiting current density ok.

So, what does really mean here, what does really mean you cannot have a current exceeding the i_L whatever be the over voltage I can keep increasing the voltage as you wish will the current increase beyond that.

Student: (Refer Time: 17:06).

It would not increase at all. So, it would not go beyond that values and that limits current the system can take beyond which it cannot really do that. So, if the system is system is totally diffusion control controlled then you can draw a plot you have like that and this current density is called as i_L. So, can you now look at the equation given above here and tell me what limits the i_L. Please air diffusion length then.

Student: Temperature is.

Excuse me.

Student: Temperature.

Where does temperature coming here?

Student: It is a D sir.

So, it is influenced by the D value the D will change if the temperature is changing so; that means, that is taking care of in the D value. So, if D can change the limiting current density can change what more?

Student: (Refer Time: 19:07).

Yeah.

Student: Length.

Length already you told right the bulk concentration. So, the concentration of species decides this one, why am I interested in this I will before I go, I will just try to clarify you why we should be worried about. Let us take the case of Fe in water containing oxygen there now this is what is the reaction here ok. So, we can balance this equation later you can balance this equation and see what it can happen right to balance this equation in terms of oxygen there you know see for example, fine ok.

So, you get this reaction right. Now the corrosion rate of this will depend upon what, depend upon how much the oxygen go and accept the e-s Fe is ready to corrode, but what is not possible the oxygen is not available to take the e-s by the process.

Now, in this case the corrosion rate of this depends on what depends upon the diffusivity of oxygen the bulk concentration of oxygen in the water. So, it is not just only Fe that is corroding which is responsible the species which are in the solution is also responsible.

Now I give another example suppose I use here let say another species at Zn suppose. Suppose I have Zn and allow it to corrode in water, assume that in both the cases the concentration of oxygen is same, diffusivity of oxygen is same, the number of e-s are same. So, what will happen to corrosion rate of the Zn, if you compare the corrosion rate of Zn and Fe what do you think, can you extrapolate?

See Zn if you look at the EMF series what is the equilibrium what is the standard potential of Fe, $E_0 = - 0.44$ volt what about Zn, $E_0 =- 0.763$ volt. Now which one is supposed to corrode more? Zn is supposed to corrode more now look at the equation now which will corrode more if oxygen is limiting the diffusion of corrosion right. So, what will happen to the corrosion of Fe and Zn will it be different?

Student: No.

No, I want answer from you.

Student: (Refer Time: 22:42).

The same, right.

Student: Yes sir.

So, even though the thermodynamic tendency for corrosion of Zn and Fe are different the Zn is supposed to corrode faster compared to Fe in this case both might corrode at the same rate might corrode at the same rate because it is controlled by the diffusion of oxygen in the system so that is why you are concerned with this actually ok. No idea, no isn’t it?

See Zn only corrodes and give rise to two e-s, Fe also corrodes and gives two e-, but these two e-s have to be accepted right by what by oxygen there, but oxygen is not willing to accept because it is not available on the in the surface. So, irrespective of the ability of the metal to give e-s the rate is now controlled now it is controlled what it is called it is called diffusion controlled reaction the diffusion controlled corrosion process. So, that is why we are interested in understanding this kinetics ok, understood not understood?

Let me just go to the next question; let us go to next question now.

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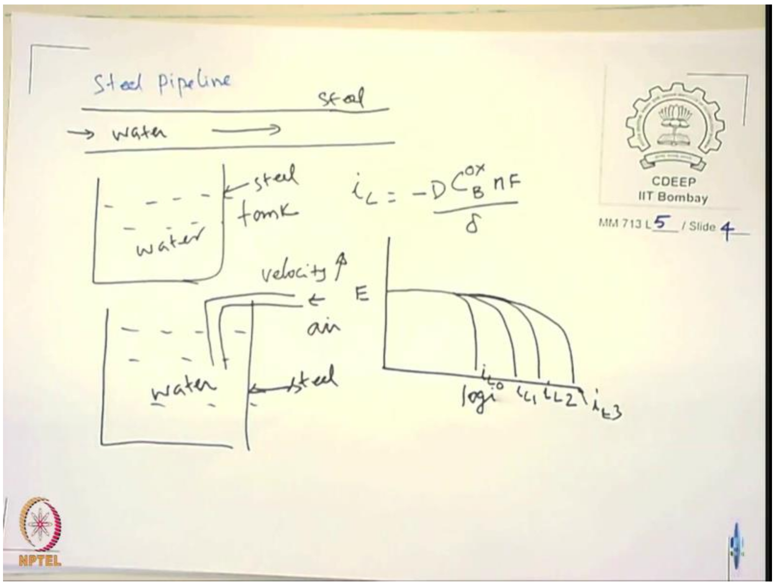

The next question is that is a steel pipeline steel pipe line it has it is through which the water is moving ok, the same water is there in a tank. So, it is steel again where will the corrosion rate be more?

Student: Pipe flowing.

Why?

Student: Velocity increases.

So, when velocity increases what happen?

Student: (Refer Time: 25:42).

Delta decreases right the delta decreases when the delta decreases the surface concentration.

Student: Increase.

Increases so, you can use the equation now you can say that i_L = - DC_B^{OX} nF/δ Now this oxidant you can replace anything you can also put reductant also I mean this is I mean anything that you want you can write it ok.

So, when you increase the velocity when the velocity is increased what will happen to i_L you get this. So, it is i_L =0, i_{L1} ,it is i_{L2} so, the rate of corrosion of this is going to be more and example also there is a ship in the sea it is at the harbor and the ship is sailing, will the ship will undergo same corrosion rate or different corrosion rates? I want an answer.

Student: Different.

Different, where the corrosion rate will be more?

Student: Sailing.

In sailing will be more because the sea the corrosion rate is dictated by reduction of oxygen in water. Now another case I take a tank I have water this is now fully aerated fully aerated now right it is water. So, what will happen to corrosion rate of the steel tank here compared to the previous one?

Student: Increase.

It will increase the corrosion rate increases. So, is the case you know you see lot of pipe lines carrying several products may be crude oil or a refinery products if it has some water, if it has some oxygen, there the corrosion rate will change, the velocity has an effect, the velocity has velocity has another effect we will see later ok. Right now, the role of velocity seen here is in terms of mass transport not more than that so that is why this particular equation becomes very important.

Now let us take the case slightly different case where the reaction partly diffusion control you can say it is a mixed control.

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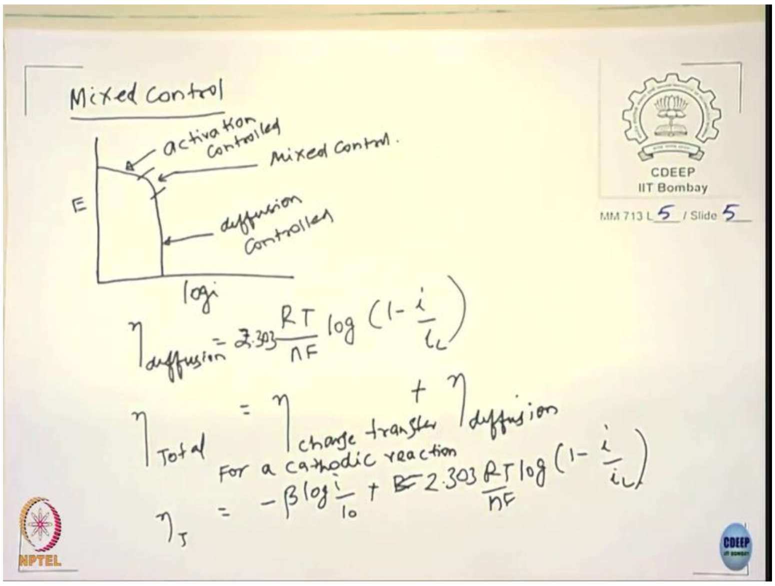

Mixed Control

$$\eta_{diffusion} = 2.303 \frac{RT}{nF} \log\left(1 - \frac{i}{i_L}\right)$$

$$\eta_{Total} = \eta_{charge\ transfer} + \eta_{diffusion}$$

For a cathodic reaction

$$\eta_T = -\beta (\log \frac{i}{i_0} + \cancel{B}\, 2.303 \frac{RT}{nF} \log\left(1 - \frac{i}{i_L}\right)$$

If I draw a diagram an Evans diagram you have an equilibrium potential this is what this is activation controlled and this is diffusion controlled and between these two mixed controls. Now, let us take the case of diffusion controlled $\eta_{diffusion}$ =2.303RT/nF log (1 – i/ i_L)

So, we can derive this equation and we do not have time to do this you can start from the Fick’s law and derive this conveniently and for the mixed control

$\eta_{total} = \eta_{charge\ transfer} + \eta_{diffusion}$ ok. So, for a cathodic reaction for a cathodic reaction

$\eta_{total} = - \beta \log i/i_0 + 2.303RT \log(1 - i /i_L) / nF$

So, this equation describes completely this curve is described by this particular equation. What about the anodic reaction, will it be diffusion control? You think so, what you think, I want a firm answer.

Student: (Refer Time: 33:17).

It would not be why?

Student: (Refer Time: 33:22).

Yeah.

Student: (Refer Time: 33:29).

For the corrosion process you have infinite amount of Fe present on the surface no matter what amount of reducing species travel, they travel from the bulk to this when they travel the mɳl is there on the surface it can give infinite amount of e-s. So, it is not generally a diffusion control process there is no transport involved there.

There is also one case where that is called passivity, we will talk about over there we will talk about somewhat similar to diffusion control otherwise anodic reaction is generally not considered as diffusion control.

We talk about corrosion not in all you know we are not talking about all electrochemical reactions no I think that is not correct to say that any electrochemical reaction anode reaction will not be diffusion control no it is not correct. We are talking about in relation to the corrosion process because the metal that is supposed to get oxidized the concentration of the surface is quite large you have infinite atoms you have actually ok.

So, this now we come to the end of the discussion on the electrochemistry of corrosion what we know need to know about electrochemistry we are now come to almost we have completed I do not say we have gone much deeper, but what is required you have seen.

So, if you summarize what we have seen, we have seen was giving a criteria for corrosion using electrochemical potential we started before, electrochemical potential, equilibrium potential is one criteria, second we talked about the reaction kinetics in terms of what in terms of the Tafel relationship where when the reaction occurs the charge is transferred across the metal solution interface.

And we also saw that if there is a migration of the species from the bulk to the interface for corrosion what kind of governing equations are available that also we have seen. So, from the electrochemistry point of view whatever you have seen so far are adequate to understand the corrosion process.

We have not of course, answered how do I calculate corrosion rate that we have not done it, we have only seen the governing equations how do I compute corrosion rates without doing experiments that was our original question I think we move towards that particular one in the subsequent lecture ok.

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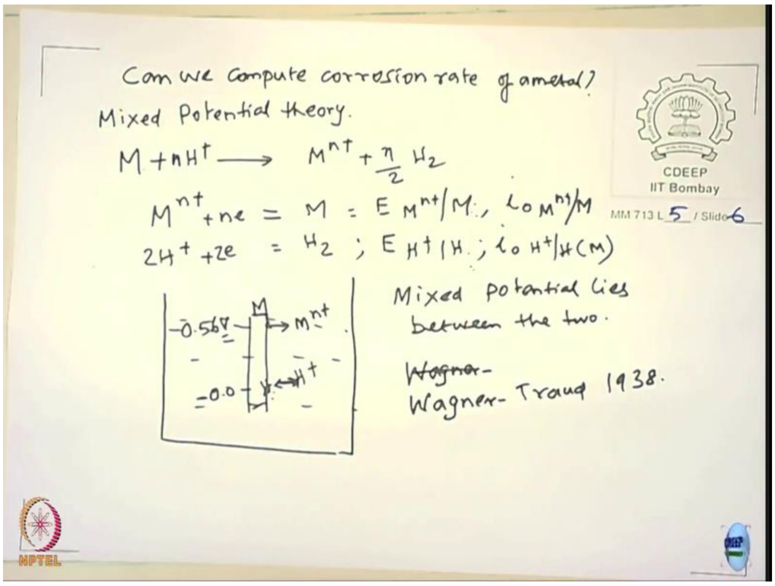

Can we compute corrosion rate of a metal?

Mixed Potential theory.

$M + nH^+ \longrightarrow M^{n+} + \frac{n}{2} H_2$

$M^{n+} + ne = M \; : E_{M^{n+}/M} , \; i_{0 M^{n+}/M}$

$2H^+ + 2e = H_2 \; ; E_{H^+/H} \; ; i_{0 H^+/H(M)}$

Mixed potential lies between the two.

~~Wagner-~~

Wagner- Traud 1938.

Now, the question is, can we compute corrosion rates rate of a metal? That is the question and that is answered by the concept called mixed potential theory, to understand the mixed potential theory let us take a corrosion reaction I involved some metal M, I am going to expose it to an acid what does acid consists of H^+ and it leads to what is called $M + nH^+ \longrightarrow M^{n+} + n/2 \, H_2$, right , can I say this. So, you have a corrosion process where in the M is getting oxidized to M^{n+} and the H^+ are getting reduced to H_2.

Why I called mixed potentials, because of the fact you start with two equilibria here $M^{n+} + ne^- \longrightarrow M$ you have $H^+ + e- \longrightarrow H_2$, the two different equilibria that we have and this has one equilibrium potential I term it as $E_{Mn+/M}$ I write like this is subscript of that and for this E is equal to what is you have a $E_{H+/H2}$ we have.

Please look at there are two independent equilibria are there on the metal surface why is they are independent, because it also has its own exchange current density $i_{0Mn+/M}$, you also have $i_{0H+/H}$ on M please look at it is on the M particular metal actually you know this is on this metal it is happening. So, these are all we know about it.

Now, what is happening M, H^+, for a moment you think that there is one equilibria here M^+ and M, there is another equilibria here H and H^+, this one taking place at two different sites you have two independent equilibria taking place. And this has one potential and one exchange current density this has got one potential and one exchange current density, am I right correct or not?

Student: Yes sir.

So, there are two independent equilibria existing on the surface. So, what happens, assume that this potential is assume that this potential is let us say - 0.56 volt for the some reason you assume that now assume that it is 0.0, metal is a conductor right will this potential here and here will remain the same, will the potential remain same they are shorted right.

So, what will happen is because they are shorted the potential start dropping towards this and this will start moving towards this and you will achieve a potential somewhere in between that is called as the mixed potentials so, the mixed potential lies between the two.

In electrochemistry and people have been talking about mixed potentials even around about 1900, but it was the Wagner and Traud at the somewhere 1938 I think if I am not mistaken in the year they formalized a mixed potential theory and it is also called as Wagner - Traud mixed potential theory.

How do you solve this problem? You have a one potential which is different, another potential is different you have different exchange current densities when you when the metal is conducting you are not going to retain all of them intact each equilibria will get disturbed by other equilibria right.

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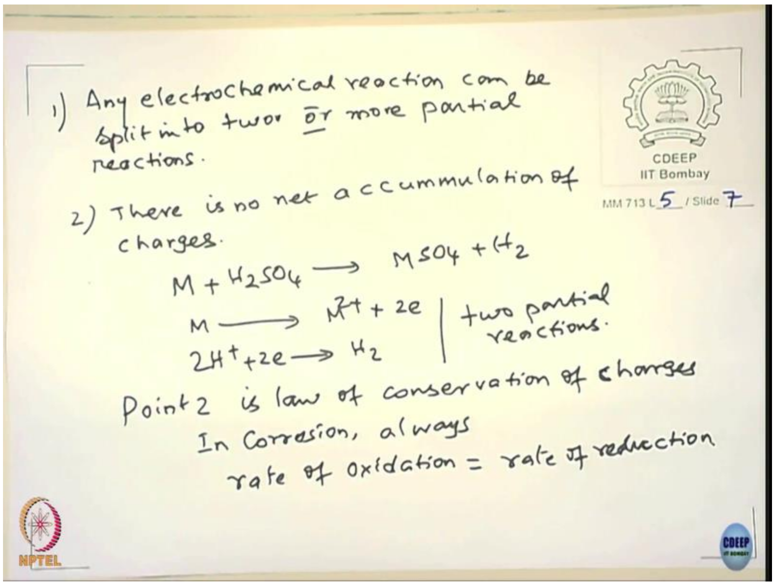

1) Any electrochemical reaction can be split into two or more partial reactions.

2) There is no net accummulation of charges.

$M + H_2SO_4 \longrightarrow MSO_4 + H_2$

$M \longrightarrow M^{2+} + 2e$ | two partial reactions.

$2H^+ + 2e \longrightarrow H_2$

Point 2 is law of conservation of charges

In Corrosion, always

rate of oxidation = rate of reduction

So, what is the basis? The basis to look forward is the following the mixed potential theory will say that 1. any electrochemical reaction can be split into two or more partial reactions to you may split into two or more partial reactions.

2. there is no net accumulation of charges these are the criteria of the mixed potential theory. Let us try to illustrate this corrosion of the metal right again you say this $M + H_2SO_4 \longrightarrow MSO_4 + H_2$ it is a corrosion reaction, am I right. I can split into two partial reaction can I, is not it. What are the two reactions

$M \longrightarrow M^+ + 2e^-$ and $H^+ + e^- \longrightarrow H_2$ they are two partial reactions.

I can make one more if you want, how I can make it one more? For example, assume that the sulfuric acid is exposed to air and what happens in that case you are going to have one more cathodic reaction going to be there. So, I can have at least two because there has to be one oxidation, one reduction, it can be more, but what is important.

The important is this there is no net accumulation of charges it is only states the law of conservation of charges ok. The 2 the point 2 is what point 2 is, point 2 is law of conservation of charges am I right, what does it mean, what is the meaning of this, we extend this in corrosion or any electrochemical process always rate of oxidation is equal to rate of reduction.

This is a very important thing the second point is very important point, what happens if one is more. Assume that I am immersing Fe in the solution right this is the Fe piece I am immersing Fe in the solution and assume that Fe corrodes at a higher rate corrodes like that. So, what will happen, it corrodes at a higher rate than the reduction process. So, what will happen to the surface yeah what will happen?

Student: (Refer Time: 47:52).

Can be precise what will happen?

Student: (Refer Time: 47:57).

Be precise exact.

Student: (Refer Time: 48:01).

What charge positive charge or negative charge?

Student: Negative.

You say that know. So, it will have more e^- on the surface then subsequent Fe cannot leave it will come back to the surface, if you will say the other way around the rate of reduction is faster than the rate of oxidation the surface will be more positive then the reducing species cannot work together. So, the rate of oxidation = rate of reduction that is the key in all your kinetic calculations ok. Now use this now let us try to understand the corrosion of metals.

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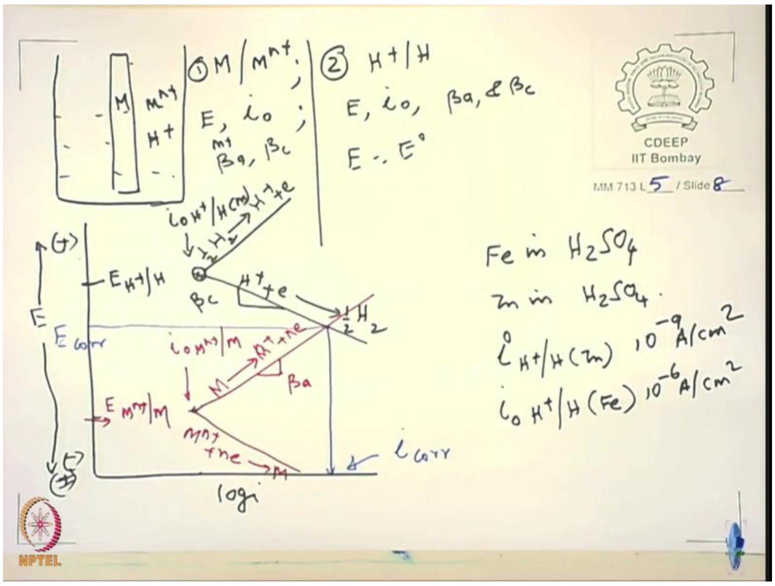

Let us continue with this example of let say some metal M in an acid how do I start with, I start with identifying the equilibrium ok. What will be the equilibria here? M is in equilibrium with M^{n+}…….. 1 equilibrium.

What are the 2nd equilibria? 2nd is H^+ is in equilibrium with the H, then what do I identify here? I identify here the equilibrium potentials for that E and identify i_0 for the M^+, I am going to divide this here and I am going to identify E for this, i_0 for that, then identify βa, βc identify β_a ,βc.

I suppose these are known to you already right how you how we plated. So, I have I can look at the Tafel here, I can look at the Tafel here and identify both of them. Now, I am going to represent this into current versus log plot, sorry now let us identify just let us first take this one let us take this case I have identified assume that it is in the standard state I take in the standard state now.

So, $E = E_0$ suppose you take this so, I have somewhere 0.0 on this, I can identify what i_0 I identified something somewhere here. So, this is in equilibrium for this and I can also draw a Tafel lines I can draw Tafel line for this. So, $H \longrightarrow H^+ + e^-$ here like this and $H + e^- \longrightarrow 1/2H_2$

I can do similar thing for the metal right here identify, this is the potential and this is it not, now can you understand this lines now. Let us take the case of hydrogen when I apply a potential above the equilibrium potential, we are going to get an oxidation reaction the current follows the potential in this manner it has got its own Tafel slope. On the other hand, I reduce it the H^+ ions get reduced and form forms hydrogen gas the same is true for a metal right.

If I apply a relatively please look at a relatively positive potential it moves up, but why I said relative positive potentials this is positive for this, but this potential is negative for this please you should not get confused right and I apply a relatively a negative potential starts moving down.

That is what will happen you have a metal here equilibrium assume that had an equilibrium here what will happened now, as a potential starts you know drifting what will happen now. This potential start moving towards this this starts moving towards this and the rate of the reaction is given by these, these, this kinetics. There is only one point in the whole diagram which satisfies the mixed potential theory tell me, what is that point?

Student: Intersection.

Yeah.

Student: Intersection.

Intersection, what intersection, this intersection?

Student: No.

No is this intersection satisfies the point right. So, that is the place it satisfies and so you have this we call them as i_{corr} and called as E_{corr}, nowhere else it will satisfy the mixed potential theory. When I say nowhere else, I am talking about nowhere else of the corroding metal we are not talking about you know otherwise even this is also in equilibrium condition, it is in equilibrium condition ok.

Now look at this now the potential lies somewhere between this point and this point, between this point and this point lies here dictated by what? Dictated by the Tafel slope of this.

Student: Exchange.

The exchange current density, the equilibrium potentials similarly the Tafel slope of this line βc and you have βa. Please understand βc of the cathodic reaction and βa of the anodic reactions are important, βa of the other equilibria and βc of other equilibria are not important these are now consequence.

So, now consequence only these two are important. So, when you are solving the problem you must know which one to use, now you guys are all good in mathematics, is it possible to compute without doing an experiment. This value is it possible to compute i_{corr}, is it possible to compute E_{corr} given this value can you, at least graphically you can do?

Student: Yes sir.

Right, if you can do graphically then you can do mathematically all you need to know is a two simultaneous equation to solve two variables how many variables are here E_{corr} and i_{corr} there are only two variables.

So, I need two simultaneous equations and to solve the two variables it is a simple mathematics it is nothing more nothing less ok, but what is required is understand the concept here ok, if you do not understand the concept you look at only as mathematics I think you will have problems either ok. So, look at what it really means is.

So, βa of corroding metal, βc of the cathodic reaction they are important for the Tafel slopes point of view the equilibrium potentials both cases are very relevant and also the exchange current densities are also very relevant for that.

Now, if you know this then it becomes easier for you to compute the corrosion rate of metals here anybody has any question let us try to sort that out ok, because you are going to now make it more and more complex is it clear to you people anybody who has any difficulty here ok.

Looking at this we have talked about the driving force for corrosion, the tendency for corrosion rate we said earlier it depends upon E_{cell} right .$E_{cell}=E_{cathode} - E_{anode}$.

So, if you consider the metal which is more having a more negative equilibrium potential you expect what happens? Can you visualize this? I am dropping a metal in acid another metal the difference between these two are one has got relatively lower equilibrium potential when I say lower it means I mean you sign also right more negative, one is relatively positive which one do you expect to corrode more in sulfuric acid ah.

Student: (Refer Time: 61:52).

Relatively more negative right, but it is not necessarily why, look at this diagram the diagram will tell you why. It is not necessary at all right of course, that is important why what are the factors involved here the exchange current density for example, if some metal has got very low exchange current density some has got high exchange current density the corrosion rate will change can it, can it not?

Student: Yes sir.

And a different Tafel slope can also change the corrosion rate. So, that is the reason why the metals behave differently I am not going to give an answer here you can if you want you can refer the Fontana book it is given there I just want to give two examples of Fe in sulfuric acid, say Zn in sulfuric acid.

So, you would expect Zn to corrode more and Fe to corrode less, but it is not going to happen you will find Zn will corrode less, the Fe will corrode more. The reason being what, the reason being is the exchange current density of H^+/H on Zn and the exchange current density of H^+/H on Fe, you guys have this handout with you, you guys have the handout, now you see the table there have you seen the table.

So, if you look at this table you will see that the exchange current density for hydrogen equilibria of various metals are vastly different.

For example, if you look at aluminum the exchange current density is what? Is 10^{-10} A/Cm^2, if you take platinum what is the value 10 to the power -?

Student: 13.

3?

Student: 13.

Platinum has 10^{-13} A/Cm^2.

Student: Yes sir.

Ok. So, you look at this you will see that the exchange current density vastly varies between metal to metal you know nickel is 10^{-6} A/Cm^2 and that of Fe is 10^{-6}, what is not given here is Zn. Zn is about you can assume that Zn is equal to 10^{-9} A/Cm^2, this is 10^{-6} A/Cm^2 ok.

If you have this and so you would expect that Zn will corrode less as compared to Fe. So, this calculation that you can do, it is not so difficult if you know and that is what the true piece the Fe will corrode less and Zn will corrode I am sorry Fe will corrode more and Zn will corrode less.

This acts as an indirect relevance to metal finishing, how many of you know of electro galvanizing, you know what is galvanizing you apply a Zn coating on steel you can do hot dip galvanizing you take it and in a molten Zn and dip it.

In electro galvanizing you make the steel and make it as a cathode you have a Zn bath, Zn solution maybe Zn chloride, Zn sulfate, whatever you apply a cathodic current Zn will deposit. It is very easy to deposit Zn, but not easy to deposit Fe because an Fe you will have more hydrogen evolving and Zn the amount of hydrogen evolution is going to be very less.

So, it is very easy to have electro galvanizing of Zn, but it is not easy to deposit Fe in the electrolytic bath, it is a technologically it is important. And, this concept is useful to say that you can deposit Zn and unfortunately you cannot deposit Fe even though it is more noble as compared to Zn actually ok.

So, this is something that you should understand, and we can stop our discussion today here and we will take it more complex things in the next class and any questions you people have.

Student: Why does exchange current density vary with different metal in different environment?

You are perfectly all right; you know exchange current density very much depends upon the solution I told you other day because it is the thing that happens with the interface. Now there are so many factors are affected by this for example, I take platinum, I take nickel, I take say Fe, I immerse in same sulfuric acid let us say, why would each of them have a different exchange current density? So, it is a very interesting question I think you guys have not asked at all.

The exchange current density is what is the ability of the metal to give e- and take back the e- am I right, that depends upon the work function; some metal can give e^- much easier some of them cannot give e^- much easier. So, it is mostly it depend upon the work function and that is the reason why some metals have high exchange current density some of them do not.

That is the reason why people use platinum as a catalyst right it is much easier for the platinum, platinum rhodium all these are catalyst they can exchange this much easier actually ok. But that is not part of a corrosion though, but that is the reason why the exchange current density vastly differs between these metals, but they have implications from the corrosion point of view.

And, we will see this when we talk about galvanic corrosion, how with the exchange current density affect the galvanic corrosion of metals you know differently ok. So, that I think we will see later, any other question?

So, then I think we will end the lecture today.