Aqueous Corrosion and its Control
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Lecture – 09
Pourbaix diagram and electrochemical corrosion

Today we will be discussing the very important concept which is on identifying a stability of a metal that is corroding; this was first you know formulated by a person called Pourbaix.

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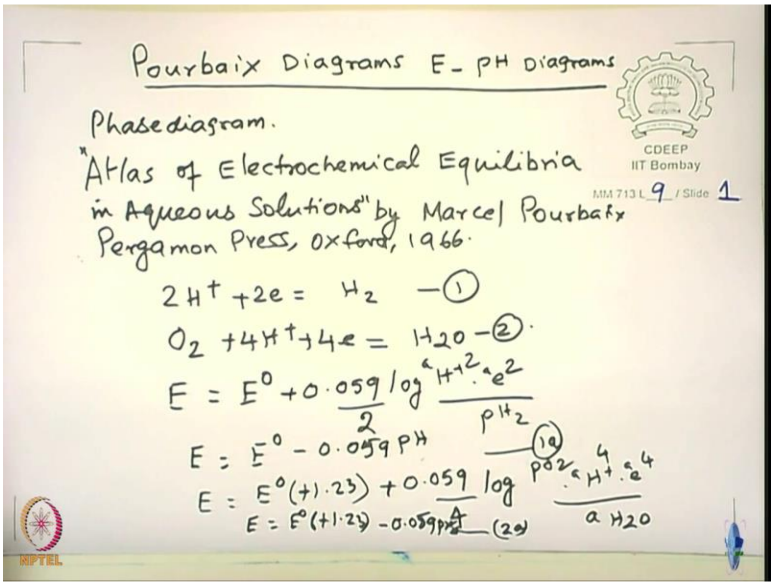

Pourbaix Diagrams E_ pH Diagrams

Phase diagram.

"Atlas of Electrochemical Equilibria in Aqueous Solutions" by Marcel Pourbaix Pergamon Press, Oxford, 1966.

$2H^+ + 2e = H_2$ — ①

$O_2 + 4H^+ + 4e = H_2O$ — ②.

$E = E^0 + \frac{0.059}{2} \log \frac{a_{H^+}^2 \cdot a_e^2}{p_{H_2}}$

$E = E^0 - 0.059\,pH$ — (1a)

$E = E^0(+1.23) + \frac{0.059}{4} \log \frac{p_{O_2} \cdot a_{H^+}^4 \cdot a_e^4}{a_{H_2O}}$

$E = E^0(+1.23) - 0.059\,pH$ — (2a)

And these diagrams are called a maps you want to call it they are named after him. So, they are called as Pourbaix diagrams, it is also called as potential pH diagrams. You guys are very familiar with phase diagrams right, you are familiar with the phase diagram. What is the use of a phase diagram? Yeah.

So, you will able to identify the probable phases that occur with respect to temperature, with respect to pressure, with respect to composition of the system. Thermodynamically you can able to calculate what are the possible phases that are present in a given system be it is a unary or binary, ternary, quaternary all kind of systems, you have a clear phase rule it defines how the phase stability should be in that case.

If I can have a similar system for me in the case of a metal corroding in a corrosive environment we define here mostly an aqueous environment we are not talking about gaseous corrosion. In this case if I can identify whether the metal will undergo corrosion or it is immune to corrosion or it can corrode at a lower rate as it happens in the case of passivation.

So, if we can identify what are the reasons that the metal would able to exhibit these properties, they are very nice, they very good for us. Ideally I want to do it for all alloys all environments all cases all different temperatures I have map and the map can give you very comfortably at this place, this temperature, pressure, pH values, chloride, sulfate that this metal is corroding non-corroding or passivating and all, but that is very complex you know it is very complex.

So, what we are going to look at here is a simple system of a water and a simple system of a metal, we are not even talking about alloys we are talking about a metal, we are talking about metallic corrosion in water and we predict thermodynamically whether the metal will corrode or will not corrode.

Ideally I should have completed this one just after we discussed about the what is called as the thermodynamics; the thermodynamics of corrosion we were talking about Nernst equation right. Subsequent to the Nernst equation we should have covered I have kept it you know so long because you need to understand the concept of passivation and also little bit more complex.

So, I thought we will do it now so that you will better appreciate the importance of these diagrams. Like all thermodynamics the Pourbaix diagrams although is very ideal conditions it is very difficult to talk about true conditions, but still they are very valuable because that gives you some perspective about whether the metal will corrode in a given condition or not.

Sometimes you can use this Pourbaix diagram in combination, suppose you take the Pourbaix diagram of a iron, nickel, chromium, put them together and say whether the alloy will corrode or not we are not going to go into that kind of complexities because it takes lot of time and involvement. This is a first course a primary course we will not be getting into that.

We also will not be getting into actual computation of the Pourbaix diagram it can be done. We have done it quite some time back you can calculate using the chemical potentials, all you need is chemical potential equilibrium constants from that you can able to calculate right. If you have a chemical potential you can calculate the free energy change, we have a free energy change you can calculate the equilibrium potentials, you also have equilibrium constant then you can talk about what all the phases which are stable.

So, all are possible for us to do this ok, but that venture I am not doing that, but those who are really are interested I will urge them in fact, you know see that book. So, we have the book in the library refer to this book this book is very interesting and important where you can make the you can see how the calculations are made.

This book is titled Atlas of Electrochemical Equilibria in Aqueous Solutions by none other than Marcel Pourbaix called Pourbaix call it. And it is published by Pergamon Press, Oxford in the year 1966 many of you would have not born I think. So, it is very old book the very nice book actually and it is worth studying this book.

So, what I am going to do today is we divide this lecture into two parts; one related to water stability, the second related to the metal corrosion. Why we talk about water stability? When you put a metal in a in water let us say I am going to dip zinc in water the corrosion occurs.

How does the corrosion occurs? The corrosion occurs by the oxidation of zinc to zinc ions at the same time you may see hydrogen may get evolved the water is unstable. The metal is unstable so as water is unstable if the water is stable then corrosion will not occur you understood, the water decomposes and forms hydrogen gas.

So, we need to understand the stability of water per se first you should also look at the stability of the metal in water. So, two things are very important to understand. So, we will first look at the water, most of you are aware of already you know water hydrolysis you guys know right.

What is water hydrolysis? Why it is used? Water electrolysis sorry water electrolysis ok. Why water electrolysis is used? To liberate hydrogen to liberate oxygen there so, you can generate hydrogen by the electrolysis of water by passing the current. So, let us look at this in this perspective how the water becomes unstable.

Now, the following equations are possible in water;

$$2H^{+} + 2e = H_2 \text{ (1)}$$

$$O_2 + 4H^{+} + 4e = 2H_2O \text{ (2)}$$

Now, let us look at these two equations and see how the electrochemical potential of the equation 1 and the equation 2 how these two really change right.

$$\mathrm{E} = \mathrm{E}^{\mathrm{o}} + \frac{0.059}{2} \log \frac{H{+}^{2} e^{2}}{P^{H_2}}$$

$$\mathrm{E} = \mathrm{E}^{\mathrm{o}} + 0.059\mathrm{pH} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1a)}$$

Let us look at the equation 1 write the Nernst equation for that right write the Nernst equation for the top 1 E is equal to E naught plus 0.059 right logarithm of what logarithm of H plus square electron square. And you have the partial pressure of hydrogen here is it right yeah thank you by 2 the number of electrons 2.

So, the activity of electron can be considered as one, the hydrogen partial pressure can be hydrogen as one atmosphere. So, this equation then becomes what is equal to E E naught minus 0.059 pH these 2 and these 2 gets cancelled off and you get this. What is pH? pH is equal to?

Student: Minus log pH.

So you get the equation 1. So, what does this equation really tell you? The equation tells you that as we change the pH the equilibrium potential for this equilibrium is going to change, right. Is very is it is not very complicated right it only says that if I change the pH the E value keep changing right.

Similarly, you can write the equation for this also right you can write the equation for the other one this is 1 a I put it here so that it becomes easier.

$$\mathrm{E} = \mathrm{E}^{\mathrm{o}}(1.23) + \frac{0.059}{4} \log \frac{P^{O2} a_{H+}^{4} a_{e}^{4}}{a_{H2O}}$$

$$\mathrm{E} = \mathrm{E}^{\mathrm{o}}\ (1.23) + 0.059\mathrm{pH} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2a)}$$

The other one E is equal to what is equal to E naught of course, this E naught is different from that of this right this is equal to this is E naught of the which is equal to plus 1.23 you should not confused with same right is equal to what is equal to plus 0.059 upon.

Student: 4.

4 great it is good then logarithm of.

Student: (Refer Time: 14:10).

Logarithm what happens logarithm of the partial pressure of oxygen and H plus power 4 and electron to the power 4 and the activity of all you can put activity you want all of them ok, please put all of them activity here and activity here and activity of the water. Now, what happens? Now, look at this if I assume the partial pressure of oxygen equal to 1, then what happens? Look at the equation what happens this equation it will becomes.

Student: E naught minus 0.059 (Refer Time: 14:59).

So, it becomes similar to that of the hydrogen equilibrium, only E naught value changes otherwise it is very similar to that of that right. So, we can write here E is equal to E naught 3 minus 0 point naught 59 pH oops. Now, there are two equations right now I am going to represent them in the diagram now.

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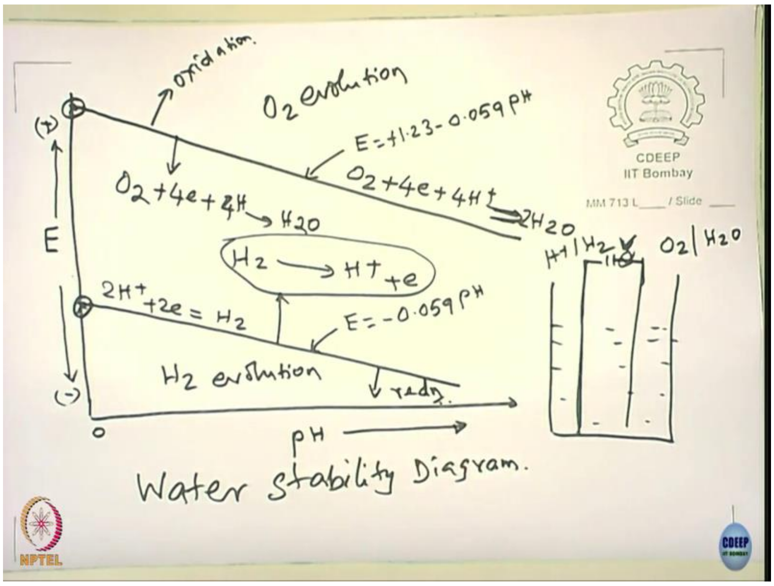

See how I am going to do that of course, it is goes increasing way and it is going to be in decreasing way. Now, I want to represent first of all the hydrogen equilibrium please see your equation you look at the equation now right. Let us look at this equation this one what a relation for that? If what is E naught for this one is.

Student: 00.

00. So, what is the corresponding value? So, I have 0 0 and the potential varies with pH what is the slope of that?

Student: 0.0.

0.059 minus 0.059 so, you find like this. So, this is the way the potential keep changing which has been. So, this is the 0 pH, the pH is now increasing in this manner. So, there is a relation if you want to have relation here E is equal to minus 0.059 pH am I correct. Let us go to the oxygen equilibrium the second one, you also have a similar thing right, what is the E naught value for that?

Plus 1.23; so, the 1.23 will come somewhere here right. How does the equilibrium potential vary with respect to pH? What is the slope here?

Student: Same.

The same so, the guy this line will goes I am not I am not good in drawing the let me try to do this, what will what the relation here E is equal to plus 1.23 minus 0.059 pH understood what is the equilibrium. So, this equilibrium can be represented as

$$O_2 + 4H^+ + 4e = 2H_2O$$

This equilibrium corresponds to

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

I think I am sorry it should be equilibrium here.

Student: Sir, oxygen should be equal to.

Yeah one second this should be equal to this line is in equilibrium.

Student: You are writing equation for a reduction reaction.

No we are writing what is this potential called?

Student: E.

E equilibrium right. So, at this particular potential it is a exhibiting a equilibrium neither getting oxidized nor getting reduced all through the line they are under equilibrium. So, this is not oxidation or reduction it is a it is equilibrium here so as this equilibrium. So, this line corresponds to equilibrium here, the hydrogen will be an equilibrium here understood or not.

Let me just illustrate further suppose I move up here what happens? If I move up what will happen? In this region if I move the potential up what will happen to this; what will happen to this equilibrium? The equilibrium will go hydrogen will become H plus plus electron agree it will move up, it will move down here what happens? What do we get? So, here move forward right. What is the over voltage for this from here to this, is it negative or positive?

Student: Positive.

Positive.

Student: Negative.

So we have only one.

Student: Positive.

What is the over voltage eta is equal to E applied minus.

Student: Minus E equilibrium.

E equilibrium right. So, when you when you go here this is your equilibrium potential this is applied value. So, what is the eta value?

Student: Negative.

Positive or negative.

Student: Negative.

So, cathodic reaction so, what happens now in this case? So, what does it mean? In this region can you just tell me what I wanted to say I want to see whether you get it or not. In this region what does it happen; what is happening in this region?

Student: Water (Refer Time: 21:45).

Water is stable right. In this region hydrogen will convert into H plus, oxygen will convert into water so; that means, it is a water stable region, nothing will happen to water if this potential between these two are lower than this here and here. When we move away from here the oxygen will evolve move away from here what will happen?

Student: Hydrogen.

The hydrogen will evolve here in this region the water is completely stable right. So, can you understand little bit more I want to say this let us say I want to understand little bit more. I have two electrodes here, one is the this is oxygen electrode and this is the H plus hydrogen electrode here, but they are in water. If I short this I measure with the voltmeter the voltage will be always 1.23 irrespective of the pH of this.

This is hydrogen this is this is hydrogen and this is oxygen here the voltage bring these two electrodes should be always 1.2 irrespective of the pH. If I make it slightly negative of this what will happen here? Hydrogen will evolve to make it slightly positive of this the oxygen will evolve here. If you make it slightly negative and slightly positive what will happen to this voltage of the cell, if I am not applying anything the voltage between these two is 1.23 you agreed this is the voltage given by this line voltage given by this line.

So, I use a voltmeter I measure the voltage the voltage is 1.23 will happen irrespective of the pH no matter what happens, if I make this potential slightly negative suppose I move here to slightly negative here I slightly make it little positive what will happen to voltage between these two. So, goes one point goes beyond 1.23. So, what will happen to water? The water start decomposing so; that means, the electrolysis will takes place. So, minimum voltage I have to keep here is 1.23 anything you go increasing beyond that water becomes unstable.

So, that is what happens so, in all your electrolysis processes you apply a voltage beyond 1.23 in order to hydrogen to evolve. Now, again there is a kinetic over voltage current do not worry about it, but this diagram only tells as long as the voltage between these two is 1.23 irrespective of the pH no electrolysis will takes place you increase it beyond that electrolysis will take place. So, here there is hydrogen evolution, here there will be oxygen evolution and this diagram is called as water stability diagram.

And this side will be reduction and this side will be oxidation I suppose now why I am giving this diagram now is because you know the concept of over voltage polarization all we know. So, you will appreciate this better than you know I would have taught you during the you know concepts of the Nernst equation ok, but again look at this is all Nernst equation and nothing more here ok.

So, the water stability is given by this particular diagram, if any of you have any questions I think you can clarify, then we can move on to metal corrosion actually because that is slightly complicated than this the procedure for that is very similar ok. Are you clear in this diagram? Ok. So, can I move to next now, the corrosion of metals?

Now, let us get into discussing the stability of a metal, I am going to take a very simple system because the idea here is only to give a concepts rather than more detailed things ok. So, I am taking a simple system, the simple system here is zinc in water.

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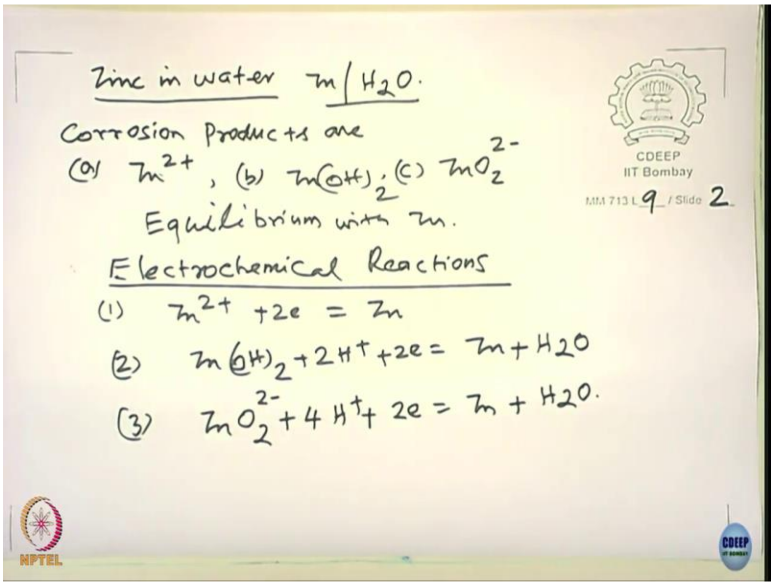

Zinc in water Zn/H_2O.

Corrosion Products are

(a) Zn^{2+}, (b) $Zn(OH)_2$; (c) ZnO_2^{2-}

Equilibrium with Zn.

Electrochemical Reactions

(1) $Zn^{2+} + 2e = Zn$

(2) $Zn(OH)_2 + 2H^+ + 2e = Zn + H_2O$

(3) $ZnO_2^{2-} + 4H^+ + 2e = Zn + H_2O$.

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How the corrosion will occur if I immerse zinc in water of different pH values at different potentials? What are the variations? pH is one variation the potential is other variation. So, with these variations how the zinc is going to corrode we are going to see now. Before we do this something that we need to know what is that? I put zinc in water what is the corrosive products what are the products you are going to get it, that you can find out from the chemical potentials actually right ok.

So, what are the product? In this case again I am taking a simple 3 products I am taking corrosion products are one zinc ions, the second one is zinc hydroxide, the third one is what you called as zincate, we have to know this otherwise we have to make some thermodynamic calculations to find out what are the likely species present in the system these are known now.

Now, what is the other so, the all are all this 1 2 3 all of them are in equilibrium with what, they are in equilibrium with zinc they are in equilibrium with the zinc, they can be equilibrium within themselves it can be in equilibrium with zinc 2 plus can be equilibrium with zinc hydroxide, zinc hydroxide can be in equilibrium with zincate or zincate can be in equilibrium with zinc 2 plus all possibilities are existing ok. So, we need to explore all the possibilities.

Now, let us look at the possible electrochemical reactions, what is the electrochemical reaction as opposed to a chemical reaction? The rate of the electrochemical reaction will depend upon the potential in addition to temperature, pressure, activity all these stuffs. The chemical reaction means it depends only on the temperature, pressure and activity, the chemical reactions do not depend upon the applied potentials I mean the chemical reaction rates they do not depend upon the potentials here.

So, let us look at the electrochemical reactions possible one the first and foremost the equilibria we have that we can talk about is zinc 2 plus is in equilibrium with zinc metal.

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

There can be a second equilibria that will be zinc hydroxide will be in equilibrium with zinc in this manner, zinc hydroxide 2 H plus 2 electron gives you and zinc plus water.

$$Zn(OH)_2 + 2H^+ + 2e = Zn + 2H_2O$$

The third equilibrium that you have here is zincate can also be in equilibrium with zinc ok.

$$ZnO_2^{2-} + 4H^+ + 2e = Zn + 2H_2O$$

So, these are the possible electrochemical reactions or equilibrium I would say where the electrons are getting transferred here right there electrons are getting transferred over here, we can also have a chemical equilibria I am going to change the slides.

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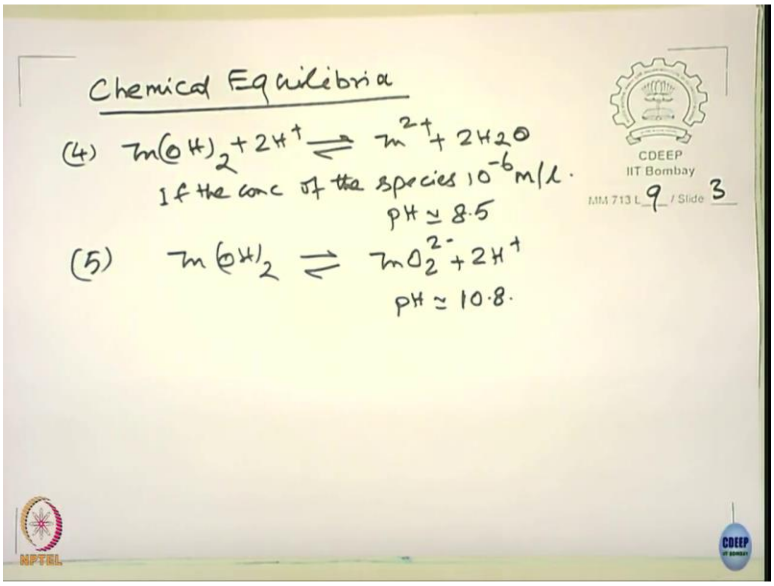

Chemical Equilibria

(4) $Zn(OH)_2 + 2H^+ \rightleftharpoons Zn^{2+} + 2H_2O$

If the conc of the species 10^{-6} m/l.

$pH \simeq 8.5$

(5) $Zn(OH)_2 \rightleftharpoons ZnO_2^{2-} + 2H^+$

$pH \simeq 10.8$.

What are they; you can have you know the chemical equilibria do not really lead to electron transfer that is in this case. These are all and we can we can say continuing the same numbers with that zinc hydroxide is in equilibrium with zinc ions 2 water and where it is stable at the pH in ok.

$$Zn(OH)_2 + 2H^+ \leftrightarrow Zn^{2+} + 2H_2O$$

Now, we can see this stability and all we can you can calculate through the equilibrium constants and all we are not getting into again not in details ok. If the concentration species are taken as 10 power minus 6 moles per liter, this equilibrium will be stable and the pH of approximately 8.5.

$$Zn(OH)_2 \leftrightarrow ZnO_2^{2-} + 2H^+$$

You can have other equilibria starts from 10.3 onwards, what is our intention. Our intention is to find out how this equilibria change with respect to potential and also with respect to pH. Now, let us take the equation 1 right let us take the equation 1.

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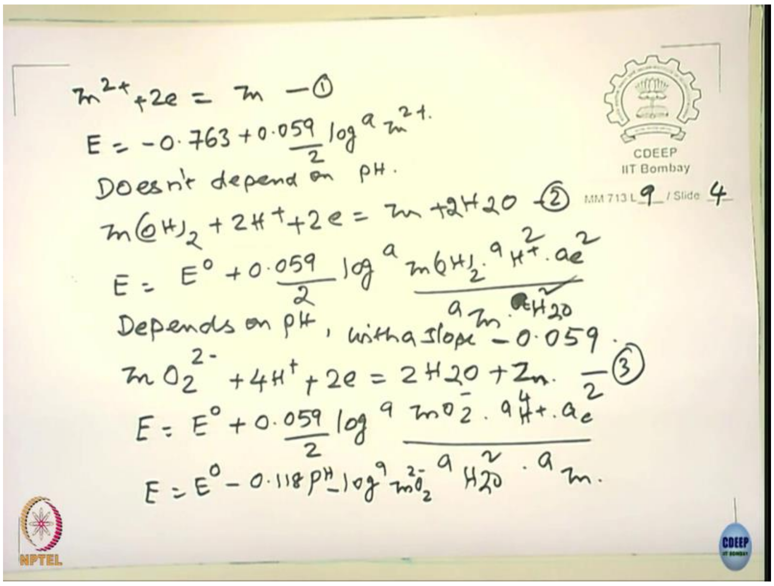

$Zn^{2+} + 2e = Zn$ — ①

$E = -0.763 + \frac{0.059}{2} \log a_{Zn^{2+}}$.

Doesn't depend on pH.

$Zn(OH)_2 + 2H^+ + 2e = Zn + 2H_2O$ — ②

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$E = E^0 + \frac{0.059}{2} \log \frac{a_{Zn(OH)_2} \cdot a_{H^+}^2 \cdot a_e^2}{a_{Zn} \cdot a_{H_2O}^2}$

Depends on pH, with a slope -0.059.

$ZnO_2^{2-} + 4H^+ + 2e = 2H_2O + Zn$ — ③

$E = E^0 + \frac{0.059}{2} \log \frac{a_{ZnO_2^{2-}} \cdot a_{H^+}^4 \cdot a_e^2}{a_{H_2O}^2 \cdot a_{Zn}}$

$E = E^0 - 0.118\,pH - \log a_{ZnO_2^{2-}}$

What is the equation 1? The equation 1

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

write Nernst equation for that. What is the Nernst equation right I am leaving the zinc there because zinc is you know unit activity right.

$$E = -0.763 + \frac{0.059}{2} \log a_{Zn2+}$$

Now, look at this equation, what do you understand from this? Does this equilibria depend on what? What does it depend on? It depends upon the activity of zinc, does it depend on the pH? So, it does not depend on the pH. So, we can write here does not depend upon pH. What is the slope with respect to pH?

Student: 0.

0 right, let us go to the next electro chemical equilibria what is the next one?

$$Zn(OH)_2 + 2H^+ + 2e = Zn + 2H_2O$$

$$E = E^o + \frac{0.059}{2}\log\frac{a_{ZnOH2}.a_{H+}^2.a_e^2}{a_{Zn}.a_{H2O}^2}$$

So, write a Nernst equation for that I think it must be 2 water I suppose please correct that please correct the make the corrections in the previous slide yeah please make these corrections.

Now, again write a Nernst equation for that see what happens is equal to E naught we do not know E naught right now right now do not worry about it, naught 59 upon 2 logarithm of what logarithm of activity of zinc hydroxide activity of H plus square activity of electron square upon the activity of zinc and and H 2 the activity H square of that sorry. Now, you can reduce the equation now see the solids here right zinc hydroxide is a solid the activity is equal to 1, zinc is a solid activity equal to 1, water the activity can be taken as a 1 and electron equal to 1. Now, how does the things change now in this case?

Student: pH change can (Refer Time: 38:47).

So, here it depends upon the pH right, what is the slope corresponding to that?

Student: 0.059. (Refer Time: 38:52).

Point minus 0.059. So, this equilibrium the equilibrium depends on pH with the slope minus 0.059 understood or not right. So, I can also write the third equation third equilibrium the 2.

What is the third equilibria?

$$ZnO_2^{2-} + 4H^+ + 2e = Zn + 2H_2O$$

Here is zinc this is between the zinc and zincate right.

$$E = E^o - 0.118pH - \log a_{ZnO_2^{2-}}$$

Now, how does this E here, E is equal to E naught plus 0 point naught 59 on 2 logarithm of activity of zincate ions activity of H plus to the power 4 activity of electrons to the power 2 and what happens the activity of water to the power the activity of zinc here.

So, here this is a unity this unity zincate is not a solid it is a complex ok. So, you can assume that the concentration is minus 10 to the power minus 6 moles you can you can assume that actually you can assume that. Now, how does this depend upon? Now, the E now depends on what? Now, E depends upon E naught what happens, minus can you tell me how depends on now it depends upon?

Student: 0.118 pH.

Yes, it is going to be 0.118 pH and minus logarithm of activity of course, we have considered zincate as a solid then I think that becomes that becomes 0 actually ok. So, you can consider this is may be solid you can consider as a solid if you want, but anyway now look at this slope here. The slope here is double the slope of the the previous one ok. So, it is changes now and this is the equation 3. So, this can be now simply presented in the in the Pourbaix diagrams.

What is the Pourbaix diagram? The potential versus the pH diagram so, let us now start presenting this and see what happens. Let us now take the case of equation 1 equation 1

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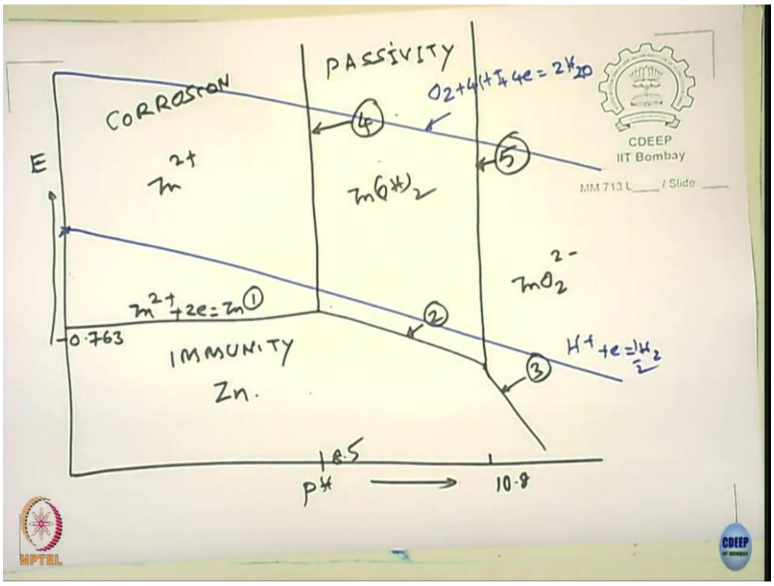

How does these relation work with pH? If I take the see what we do normally we take the activity is equal to 10 to the power minus 6 when you take activity equal to 10 to the power minus 6, then what happens? This guy will start changing right the E value will not be minus point 7 6 3 it will be you know you have to add minus 0.059 upon 2 multiplied by the minus 6 right.

So, the E also going to change so, you can able to you know it I mean you can you can keep it as unity also not a problem. So, you can keep it as a unity if you like you can make it as let us say minus 0.763 considered as a unity here.

So, it is not changing what is this one? This is now zinc is in equilibrium with zinc zinc ions are the equilibrium with the with zinc here not changing at all. What is the next one? Next one is going to change is going to change with a slope of isn't it, this one right and what is this, this is equilibrium.

This equilibrium is this is the equilibrium 1 you can say, this is the equilibrium 2 it is not easy to represent all the equations here so write equilibrium 2. What is the third one the slope becomes

Student: Positive.

No not this is negative only now it becomes double the slope like this. So, this is the third equilibrium this corresponds to the pH that is given there because when is the look at this 2. What are the species in 2? The 2 the species in 2 are zinc hydroxide right.

So, zinc hydroxide when this is stable, zinc hydroxide is stable only at 8 point.

Student: 5

5. So, 8.5 only comes right. So, it becomes 8.5 somewhere in the range anyway we can always do that this is your zinc hydroxide. And what is this one, this corresponds to equation 4, this corresponds to equation 5 right. So, I have now represented here right now same thing all the equations are there this particular equilibrium.

Please look at this equilibria it does not depend upon the potential it is not going to change, irrespective of the potential, potential whatever be the potential it is not depending on the potentials it is parallel to the to the potential axis.

So, it is independent of the potentials, parallel to the potential axis independent of potentials, parallel to the pH axis is independent of the pH, this guy depends upon the pH as well as the potential, this guy depends upon the pH as well as the potentials. So, please understand that how this really form here.

So, what it means is that I take a zinc I place a zinc in water ok. Now, I place a zinc in water. This is let us say 8.5 or something the range and this is what is this value.

Student: 10.8 sir .

It is about it is not properly scaled it is not properly scaled. So, if I take zinc and keep it in the pH range of let us say about 4 and the activity of zinc ions are considered as unit activity if I keep the potential as minus 0.9 what happens?

Student: It will not corrode.

It will not corrode right so, it will not corrode. If on the other hand in this pH range if the potential is let us say minus 0.6, what happens to the corrosion they start corroding or non corroding?

Student: It is corroding.

Corrosion. So, it is called corrosion here it is called immunity it is thermodynamic immunity we do not corrode a single bit what about in this region, in this region it forms zinc hydroxide, if the zinc hydroxide is continuous not allowing the environment to interact with the zinc, not allowing the electrons to flow through, not allowing the zinc plus ions to go through the film, film is quite impervious. So, what will happen to corrosion?

Corrosion will decrease. So, this is called passivity. So, this is the region which is passivity. So, we have a passivity here the metal will remain less corrosive, what is the difference between this region and this region, can you tell me between these two and these two, what are the difference between these two?

Student: (Refer Time: 49:50).

Yeah.

Student: This region. (Refer Time: 49:51).

It remains it is complete immunity it would not corrode at all, in the passive region it will corrode, but it will corrode at a rate much lower than what happens in the corrosion region.

The corrosion region will corrodes much higher rate the passive region it will corrode at a very low rate to what extent it will corrodes if the corrosion is more less or the least depend on what. It depends upon the film that is formed if the film is protective very good then the rate of corrosion will come down. The Pourbaix diagram does not tell that the Pourbaix diagram only tells that it forms an oxide film on the surface.

It does not tell you to what extent the corrosion is suppressed whereas, in the immunity region it says very clearly the metal will not suffer any corrosion at all. I hope I hope you got the point.

Student: But in reality within passivity region it will corrode.

It will corrode, but very low rate, you know you go back to our discussion on mixed potential theory Evans diagram right, corrosion rate depends on what, corrosion rate of a passive metal depends on what parameter?

Yeah?

Student: Electrochemical parameters(Refer Time: 51:22).

No what is electrochemical parameter?

Student: It is critical current density. (Refer Time: 51:28).

What current density, is critical current density is a.

Student: Passive.

Is a passive current density right, the corrosion rate of the metal depends on the passive current density provided is spontaneously passivating right, is not it? So, and in that case IP is equal to I corr it does not tell you what rate it is corroding. So, that is not thermodynamics it is kinetics now. The film is very good the IP will be very very low, the film is poorest or then of course, the IP will be very high ok.

All it says that in this region the metal will passivate, what quality of the film it is, how protective it is, the in the in the Pourbaix diagram does not tell you that information there is not simply available for us ok.

So, you know this is advantage of I mean I mean there are limitations; obviously, ok, but there is real advantage of using this diagram because it can identify the regions of immunity, corrosion, passivity and all the stuffs. In fact, we will talk about what is called a cathodic protection later, the cathodic protection lie in this region called as the immunity region actually here we will talk about and when you talk about uniform corrosion.

So, this is a simple map of it now this map if you see in the literature it can be very complicated, why it can be complicated these lines for example, this line will change depending upon the activity of zinc ions if the activity of zinc ion is minus 6 this line will start shifting down. Similarly these guys will start shifting left side right side depending upon the activity of the species because you know you know the k right k depends upon what the k depends upon the concentrations or the activity of the species.

So, these lines can be changed depending upon what activity they are, but basically the trend would remain more or less are similar. So that I think you should be knowing, before I close you know the discussion it is necessary to understand where does the water stability lines lie in this Pourbaix diagram. Now, where does it lie can you just tell me.?Suppose, you take water it is going to be.

Student: At 0.

At 0 here right it is going to go somewhere here it is going to be somewhere 0 here and and you will have a slope somewhere very similar to this slope. So, this is

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

your H plus plus electron gives you hydrogen, I can also have one more line for the oxygen water equilibrium right because I do not know it must be somewhere up.

But I think we will write somewhere here this we close to this something like that and this will be your equilibrium. What is equilibrium?

$$O_2 + 4H^+ + 4e = 2H_2O$$

Oxygen plus 4 H plus plus 4 electron gives you 2 water; please look at this region is the water stable regions right [noise] and this region is water unstable region.

So, suppose you put you drop zinc now look at this diagram now you drop zinc in water of different pH. So, what are the reactions will occur can you tell me, will the oxygen evolve on the surface and if you have question. Look at the you have to look at the Pourbaix diagram only right you look at the Pourbaix diagram and tell me what happens there you know what happens in water; what do you think will happen?

So, hydrogen evolution takes place right the hydrogen evolution takes place ok, because the zinc is dissolving. So, it will be the potential will be somewhere between in this point and this point between these two it will be there it would not be it would not go here is not it, this is one potential other potential. So, it will be somewhere here the hydrogen will evolved this zinc will get oxidized ok, the oxygen will not liberate because you need a very high potential you cannot go up not possible to do that ok.

What is anodic reaction? The anodic reaction is zinc oxidation and the cathodic reaction is your your you know water is splitting into to hydrogen thing. You will not get oxygen evolution because oxygen evolution is another is the anodic reaction or the cathodic reaction, oxygen evolution is a cathodic reaction or anodic reaction? I am saying oxygen evolution from water.

Student: Anodic.

Anodic reaction ok. So, that anodic reaction will not occur ok. So, it is between anodic reaction is zinc is getting oxidized as zinc 2 plus and cathodic reaction is H plus getting reduced as hydrogen ok. So, water is unstable it does not mean there is oxygen evolution no it means hydrogen evolution takes place the zinc is getting oxidized to zinc ions so, that is possible to look at from this diagram.

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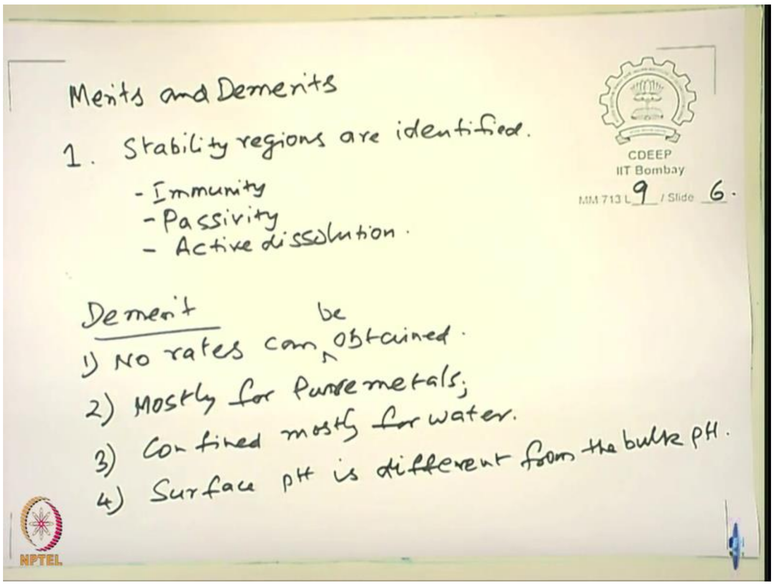

Merits and Demerits

1. Stability regions are identified.
   - Immunity
   - Passivity
   - Active dissolution.

Demerit

1) No rates can be obtained.
2) Mostly for pure metals;
3) Confined mostly for water.
4) Surface pH is different from the bulk pH.

Now to complete this before we complete it is necessary to at least understand what is the; what is the usefulness of the Pourbaix diagrams merits and demerits? The real merit is get the stability regions are identified, stability means corrosion what is mean with that? Immunity, passivity, active dissolution are identified.

What is the demerit? No rates can be determined no rates can be obtained when I say rates it is a corrosion rate can be obtained. Again mostly for pure metal and mostly for pure metals and again confined mostly for water, the fourth is you know the surface pH is different from the bulk pH.

So, there are some issues in that actually because you may not know the metal for example, you take zinc and dip it in water what will happen? What do you think will happen to the surface pH?

Yeah.

Student: Will low.

Will low think about it, it can be true of course, there can be one more option not changing at all. Now, why do you think it will increase? Who said it is increasing? Why do you say it is increasing?

Student: Because H plus ions will be accumulated (Refer Time: 60:35) surface. So more (Refer Time: 60:37) H plus ions present

Yeah H plus ions are consumed on the surface not accumulated.

Student: (Refer Time: 60:43).

If H plus ions are accumulated the pH will drop.

Student: pH will drop.

The corrosion process involves consumption of H plus ions and so there is going to be increase in the pH provided of course, if the H plus ions are not keep in pace with the consumption, but mostly you will find the surface pH is slightly higher than that bulk pH you can also do agitation all these kind of thing it will lower the pH accumulation, now that is a different subject altogether ok.

So, I think I hope you guys have some clarity about what this the Pourbaix diagram means to from the corrosion point of view, you do not have to say it is a solution for everything no that is something we should not think about it.

But certainly it gives you a flavor an idea a concept about whether the metal will be suffering passivation I mean corrosion or it will be undergoing passivation or it will be immune to corrosion it depending upon the potential and pHs that kind of information that we can get from the Pourbaix diagrams.

So, with this I think we will complete the discussion on electrochemical thermodynamics and kinetics ok. So, probably we have spent nearly about 8 lectures, the first lecture we had given a very broad outline about the course, from the second lecture onwards we start to looking at the thermodynamic starting from where starting from the free energy concept is not it. We said the what free energy concept means it is applicable to corrosion, it is applicable to chemical equilibria, it is applicable to almost all systems.

We said that corrosion is a spontaneous process and so, if you use the criteria of free energy change the corrosion is characterized by the a negative free energy change free energy change has to be negative for any spontaneous corrosion process, we gave an example of magnesium and steel or iron that they will give you a free energy change which is negative.

We also gave a an example how the gold if it has to corrode the delta g is going to positive and said that corrosion will not occur. We also said that measuring free energy change and then telling that metal will corrode or not it is a very complex process.

So, we wanted to move over to a simple concept which is very easily measurable in the laboratory that is using the potentials. So, we visualize that electrochemical corrosion processes in aqueous corrosion, all this aqueous corrosion involves an electrochemical equilibria there is electrochemical corrosion processes are taking place.

So, we start defining what the electrochemical equilibria really means is in terms of equilibrium potential right, the equilibrium potential what is defined actually and that can be related to free energy change using the Nernst equation.

Now, we also know that the you can obtain the equilibrium potential for any equilibrium by knowing the standard potentials, by knowing the other other component of Nernst equation what is that concentrations and the partial pressures all these stuffs.

So, when you know the equilibrium potentials of the system you can use that as a criteria to find out whether a metal will not go corrosion or not by subjecting into this concept E cell is equal to E cathode minus E anode these things and that has to be always positive.

So, by defining that you can able to say whether the metal will corrode in a given situation or not and that is only talks about the metal will corrode or not, but you do not know what rate it is corroding in order to know in order to predict or in order to calculate the corrosion rate we got into the kinetics electrochemical kinetics.

So, electrochemical kinetics we started using simple concept from there using the Tafel equations, how the Tafel equation can takes place you know. See, all the Evans diagrams are all based on the Tafel equations actually we did not go into Butler Volmer equation complexities and all we made it simple and then we say that that the we first of all looked at the the kinetics in terms of charge transfer kinetics which is governed by a Tafel equation.

We also look at the diffusion kinetics which are given by Fick’s law right, from Fick’s law that you can look at what the limiting current density is. Now, we said that any current corrosion processes you have to have minimum at least two equilibria start with one of it should become a cathodic reaction, other will becomes the anodic reactions.

So, we have seen the governing equations and if you solve the governing equations you can able to get E corr and i corr that is decided by what they decided by mixed potential theory which says that at E corr or at i corr the rate of oxidation must be equal to rate of reduction, that is that is sets the criteria for what is E corr and what is i corr, how to get these things now.

So, having seen that they we use this same concepts in order to understand how the corrosion will occur when you add an oxidizer when you velocity is changing all this we looked at it. We also looked at a special form of corrosion of metals which is a passivity where the passive film is is formed and where in the anodic dissolution rate is brought down because of the formation of the passive films ok.

So, the passive films are very essential for engineering materials, because most of the engineering materials when you are going to use they form passive film the corrosion rate drops actually. In fact, they are all belonging to the active metals they are not belonging to the noble metals at all. So, that is what we we saw that how the passivity is very important.

Again we apply the mixed potential theory to the to the passive systems also and show how the E corr value I corr values will change in all these cases same governing equations are applied same mixed potential theory is applied we can able to see that how E corr and I corr can happen things are of course, complex here because in a metal showing active passive, transpassive dissolution then you find that the mixed potential theory can be applicable at any complex manner actually that also we started.

So, having said that we understood all these we moved on to determining actually how the corrosion rate can be can be measured in the laboratory using electro chemical techniques, there also we saw that using what is called as what is called as Evans diagram and how the evans diagrams can be can be used to understand real plots the here the polarization plots.

I did not even go in details about how to get the plots you know galvanostatic potentiostatic you will see that in the other course and so using these plots how to get exchange current density Tafel slope E corr values you know and I corr values all this you have seen. Lastly and we also looked at the other part of thermodynamics that you can identify the regions of passivity, active corrosion and immunity using a simple thermodynamic concept of Nernst equation and the equilibria involved in the systems actually.

And these diagrams are all somewhat similar to phase diagrams and they are all called as the Pourbaix diagrams and we also know how the Pourbaix diagrams have its own limitations despite that it is useful in getting a picture about when the passivity can occur and when that may be active dissolution.

I think with this we I hope that you people have reasonable clarity in terms of getting the fundamentals of the electrochemical aspects of corrosion which will be useful in understanding various forms of corrosion including uniform, pitting, galvanic corrosion, crevice corrosion in all the cases most of the cases you can apply these concepts. So, that we get better clarity in terms of in terms of understanding these mechanisms. In fact, that is useful even to prevent corrosion actually ok.

So, that is why these concepts are very essential that is why you spend nearly about 9 lectures and I would urge you strongly please go through this again get the concepts very clear ok, if these concepts are clear I think your understanding of corrosion aqueous corrosion would be very easy actually and these concepts are not difficult, but you have to be very systematic.

Do not jump into conclusions we for example, we saw standard potential is not reduction potential is not oxidation potential we say it is equilibrium potentials there are books we say is that you know there is a sign invariants, you know sign variant, we consider sign sign invariant actually right.

So, these concepts have to be clearly brought in you should know clearly what is mean by over voltage there should be no sitting you are going to have you know no clarity and over voltage you may not be able to even solve many of these things at all.

So, you will understand what over voltage means really overall voltage it can be positive or it can be negative. So, you cannot just you know you cannot just say that over voltage always means higher voltage you know you cannot just talk about that kind of things.

So, get into the concepts I think it it becomes much easier for you to understand the aqueous corrosion and next class we will start looking at the practical forms of corrosion how they are really happening on the field. So, with this I think we close this and wish you of course, a very good happy weekend the remaining weekend.

Thank you very much ok.