Aqueous Corrosion and its Control
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Lecture – 03
Can we predict if a metal corrodes? (Part–II)

In the last class, we started discussing to find out if we can predict whether a metal will undergo corrosion or not. We will continue that one to make these concepts clear. Before we do this, I like to summarize what we discussed in the last class. We said that for any reaction be it a corrosion or be it a chemical reaction or a physical transformation, the first criteria for spontaneity the reaction to occur spontaneous in the corrosion is the free energy change.

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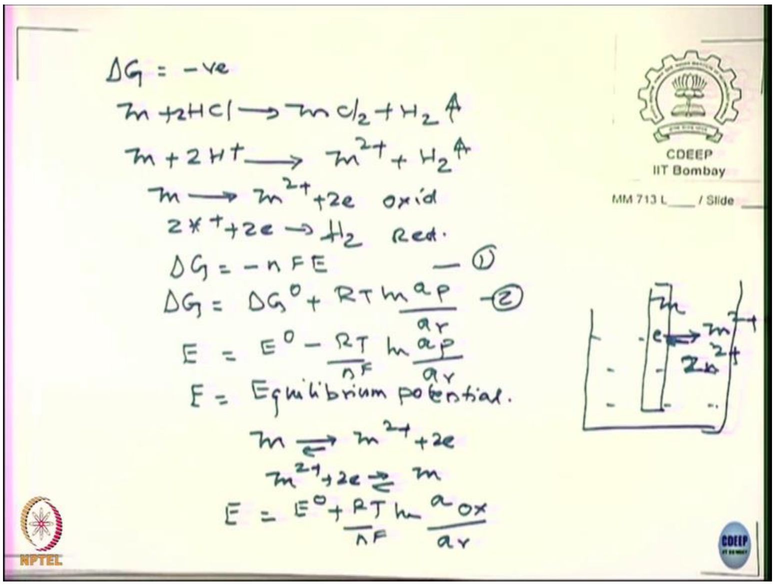

$\Delta G = -ve$

$Zn + 2HCl \rightarrow ZnCl_2 + H_2\uparrow$

$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2\uparrow$

$Zn \longrightarrow Zn^{2+} + 2e$ oxid

$2H^+ + 2e \rightarrow H_2$ Red.

$\Delta G = -nFE$ — ①

$\Delta G = \Delta G^0 + RT\ln\frac{a_p}{a_r}$ — ②

$E = E^0 - \frac{RT}{nF}\ln\frac{a_p}{a_r}$

E = Equilibrium potential.

$Zn \rightleftharpoons Zn^{2+} + 2e$

$Zn^{2+} + 2e \rightleftharpoons Zn$

$E = E^0 + \frac{RT}{nF}\ln\frac{a_{ox}}{a_r}$

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The free energy change delta G has to be negative. This what we saw in the last class. But, if you talk about a corrosion measuring the free energy change is more difficult for every corrosion processes. So, what we did? We looked at the corrosion processes especially the aqueous corrosion processes in detail. We said that the electrochemical corrosion, the electrochemical reaction is the basis for aqueous corrosion right.

You may take for example, Zn reacting with HCl giving rise to $ZnCl_2$ and the H_2

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

This may look like a simple chemical reaction, but in essence is an electrochemical reaction, right. If you recollect you said that you can write this as Zn interacting with $2H^+$ ions in the solution and then Zn is getting oxidized and the H^+ are getting reduced to form H_2

So, there is an oxidation process, there is a reduction process. So, you can separate this into Zn going as $Zn^{2+} + 2e^-$ and $2H^+ + 2\ e^-$ giving as the H_2 process and we call this in oxidation, and we call this as reduction process. So, we assume that that this is in an electrochemical process, we go for electrochemical criteria. It is easy to measure the potential of electrochemical systems.

How do you measure these potentials? How do you relate it to the free energy change? We also saw that we use the Nernst relationship. What is the Nernst relationship? It is between the free energy change

$\triangle G = - nFE$….1

is what we saw in the last class. So, we can relate the free energy change to the potential using this Nernst relationship right.

Now, for a chemical reaction you have a relationship

$\triangle G = \triangle G^0$ + RT ln(activity of the products/the activity of reactants) ……………2

we saw that right. For any reaction we can write like this and using the equation 1 into 2 to do this, you can convert this into

$E = E^0$ – (RT/nF) ln (activity of the product/activity of the reactants). And, this is the Nernst equation right this is the Nernst equation.

How do you read this equation? Let us take the example given here Zn right. Let me look at Zn immersed in Zn^{2+} right this immersed with Zn^{2+} right. This is the Zn metal the Zn solution. It establishes in equilibrium right wherein Zn goes as Zn^{2+} and again it comes back.

In the process the e^- are getting exchanged between Zn ions and the Zn metals. The potential is so established between the Zn and the solution containing Zn ion, we call them as an equilibrium potential right and this potential E is called as what is called as equilibrium potentials ok.

Please understand, it is neither oxidation nor reduction right; the reaction occurs forward the reaction occurs backward. So, you cannot call this potential as either an oxidation potential we do not call either as a reduction potential. We call them as what? We call them as the equilibrium potentials. This is a very important thing in understanding the electrochemical equilibrium.

So, what I mean by that? If I write an equilibrium in this manner or you write like this both of them would exhibit what? Both of them would exhibit same potential irrespective of what? Irrespective of the way you write it. So, the potential is sign invariant we saw that in the last class.

So, how do I get the equilibrium potential? What is the criteria for that can anybody recollect? How do I get the equilibrium potential if I give you a concentration of Zn let us say 0.1 molar suppose I give 0.1 molar, I substitute in the equation right, but equation will be always written in such a way that

$E = E^0 + (RT/nF)$ ln (activity of oxidants/the activity of reductants).

So, only when you write like that you will get E value correctly, otherwise E value could be changing ok. So, this is the most important thing in determining the equilibrium potential for any electrochemical system alright. We discussed this in detail in the last class right and if you have any questions on this? No questions. So, let me proceed now.

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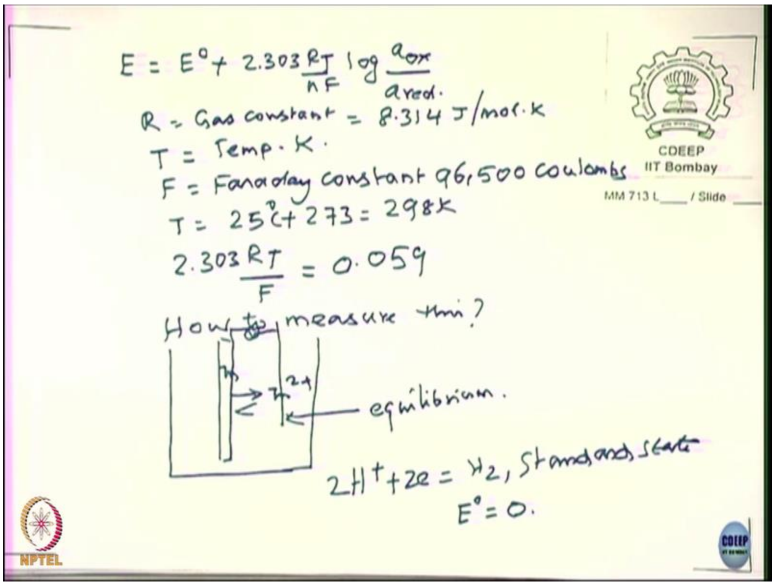

$E = E^0 + 2.303 \frac{RT}{nF} \log \frac{a_{ox}}{a_{red.}}$

R = Gas constant = 8.314 J/mol.K

T = Temp. K.

F = Faraday constant 96,500 coulombs

T = 25°C + 273 = 298K

$2.303 \frac{RT}{F} = 0.059$

How to measure this?

equilibrium.

$2H^+ + 2e = H_2$, Standard state

$E^0 = 0.$

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Now, let us go into this the Nernst equation right, like we have seen

E = E ^{0} + 2.303 (RT/nF)log(the activity of oxidants/the activity of reductants)

right. You know what R is, right? R is what? R equal to the gas constant.

Student: Gas constant.

Which is equal to 8.314 Joules per mole K per Kelvin.

Student: (Refer Time: 11:11).

Ok ah this joule or kilo Joule? Joule it is a Joule it is ok.

Student: (Refer Time: 11:21).

You can also see you can represent as low calories that I mean this is I mean it is fine and T is a temperature in Kelvin, right. What is F? F is equal to Faraday constant is given as roughly 96,500 coulombs right. If temperature is assumed to be is equal to 25 degree Celsius, you have 273 convert that into it, what happens? Is equal to 2?

Student: 298 Kelvin.

298 Kelvin, then you substitute everything in this here

2.303 RT/F. So, 2.303 RT/F turns out to be 0.059. You can calculate this at leisure time and you see that the number that is given is the correct number or not. So, now, using this you should be in a position to calculate the equilibrium potential for any electrochemical system right, be it Fe^{2+} + e^- is in equilibrium with Fe^{3+}; Zn is in equilibrium with Zn^{2+} ions. No matter what the equilibrium is you should be in a position to determine clearly what the equilibrium potential is this calculation.

How to measure this? How do you measure this? How do you measure this? Is it a measurable quantity or I say no, no it can be only calculated, can we measure this? right. So, I should be able to measure this.

We have seen in the last class again that it is not possible to measure the absolute value. Why? If you are going to use another probe in the in the electrolyte, for example, if I consider an electrochemical system some metal take for simplicity same Zn is in an equilibrium with Zn ions. were to measure it, I need what? I need a probe. If the moment I put a probe here and I measure with the voltmeter and this probe also will have one equilibrium.

So, you are going to measure only a potential difference, you cannot actually measure the absolute values. It is not possible right. So, how does one solve the problem? The problem is solved by considering this equilibrium H^+ + 2 e^- giving rise to H_2 in the standard state. You consider E for that is considered as a 0 here. So, we considered that E is a 0 and all the potentials measured are in relation to hydrogen right. So, in relation to hydrogen that you can measure it. So, you need an electrode. You need an electrode which is also in equilibrium.

So, how do you visualize this? Can somebody visualize an experiment, measurement of equilibrium potential? Yeah, we have cell. So, let us say I want to measure the electrochemical potential of ion immersed in Fe^{2+} ions. What do you do? I take a beaker; I put Fe^{2+} ions of the given concentration. I dip ion electrode and other side what I will have? I will have an hydrogen electrode; the hydrogen electrode in what state? In the standard state. What is the standard state? The activity of H^+ ions equal to unity.

The hydrogen partial pressure is equal to 1 atmosphere and I use a voltmeter; what is that voltmeter? An high impedance voltmeter; the measured potential between these two are called as the equilibrium potential of the ion Fe^{2+} system. very simple. But, in practice, if

I have to if I have to measure the potential by use the hydrogen electrode very complicated. Why it is complicated? What is the hydrogen electrode? I just define to you what the hydrogen electrode is ok.

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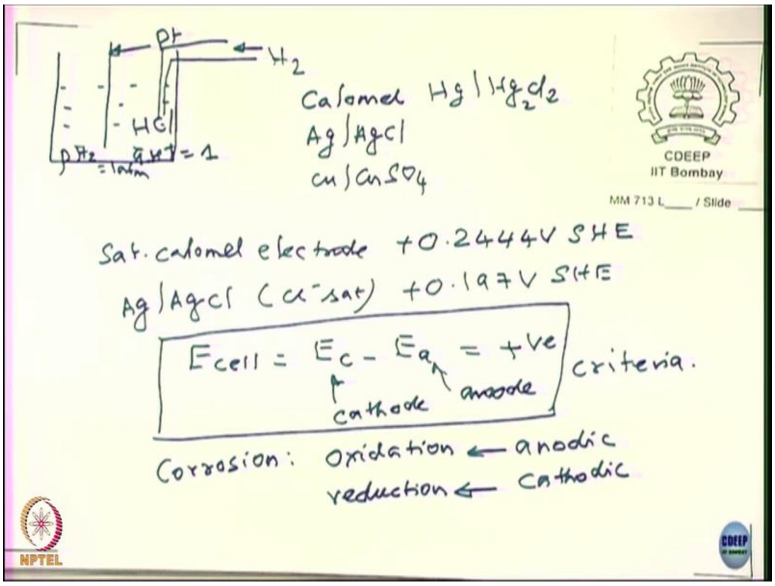

Calomel $Hg | Hg_2Cl_2$
$Ag | AgCl$
$Cu | CuSO_4$

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Sat. calomel electrode +0.2444V SHE
$Ag | AgCl$ (Cl^- sat) +0.197V SHE

$$\boxed{E_{cell} = \underset{\text{cathode}}{E_c} - \underset{\text{anode}}{E_a} = +ve}$$ criteria.

Corrosion: oxidation ← anodic
reduction ← cathodic

I would say you would have some beaker made up of let us say glass. I immerse a platinum electrode here, right and then what I do? I take an acid let us say hydrochloric acid wherein the activity of H^+ is equal to 1. I pass through this hydrogen gas what should be the partial pressure of hydrogen here? The partial pressure of hydrogen here has to be 1 atmosphere. The potential is so measured equal to standard potentials.

If I have to do this in the lab is very cumbersome, not very easy right. Can you do this very easily? Not very easy. So, you are going to use reference electrode which are easily can be made very easily and these reference electrodes are what? There are some of them called as calomel electrode. And, you can also have silver, silver chloride electrodes. You can also have copper, copper sulphide electrodes. There are several of them are there right.

What is the calomel electrode? It consists of mercury and mercurous chloride like this and these electrodes have potentials depending upon the concentration. In this case concentration of chloride, concentration of chloride here and if you are going to use a saturated calomel electrode saturated calomel electrode the potential is + 0.2444 volts with respect to standard hydrogen electrode.

Similarly, you can also have silver, silver chloride and the chloride is saturated. Then, the potential is equal to + 0.197 volt ok. I have just give an example and there are several electrodes, you should refer this in standard books ok. In fact, there is a book on reference electrodes only, how to make this reference electrode in the in the in the lab. We can you can construct these things yourself only. So, these values you can obtain from any books any standard books. So, there is no problem ok.

So, so far I suppose you are clear about how do you calculate a reference I am sorry how do you calculate a equilibrium potentials. You know how to measure the equilibrium potential of the systems ok, then how do you use this potential to predict if the corrosion occurs or not that is given by this concept what is called as E_{cell} is equal to what?

E_{cell} = Ecathode - E_{anode} here right.

This is for the cathode and this is for the anode. And, by convention this has to be always positive, it cannot be negative at all. It has to be only positive right. So, use this criteria. So, this is the criteria. This is the criteria for that right.

Now, what is the corrosion? In corrosion you have two reactions one is oxidation we call as anodic and other is a reduction which is what? Which is cathodic. The only thing is we do not know which will be cathode and which will be anode that we do not know ok. Now, let us take this example and see how this can be used to predict if the corrosion occurs or not. I have given you a handout ok; please take this handout. What is given there? What is given is the standard oxidation reduction potentials it is also called redox potentials I would simply call it as standard potentials.

What is the standard potential? What is the standard potential?

Student: (Refer Time: 24:36) iron is 1.

Yeah. So, let us go back to this equation. You, go back to this equation what you have seen before, you go back to this equation here right. Let us take this equation.

One of this you take this equation here and the activity of the of the reluctant, the activity of the oxidant or you can take this equation. The activity of oxidant and reductant, they are unity the equilibrium potential equal to.

Student: Standard potential.

Standard potentials, please remember this. So, it is a special case of the equilibrium potential right is, it is essentially equilibrium potential the special case of the equilibrium potential right. So, that the thing is what you should got it.

So, what I shown here take this table ok. Now, in the table let us take two cases; take the case of say copper, take the case of let us say iron 2 and I am going to take copper and would immerse in sulphuric acid. So, I have also going to take iron and immerse in sulphuric acid ok.

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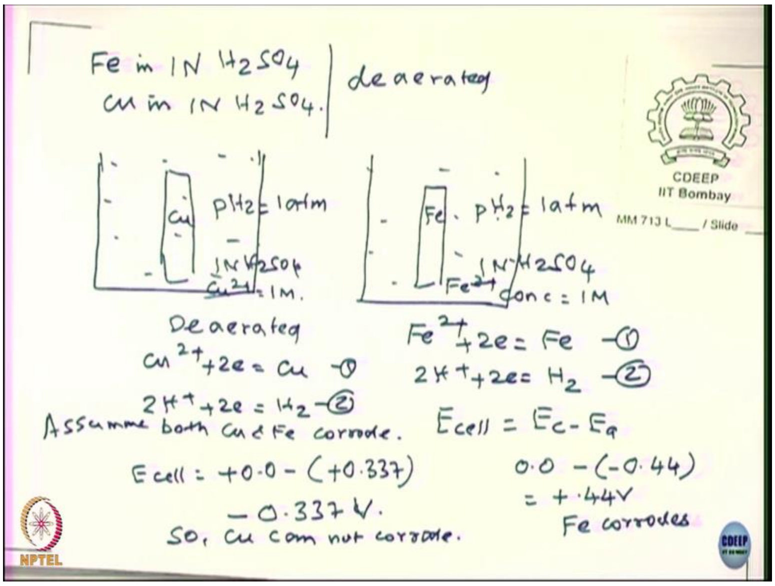

Fe in 1N H_2SO_4
Cu in 1N H_2SO_4. | deaerated

Deaerated
$Cu^{2+} + 2e = Cu$ –①
$2H^+ + 2e = H_2$ –②
Assumme both Cu & Fe corrode.
$E_{cell} = +0.0 - (+0.337)$
$-0.337\ V.$
So, Cu can not corrode.

$Fe^{2+} + 2e = Fe$ –①
$2H^+ + 2e = H_2$ –②
$E_{cell} = E_c - E_a$
$0.0 - (-0.44)$
$= +.44V$
Fe corrodes

So, two cases iron in one normal sulphuric acid. So, and copper in one normal sulphuric acid. Some of you would were not familiar with this normality, molarity I think you should read and maybe discuss with yourself and it will be hard for me to discuss here actually ok.

So, please get yourself familiarized with the with this units of concentrations how do you really represent them actually ok. Let us take two cases. So, I am going to have put it in this form of a diagram take here. I am going to immerse copper here, 1 normal sulphuric acid. I am going to have iron in one normal sulphuric acid. Please notice they are deaerated; it means these are all deaerated. No dissolved oxygen present in both the cases.

Now, we need to predict if the corrosion occurs. I make your life more simpler for you. I will say that the partial pressure of hydrogen here is equal to 1 atmosphere and the partial pressure of hydrogen here equal to 1 atmosphere. I make it quite simple right.

Now, you tell me how do we really solve the problem let us take this the table where you have standard potentials given for the host of equilibrium an iron and an copper equilibrium also given in this. Please tell me how do we solve this problem.

So, what you have to do first of all? First of all you have to write the corrosion equation right. What will be the corrosion equation in both the cases? Let us say in the case of iron what will be the corrosion equation here. What do you think happens, if you put iron in sulphuric acid, what do you think will happen? It corrodes.

Student: Oxidizes.

What oxidizes?

Student: Iron may oxidize.

Iron will oxidize as Fe^{2+} and hydrogen?

Student: Produce the gas.

Will as if iron corrodes.

Student: Yes.

Similarly, what will happen in the case of copper? So, copper should get oxidizes Cu^{2+}or maybe copper the single + and let us by say iron should get reduced as hydrogen gas if copper is corroding.

So, you start with the two equilibrium two equilibrium in this case. What are the equilibria let us take the case of iron, for example? What are two equilibria involved here that leads to corrosion? You have to start with two equilibria right what are the equilibria that are involved here right. Before corrosion there are two equilibria coming to picture: one is iron is in equilibrium with the Fe^{2+} ions again to make it simple I want to make this one more variation here.

You immerse iron in Fe^{2+} and the concentration is equal to 1 molar, right. Similarly, in this case I have a copper and Cu^{2+} equal to 1 molar, I assume this make assumption right. So, make more simpler for you ok. So, how do I start with? How do I start?

Yeah?

Student: (Refer Time: 31:05).

So, you first of all you calculate E_{cell} right. So, before calculate to get E_{cell} what do you need?

Student: (Refer Time: 31:15).

Yeah, you need the equilibrium potential for two independent equilibria right, is it not?.So, you need to calculate E_{cell}. To calculate E_{cell} you need what? You need equilibrium potential for? 2. What are the equilibria here in, can you write what are the equilibria involved in the case of iron? Can you please right here in your papers what is the equilibria involved here?

So, involved are

$Fe^{2+} + 2e^- = Fe$ …1 ,is 1 equilibria what are the other one $2H^+ + 2e^- = H_2$……2, it is 1 equilibrium right. So, equilibrium 1, equilibrium 2 for this right. What is for

$Cu^{2+} + 2e^- = Cu$ …….1

$2H^+ + 2e^- = H_2$. ………2

Now, these are the equilibria now, one should become cathode other should become am I right or not?

Student: Yes.

So let us take the case of iron and try to solve the problem. So, what is the equilibrium potential for $Fe^{2+} + 2e^- = Fe$ with respect to this problem?

Student: -0.44.

Why you take - 0.44? Why did you take that yeah, why did you take that?

Student: (Refer Time: 32:52).

You are right I mean why did you take - 0.44?

Student: (Refer Time: 32:56).

Yeah, reduce also will have same potential only.

Student: Sign.

Student: Sign. Sign will (Refer Time: 33:07).

Same. The sign will change if I am going to take iron as getting oxidized or reduced is equilibrium potential sign invariant or sign variant right.

Student: Invariant.

Invariant, right? So, - 0.44, but why not - point something else why did you choose? You are right. Why did you choose you look at the problem there?

Student: Standard.

Yeah, you are talking about a standard here. You see iron is immersed in activity is equal to 1 that is why you are taking – 0.44. If the concentration is different for example, if I say it is 0.1 molar would do you have - 0.44?

Student: Yes sir.

What happens in that case? You have to now calculate that actually right you have to calculate it. So, please understand. So, you need to calculate that in order to get the values. So, I made the life simple by assuming that both equilibria and the standard state so, we are reducing the standard potentials. So, let us assume that both copper is corroding and iron is corroding let us assume that. Please find out whether corrosion occurs or not. Can you please make a calculation and see?

Assume that assume both copper and iron corrode. So, what happens? Can you find a E_{cell} if you assume that that iron is corroding and copper is corroding what happen to E_{cell}?

Student: Since E_{cell} of iron is positive, therefore, iron is corroded.

Student: Corrode.

Will corrode.

Student: But, E_{cell} for copper is negative therefore, copper is not corroded.

Right, it will not corrode right. So, it is possible that you can come to a right conclusion you may assume whatever you like. You may you may even assume that iron is not going to corrode and say that it is $E_{cell}=E_c - E_a$, then you will get into a negative sign. So, it is possible to compute and say that the metal corrodes or does not corrode. I hope each of you label to make these calculations $E_{cell} = E_c - E_a$.

So, what happens we assumed that say iron is corroding. So, what happen $E_a=- 0.44$ and your $E_c =0$, then $E_{cell} = + 0.44$ volt. So, iron corrodes ok. In this case you take this case E_{cell} equal to what? Is equal to you assume that copper is corroding; that means, E_{cell} in this case is equal to,how much?

Student: 0.337.

-0.337. So, E_{cell} is equal to - 0.337. So, is this is a volt. So, copper cannot corrode. So, understood? Ok. So, it is possible for us to predict if a metal will undergo corrosion or not.

Now, measurement of electrochemical potential is much easier and it is very easy you go to lab and in about 5 minutes you can measure it ok. All you need to have is a voltmeter of impedance value, you need a reference electrode and the metal that you are interested to measure the metal or other system whose potential required to be measured.

So, I suppose you people now are now clear in terms of the first concept of how do we really predict if the metal will undergo corrosion or not. We will extend this argument I want to pose a problem to you.

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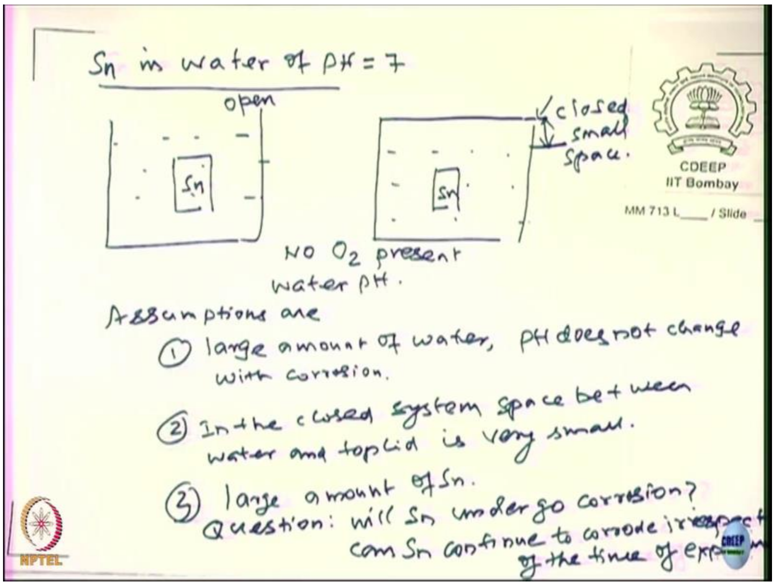

Sn in water of pH = 7

No O_2 present
water pH.

Assumptions are
① large amount of water, pH does not change with corrosion.
② In the closed system space between water and top lid is very small.
③ large amount of Sn.

Question: will Sn undergo corrosion?
can Sn continue to corrode irrespect of the time of exp

The problem is I take Sn in water of pH 7 ok. Two conditions take water and immersed in here in another case I take water I have Sn, I close this here; this is open ok. This what about here in this case? Is closed, no oxygen present, no oxygen present and the water of pH is about 7. So, the pH of the water here you know the water pH is 7.

I make the following assumptions. What are the assumptions here? The assumptions are 1 – large amount of water, pH does not change with corrosion ok. 2 – in the closed system in the closed system what you see here the space between water and the lid, and the top lid is very small and you have large amount of tin in the system. You understood the problem? ok. I have given you pictorially how they are looking like one beaker where I put tin I have taken in water of pH 7.

Other case I have taken tin in water, but it is closed, and this space is very small I would and it is no oxygen present. I have two questions for you. The question is will tin undergo corrosion or not? One this now the questions are question will tin undergo corrosion? Ok, first thing; the second thing is can tin continue to corrode irrespective of the time of the time of exposure? You understood the problem? How do you address this problem? How can you solve this problem?

The first question for example, what I can give you is I can give you one more information for you. I can or the information that I would like to give you what information that you need because it is not sufficient.

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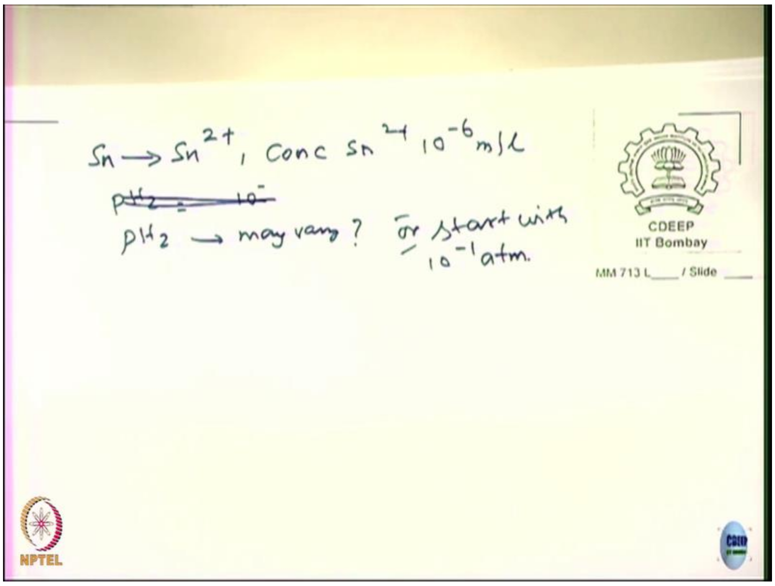

$Sn \rightarrow Sn^{2+}$, Conc Sn^{2+} 10^{-6} m/l

~~$pH_2 = 10^{-}$~~

$pH_2 \rightarrow$ may vary? or start with 10^{-1} atm.

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The other additional information is Sn is corroding if at all if it corrodes it is going to be as Sn^{2+} and the concentration of Sn^{2+} always reminds 10^{-6} moles per litre ok. The partial pressure of hydrogen can be considered as say 10 power - now this am not going to change this ok, these left out ok.

Now, what do you think will happen in this case? So, partial pressure of hydrogen may vary I put this way I done part the partial pressure of hydrogen may vary or you start with let us say you can start with or start with let us say 10^{-1} atmosphere. I put this I will go back to this problem. I had defined this problem in this manner, and I have tin here. I have tin exposed to water one case vessel is open to atmosphere and the other case vessel is closed.

The space between water and the top plate in this case is smaller the pH of the water remains same all the time at 7 and Sn^{2+} in this case is said 10^{-6} moles per litre right and the opposed there is no oxygen present.

If that is the case and can you say how these systems are going to behave in terms of corrosion. Are they going to behave corrosion with the time same manner or it is going to be different? If so, how they are going to different or to start with can you think that tin will undergo corrosion or not?

So, that prediction you should be able to now do that I think you are you know having enough understanding of what electrochemical equilibrium is; you understand what the corrosion is. With the equations that you have the relationship that you understood you should be able to tell how these systems are behaving in the corrosion point of view.

Now, I just want to know I just want to give this your assignment for you and I want to see this answer when you come to the next class ok. So, please do solve the problem and you know send it by email and the TA will able to go through and correct it. You all can discuss. Please everybody discusses, but do not copy your answers ok. Understanding is free you should always discuss, then only you will able to understand the concepts ok, but solve the problem yourself independently do not do that ok.

So, please do this and tell me how these systems will respond with respect to time that way we can do that. And, based on this I will give you some more problems and I think we can work on that to make your understanding better and better. Before I move on to the next topic of how do you calculate the corrosion rate, we talked about to predict corrosion rate how do you calculate corrosion rate.

I want you to understand one concept ok. See they are very elementary you know I am not supposed to discuss in this course, but they are very vital if you need to understand corrosion that is the concept of pH.

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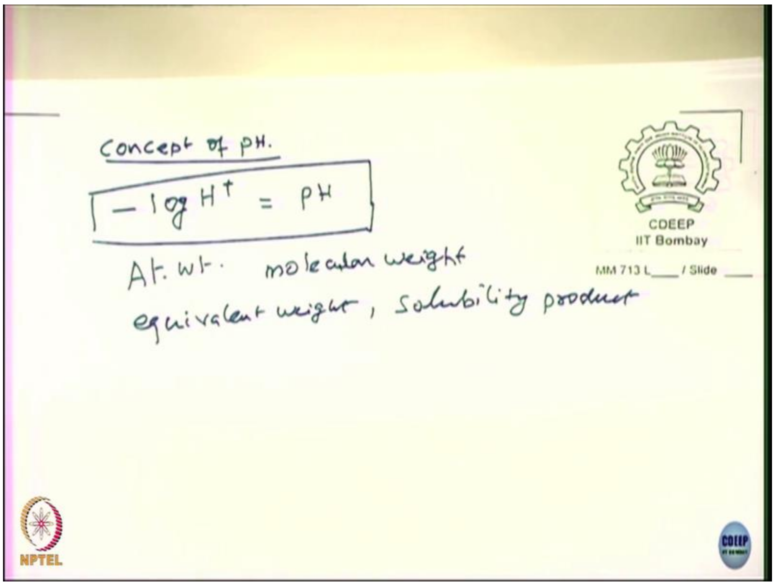

Concept of pH.

$$\boxed{-\log H^+ = pH}$$

At. wt. molecular weight

equivalent weight, Solubility product

What is pH? Yeah.

Student: Potential(Refer Time: 48:35).

Yeah?

Student: potential for the hydrogen ion.

Yeah, it is related to the activity of hydrogen ions in a solution. So, it is a concentration of hydrogen ions in solution. Please I am going to use activity and concentration in a synonymous manner because otherwise our life is going to be complicated we cannot solve any of the problems ok. So, here is related to hydrogen ion concentration. How is it related to?

Student: (Refer Time: 49:08).

Yeah, it is negative.

Student: Log.

-Log H^+ = pH please understand this. Please look at. So, when I when I say pH= 5 and pH= 9 please understand the question. When I say pH= 5 and pH= 9 how many times the hydrogen concentration change?

Student: 10^{-4}.

10^{-4}. So, it is very important. People think the corrosion of steel is happening at 4 and they will get surprised it does not happen at pH= 9. It is only 5 you know it is 5 orders are difference in the hydrogen ion concentration. Corrosion involves reduction of the H^+ ions.

So, please get that feel of it what I am talking about it. You also try to get the feel out what is molar and what is equivalent weight. Please understand, these are all the terms you should know I am not going to talk about here atomic weight, molecular weight, equivalent weight ok.

These are the terms I think you people should for a time period get familiarized with and even the concept like solubility product ok. They are typical terms, but they are very very useful for us to understand why corrosion occurs in some conditions, why corrosion does not occur in some other condition right. See, please look at we are scientists as much as engineers you need to understand why. Why is not there I think you no point is studying M Tech corrosion course.

Student: Yeah.

There is no dos and don'ts for you guys. These for you to get analyse tell what happens based on what you see in environment. You go to industry it is not simple you know. You find the reaction occurs some reaction vessel corroded you know and you say you know this company will be using another company say it is failing here. They rise the temperature only by you know 5 degrees start cracking unless you understand the relation between the parameters that affect corrosion you cannot really give a solution to the problem ok.

So, we need to understand the interrelation between corrosion and various factors affecting the corrosion processes. So, we will end our discussion related to what is called as the prediction of corrosion.

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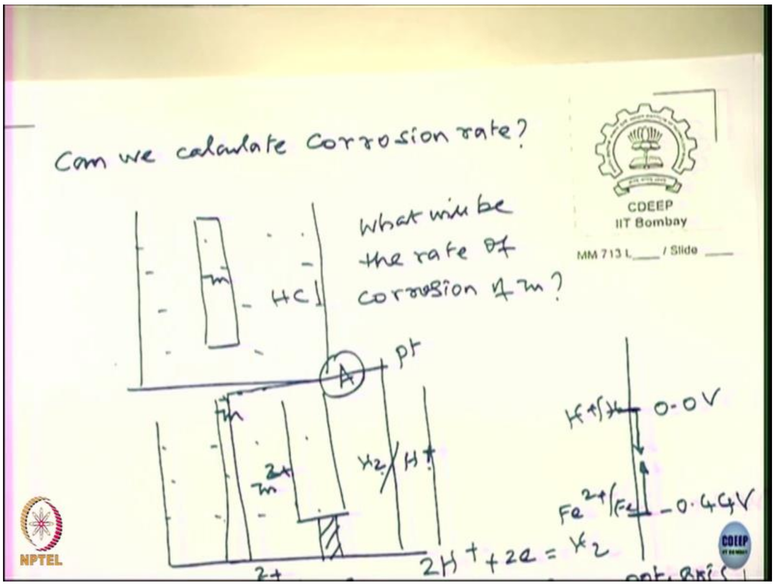

Now, comes can we calculate can we calculate corrosion rate? Say, I have immersed Zn in let us say hydrochloric acid. You know how to compute whether it corrodes or not rather corrodes or not use the Nernst equation. Now, in Zn in hydrochloric acid what will be rate of corrosion ok. So, what will be the rate of corrosion of Zn? So, question, can you make a calculation?

what are the governing equations? What are the governing principles for that that is our next step.

Now, let us look at the corrosion and in details right. Let us let us look at the corrosion here. I am looking at corrosion like this. I am illustrating this corrosion process in simpler terms right before corrosion occurs Zn is in equilibrium with the Zn ions right see that. Hydrogen is in equilibrium with the hydrogen ions. Both of them establish potentials what do what do they call that potential called? Equilibrium potentials right.

Now, does it corrode here? Does Zn corrode here? Does not corrode, rate of forward reaction equal to rate of backward reaction. Will there be any hydrogen evolution here? No hydrogen evolution because hydrogen ions combined with e- form hydrogen gas and hydrogen gas in turn give e- and form H^+ they are equilibrium condition.

So, I define this as $2H^+ +2e= H_2$ and define this as $Zn^{2+} + 2 e- = Zn$ is here. These two happens now why and if they are in the standard state for our assumption the voltage E for that is equal to 0 and a standard state E is equal to - 0.44 and I short this what happens? I use an electrical cable i connect these two what will happen? Yeah.

Student: Same.

What will happen? The potential of this is 0 and potential of this is - 0.4. Now, I just shorting these two. So, what do you think will happen? When you when you take a say copper wire, I have a resistance in the in the in the copper I have a resistor ok. Resistance is infinite and this side I have voltage which is let us say - 0.4 and this side the voltage is 0. And now I lower the resistance right I make it 0 like. So, what will happen? Current will be the current flow or not?

Student: Yes.

The current will start flowing. The moment you remove the resistance the current starts flowing. Am I right or not? So, you have a infinite resistance they are not connect talk to each other. Now, they have independent potentials, the independent equilibrium that you have right and I shot this with a wire this will start moving towards what happens let us look at this. I draw like this. This is called a potential axis. This is a potential axis. This is 0.0 this is H^+ /H and there is - 0.44 volt or this is Fe^{2+}/Fe.

I remove a resistance what will happen? This potential will starts moving towards this and this will start moving towards this, that happen or not? Is it not? So, the 0 the potential of the hydrogen electrode will tend towards positive. I am sorry the potential of the hydrogen electrode tend towards negative, and that of Zn will tend towards positive move towards like this and the current will starts flowing. Am I right?

If I put an ammeter here I can measure what is the amount of current that is flowing I can use Faraday's laws and I can determine the rate of corrosion, can I not? Right. So, if I can use an ammeter here I measure the current and I know the current I can use the Faraday's laws I can determine the corrosion rate, measure it is called measurement. Can you calculate it without measuring using ammeter can I determine what will be the amount of current that is flowing between this and this? If there are governing equation then that governing equation will tell us so, what should be the amount of current flowing here and that current can be used to calculate the corrosion rate based on the Faraday's equations.

So, what we are going to do in the in the subsequent lecture is to find out the governing equations here between the voltage and the current. See please notice when the potential is start moving from here to this the current is going to move more the potential is moving more will be the amount of current that is flowing in the system. So, my idea is can I get a relation between the potential that moves up, coming down and the current that is flowing on this electrode on this electrode.

If I know it I can calculate it. I do not have to go and do an experiment in the laboratory actually right I do not have to do that. So, our task now is to find out the governing equations and then use that equations to compute the corrosion rate of metals am I clear? Am I clear to you? Ok that is what we are going to do that. So, then we can answer this question can we calculate the corrosion rate. This of course, is a it is a very involved you know derivations.

If you take the Bockris and Reddy book on Modern Electrochemistry, the kinetics are very well derived and nice things are there and that is called as Butler-Volmer equation. I am not going to derive the equation and those who are interested please read that book read other books as to how the Butler-Volmer equation is going to be derived.

I am going to make a very simplistic approach, so that now you are from somebody from you know metallurgy background, or somebody from electrical engineering background somebody with mechanical background.

So, I do not want you to flood with the equations, but yet I want you to appreciate the governing relationship the governing equation, so that you can able to calculate yourself tomorrow ok. So, that is our next task of how do we really compute the corrosion rate of the metals. Am I right actually, am I clear to you? ok. So, far what we discussed are you people clear ok?

So, let us go to the next step of how we compute the corrosion. Let me start with the equilibrium condition right. Let me start with the equilibrium condition. What is the equilibrium condition? Let me take a simple electrochemical equilibria. What is that equilibria?

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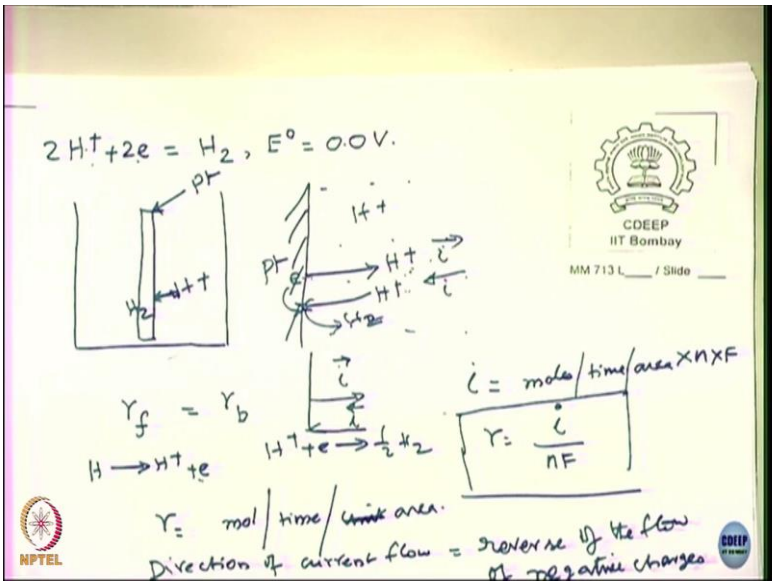

Let us take this equilibria. $H^+ + e- = H_2$ it is very known to you. In the standard state in the standard state what is the E value for this, (are you clear?

Student: Yes sir.

This is an equilibrium. What does it mean? The hydrogen releases e- it forms H^+; H^+ accept e- and forms hydrogen gas. So, it is an equilibrium condition.

So, how do I pictorially put this? I put this pictorial like this ok. This is a platinum wire a metal and I have H^+ I have H_2. Now, here takes place. Now, what is happening please look at if I able to visualize if I have the ability to go and see through my eyes what is happening at the interface right, this is the interface right. What is the interface? This is by platinum metal and this is the acid I have right.

So, what is happening? One reaction is going as H^+ the other one H^+ goes like this. e- are there, the e- come over here only right and it becomes what? It becomes now the hydrogen molecule.

Please look at the rate of forward reaction equal to rate of backward reaction. Can I say this? So, the rate of forward reaction is equal to the rate of backward reaction right. What is the forward reaction? The forward reaction here is what is H going as H^+ + e-; what is the backward reaction? $H^+ + e^-$ going as H. What is the unit for rate of reaction, any of you guys know?

What is the unit for rate of reaction? r equal to is given as rate of reaction is equal to what? is equal to moles and unit time. Now, we are going to do it in a area, do not we? Unit area, am I right? What do moles may given you before how many units of hydrogen is getting transformed to H^+. So, mole per unit time per unit area is what is going to be it is not unit very simply say you area here not unit area it is the area right mole time area gives you this.

Now, what is happening here? Please look at please you have to be with me now in this reaction $^{e-}$ are released; in this reaction e^- are accepted. So, what does it mean? It means what is the direction of current in normal electrical engineering? What is the direction of current? The direction of current flow right direction of current flow is equal to reverse of the flow of negative charges why negative charges it can be e^- it can be any ion, it can be anything right. So, it is the direction of flow current is the opposite of the direction of flow of negative charges.

Now, please look at this interface, we are talking about electrochemical reaction. Now look at the interface now. Now, current in this case current how does current flow? The current is flowing from the solution to the metal. Here the current is I am sorry in this case the current is flowing from the metal to the solution in this case the current is flowing from solution to the metal right. Am I right or not? Is it not ok? I am not seeing any response from you people.

So, it is electrochemical equilibrium, what is electrochemical equilibrium? There is a flow of current associated with the reaction rate. Now, now when hydrogen gas is converted to H^+, H^+ ion moves from the metal surface to the solution. It moves like that. So, it carries a current in this direction. When H^+ ions are getting reduced it carries a charge in the opposite direction; that means, the current is now flowing like this.

So, that means, the equivalent of that is going to be i like this, here i is going to be. Can I write like this ok? In the first case i is in this direction; in this case in this case i is in the this direction, current moves differently because the charges are different in these cases. Am I right or not? Understood? Now, let us put all of them together, what do you understand? You understand that at the interface there is no net oxidation then no net reduction, but the current is flowing back and forth; goes forward it goes backward net amount of flow is 0.

So, net amount of reaction is 0. So, no corrosion, no reduction, no oxidation taking place system is under equilibrium condition, am I right or not? So, system is now defined as under equilibrium condition. How do I calculate i? Can I calculate i here? Is it possible to calculate i? I can calculate i if I know the rate of reaction. How do I do that ok? i is equal what is the equation for i? i equal to what?

Student: 2.

Moles about per time per area multiplied by what? number of e^- into Faraday am I right?

i equal to the moles per unit area the number of e^- this am I right or not? So, this is i right. So, $r = i/nF$. Have I made clear to you or not? Too much too much of electrical engineering, too much of electrochemistry I suppose this would be easier, right? I have converted this rate of reaction into current using this equation now. So, i/nF is your these are all you might have studied in 10th or you know 11th and 12th and all I suppose ok.

So, what I am trying to say now the rate of reaction is related to the current here current here. Please notice in this case what happens? The rate of forward is equal to the rate of backward and so, the i is equal to i_0.

Student: Sir.

Yeah.

Student: (Refer Time: 72:37).

Oh, I am sorry. Yeah, I go back now in that case it is good. It is good, that you guys are telling that.

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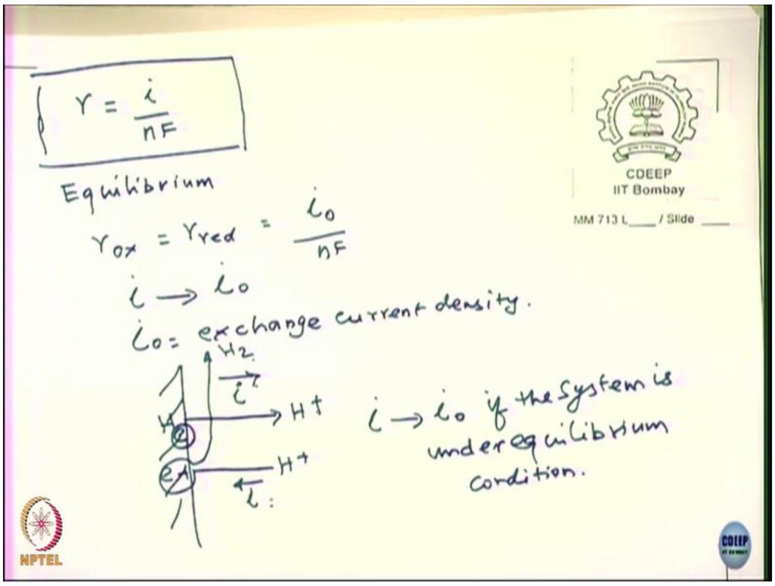

$$\boxed{r = \frac{i}{nF}}$$

Equilibrium

$$r_{ox} = r_{red} = \frac{i_0}{nF}$$

$i \rightarrow i_0$

i_0 = exchange current density.

$i \rightarrow i_0$ if the system is under equilibrium condition.

Yeah, now we have seen now the rate of reaction r = i / nF. Under equilibrium what happens? The rate of oxidation is equal to rate of reduction then what happens? Then and what happens now i_0 /nF that means, i tends to become i_0. What is i_0? i_0 is defined as exchange current density ok.

Suppose you guys now get a clear picture about what is an electrochemical interface. What is an electrochemical interface? I stop here now. What is an electrochemical interface? The electrochemical interface is where there is oxidation and reduction taking place right, am I right or not?

Student: Yes sir.

And, so, the current flows back and forth. If the rate of forward reaction equal to rate of backward reaction, then the system is under equilibrium conditions. At that condition the amount of current transfer is equal to exchange current density ok.

Let me just draw here ok. Let us take the case of hydrogen gas converted to H^+. Now, what is happening? Now, the e- are released on the surface right. Now, please look at hydrogen here is moving here as H^+, where do they what is the direction of current? This is the direction of current. It is going please current is a vector now please look at current is a vector.

Student: Yes sir.

Ok. Now, H^+ moves here and accepts one e^-, what happens? It goes out as a gas. What is the direction of current here? i is moving.

Student: Towards the i.

Towards the i. Now, this i and this i must be same or same? Should be different? It should be same if the system has to be under equilibrium and so, and this i is equal to i_0 ok. If the system is under equilibrium condition and this i_0 is related to rate of reaction through this equation this equation right i_0 upon n and F, look at this ok.

So, today I think we should stop here. The exchange current density is an equilibrium parameter, please understand. The exchange current density is an equilibrium parameter similar to what? Similar to the equilibrium potentials. Can I say that? The exchange current density is a parameter similar to equilibrium potentials. The only problem is it is not easy to compute i_0.

We will we will try to talk later, but this is a difficult subject it is not easy to compute n i_0 that is the real difficulty that we have ok, but it is enough for us to say that i_0 represents the equilibrium existing of the interface between the solid surface and the electrolyte divided into we are discussing ok.

So, with this I will stop here. We will continue in the in the next class and I hope that in a in one or two classes we should able get an answer how do we compute corrosion rate for a given metal because you know that corrosion is a non-equilibrium state, it is a spontaneous one right.

So, first you define what equilibrium state is, then you start deviating from the equilibrium then you are going to get into corrosion right. So, first definition is how do I define an equilibrium condition. If I define an equilibrium condition, then I think I will know how it deviates and that deviation is going to be now computed ok.

So, today we will stop here. Please do go through these notes actually and understand what you are discussing as you see that the complexities of electrochemistry will keep building up ok. And, it will be very easy provided you understand step by step this concepts ok. So, concepts is the key, without concepts it is very difficult for you to make any calculations or computations because corrosion is there are so many variety of forms of corrosion different environments, different metals so many of them ok.

You cannot give a table and then tell you know please make a computation. You must know the governing equation and then try to use the equation, so that the corrosion rate can be calculated for any system that you are interested actually right. So, that is the purpose of the this particular lecture ok. So, please go through that and you please solve the problem which I given you, so that that gives you a clear understanding of how we predict a metal will undergo corrosion or not ok. So, today we will stop it.