Corrosion – Part I
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Lecture – 16
Limitations of Standard Reduction Potential Series of Pure Metals

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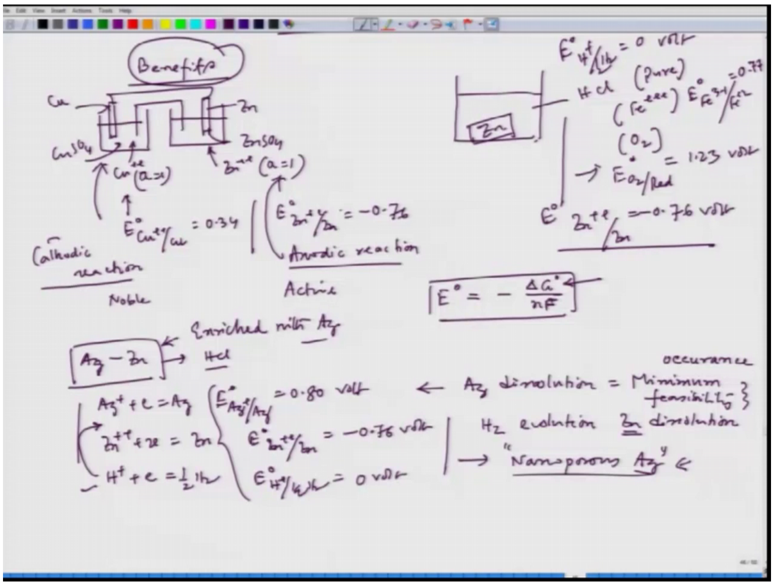

Well, let us begin lecture 16. In last lecture, we have seen two series. One is based on elements, and of course pure elements. The most of the cases in the first series we saw that metal ions are reducing and then going to a metal with the oxidation number 0. In the second series we saw that some of the reduction reactions are distributed. And one of the reduction reactions in hydrogen reduction as well as oxygen reduction, we saw that they are also positioned in that particular series. We had also reduction of metal ion to another metal ion, which is nothing but the reduction of the ferric ions to ferrous.

So, those reduction reactions are mentioned in the second series. And both the series are based on our theoretical situations, where we have activity we can find out that value from chemical potentials of those species involved in that reduction reaction. We have calculated for some metals as well as for four reactions that could possible that could be possible in water system. And those E 0 values for both the series are valid when the activities of ions as well as metal are maintained at 1.

Now, after that we started talking about the benefits as well as some of the issues with standard reduction potential series. So, benefit definitely we have benefit for example, when we have metal ions present, and we can definitely decide, which one is going to get deposited, which one is going to dissolve. For example, in case of this cell where we have copper and copper plus plus, copper sulphate solution and this is zinc and zinc sulphate solution.

In both the cases, now if we connect them, and then also we connect them with a salt bridge; since, this particular solution contains copper plus plus ion, and here also it contains copper plus plus sorry zinc plus plus ions. And if activity is 1 and here activity is 1, then definitely we can achieve standard reduction potential. And then if we join them, this reduction reaction E 0 for this equal to 0.34 and E 0 for zinc plus and zinc equal to minus 0.76. So, this here on this side, we have cathodic reaction; and this side we have anodic reaction ok. This side we have cathodic, and this side we have anodic reaction.

So, also we can see that this part this side is noble and this side is active. So, these two information definitely we can get. At the same time, it also gives an idea that let us say silver zinc alloy, silver zinc alloy if we put it in HCl, then we can get to know that even there are no ions of silver and zinc in the beginning in the HCl, but since A g plus plus e equal to A g this reaction we have E 0 equal to 0.80 volt. And zinc plus plus plus 2 e equal to zinc plus plus sorry zinc E 0 equal to zinc plus plus zinc equal to minus 0.76 volt.

And since it is acidic medium we have another reaction E 0 0 volt. From the standard reduction potentials we can make out that this one is lying in between. So, I can have this reaction and this reaction. So, we can have H 2 evolution and zinc dissolution. This information can also be obtained, but of course silver dissolution is impossible or rather I should not mention impossible, because the de alloying mechanism we have a different, but at least we can say that silver dissolution by looking at these 3 reduction potentials, minimum feasibility, minimum occurrence. So, once we see the zinc dissolution is taking place that is what this particular situation gives rise to nanoporous silver.

So, silver remains in the is not dissolving rather zinc dissolves, and that makes this particular alloy enriched with silver. And of course you will see hydrogen evolution reactions on the surface of that particular zinc silver alloy, that information also we can snatch out from this. So, here I have written minimum feasibility.

So, their reasons for this actually the modern mechanism for de alloying in silver zinc system, there are several proposals or several mechanisms some people say that zinc and silver both dissolve in the beginning and then silver deposits back, because of its higher reduction potential and zinc iron stays back so that option is also there. But finally after the formation of nanoporous silver we get to see there in the solution silver content is as minimum as possible. So, this information can also we make out. One thing of course we know what is active and what is noble so these are the benefits.

And on the second series what we have seen at least we can tell that what reactions are going to happen. For example, if we have our acid medium Hcl, and there if we have a silver plate a zinc plate sorry zinc plate and if we have pure, Fe contain Fe plus plus ion, and Fe content dissolved oxygen, the dissolution rate of zinc would increase, because the reduction potential is E0 for Fe plus 3 Fe 3 plus plus 2 equal to 0.77.

Here since it is an acidic medium, so E 0 oxygen red it becomes 1.23. If we have unit activities of oxygen this is E 0, and hydrogen ion 0 volt these are all in volt, but if we compare zinc plus plus zinc E 0 equal to 0. minus 0.76 volt. So, this is highly active, this zinc would behave active, and other all three reactions have got higher standard reduction potentials. So, we can make out that yes zinc would dissolve, and there could be possibility of all those 3 reactions, and that would actually increase the zinc dissolution rate or zinc corrosion.

So, this information we can also snatch out from this. Of course, the quantification is difficult we cannot say that how much zinc would dissolve by looking at this standard reduction potential. We cannot have for that we need to get into the kinetics part, but from thermodynamic concept, because E 0 is a thermodynamic quantity, why E 0 is a thermodynamic quantity, because E 0 equal to minus delta G 0 by n F. So, this, and this is a thermodynamic state function change, which is the Gibbs free energy change in the standard condition; n is the number of electrons associated with that reduction process. And F is the 1 faraday. So, this is at least from this we can tell that thermodynamically zinc dissolution would happen, and other reduction process would take place, but there are limitations.

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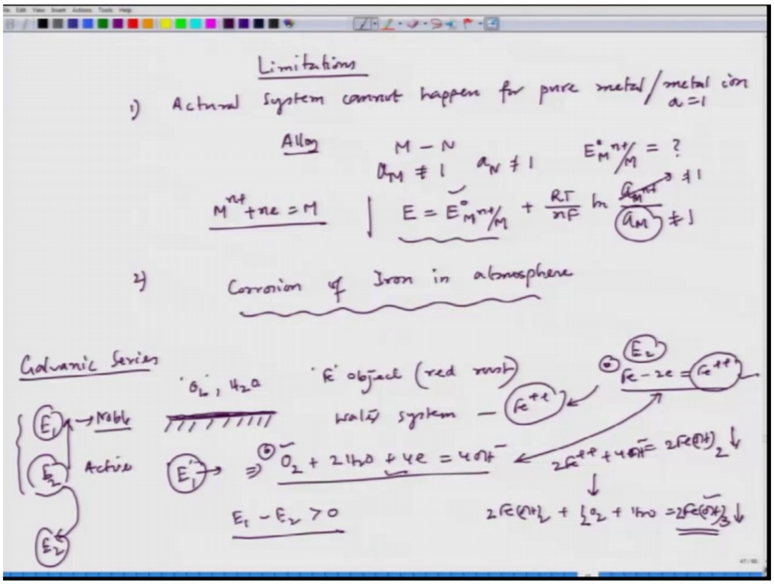

Limitations

1) Actual system cannot happen for pure metal/metal ion $a = 1$

Alloy $M - N$

$a_M \neq 1$ $a_N \neq 1$ $E^{\circ}_{M^{n+}/M} = ?$

$\underline{M^{n+} + ne = M}$ $E = E^{\circ}_{M^{n+}/M} + \frac{RT}{nF} \ln \frac{a_{M^{n+}}}{a_M}$ $\neq 1$ $\neq 1$

2) Corrosion of Iron in atmosphere

Galvanic Series

E_1 → Noble

E_2 Active

E_2'

'O_2, H_2O'

'Fe' object (red rust)

water system — Fe^{++}

$\ominus$ $Fe - 2e = Fe^{++}$ E_2

$E_1' \rightarrow \Rightarrow \oplus$ $O_2 + 2H_2O + 4e = 4OH^-$

$2Fe^{++} + 4OH^- = 2Fe(OH)_2 \downarrow$

$2Fe(OH)_2 + \frac{1}{2}O_2 + H_2O = 2Fe(OH)_3 \downarrow$

$E_1 - E_2 > 0$

So, the limitations one is of course actual system cannot happen for pure metal, and metal ion of activity 1. Actual system does not happen like that for example let us let us say if I considered alloy if I consider M and N, alloy these are two metals. So, M activity of M in the alloy would not be 1 And also activity of N will not be would not be 1 so that case if I try to find out E 0 M n plus M or I can put it as n plus M, we cannot find out, because if I try to see the Nernst equation provided, we have this reactions that time this is not equal to 1, since it is an alloy, and this also not equal to 1, so that case we cannot find out this so we cannot find out this, so that case this standard reduction potential would not exist.

Now, similarly in some situations we may not have in the beginning we may not have metal ion present. For example, a classic example is the corrosion of iron in atmosphere. So, we would have few case studies on this corrosion of iron in atmosphere. So, first case studies let us say we have an iron object. Now, we have a moisture. Let us say this is a moisture layer there is a small moisture. This is iron object. And we do see on the on the in our localities that iron object have red rust on top of a iron object, so that is the corrosion product.

Now, there in the beginning, and even if we take a pure iron. So, in the beginning in the water system we do not have iron ions. And later it of course it comes from iron by this reaction these reactions. So, the standard reduction potential we cannot calculate, because this activity of this in the beginning is not 1. Rather activity of this iron in the beginning where water does not contain any iron is 0 there is nothing.

Now, if we, but there are oxygen dissolved oxygen as well as water, and since if the earth atmospheric water is mildly acidic, so we can consider it to be neutral. So, the neutral medium we know that there is a possibility of this reduction process. See if we have this reduction then this oxidation reaction must happen in order to supply electron for this reduction reactions. And then we have combination of to form whole 3, and later it goes to it again gets oxidized. So, Fe OH whole 2 plus half O 2 plus H2O equal to Fe OH whole 3. If I try to balance it, so if I put 2 here 2 here so, then 6 oxygen ion, so this is 4, this is half, this is half hydrogen ion there are 6 also 2 and 4 yes this is balanced. So, we have this ferric hydroxide which is nothing but the red rust.

So, then we have formation of corrosion product and the corrosion of iron, but here also we do not see the possibility of attainment of standard reduction potential, because the iron ion activity will not reach 1, because as it is trying to reach 1. This product is forming, and this product is this product precipitates out. So, it would further reduce the concentration of iron ion. If there is a possibility of equilibrium, will be decided by the dissociation of this ferric hydroxide or ferrous hydroxide sorry this is 2 sorry I put 3.

So, ferrous hydroxide or ferric hydroxide this also has a very low solubility. So, the iron ion activity may not reach or will not reach 1. So, we cannot have standard reduction potential development or standard reduction potential. So, there we have to see as we have earlier discussed the potential difference between this and this. So, if the potential difference for example, here we can have a reduction potential developed.

And here also this is E 1 and here also we have a potential developed. So, if E 1 less than E 2 greater than 0, then we can say that iron corrosion would be a possibility. And then since it has got a higher potential, this particular reaction has got a higher potential, this is having higher potential than this. See if we distribute E 1 and E 2, so E 1 would be since it has higher potential, it will be lying on top of it. So, this would be noble then and this would be active.

And the cathodic reaction would be this and anodic reaction would be this. So, these series what we have discussed before is basically nothing but galvanic series. Here we do not mention potential. We just distribute a potential as per the difference in potential we distribute those reduction processes like the way we have distributed these two reactions. And then we try to see that whether one reduction one is on top of other.

So, if one is on top of other the one which is below will act as active and one which is above will act as noble. And now if this gap is very wide say let us say this E 1, E 2 position is here. So, this gap is huge so that means there is a possibility of higher degree of corrosion or higher degree of reduction and as well as oxidation reactions. So, here we only have a distribution of cathodic reactions. We do not have any potential value, but in case of reduction standard reduction potential series we do have a potential values mentioned there, but here we do not have to have potential values mentioned. So, we will talk about this finally but, one thing is there for example, E 1. So, when we try to find out E 1 definitely we have to get the help of Nernst equation.

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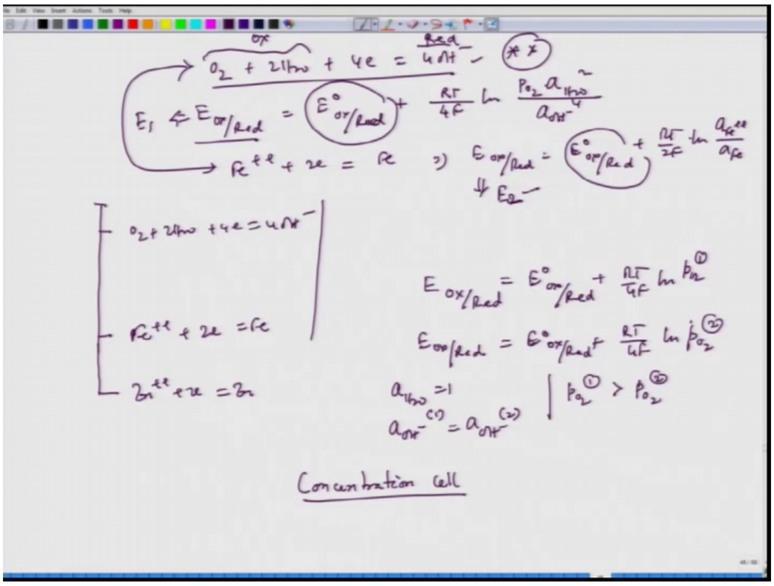

$\overbrace{O_2 + 2H_2O}^{ox} + 4e = \overset{Red}{4OH^-}$ (**)

$E_1 \Leftarrow E_{ox/Red} = E^\circ_{ox/Red} + \frac{RT}{4F} \ln \frac{P_{O_2} a_{H_2O}^2}{a_{OH^-}^4}$

$Fe^{++} + 2e = Fe \Rightarrow E_{ox/Red} = E^\circ_{ox/Red} + \frac{RT}{2F} \ln \frac{a_{Fe^{++}}}{a_{Fe}}$

$\Downarrow E_2$

$O_2 + 2H_2O + 4e = 4OH^-$

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

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

$E_{ox/Red} = E^\circ_{ox/Red} + \frac{RT}{4F} \ln p_{O_2}^{①}$

$E_{ox/Red} = E^\circ_{ox/Red} + \frac{RT}{4F} \ln p_{O_2}^{②}$

$a_{H_2O} = 1$

$a_{OH^-}^{(1)} = a_{OH^-}^{(2)}$

$p_{O_2}^{①} > p_{O_2}^{②}$

Concentration cell

And now if you see the Nernst equation for this reaction oxygen plus 2 H2O plus 4 e equal to 4 H minus, so there E 0. I am just writing E ox red equal to E 0 ox red minus 0.0591 p H or if I write plus RT 4 F L n, PO2 activity of H2O divided by activity of OH minus to the power 4. So, this is the potential we are trying to see there with reference to the standard reduction potential for this reaction. And again for iron here also we are writing E 0 ox red equal to E 0 ox red plus RT 2 F l n activity of Fe plus plus activity of F e. See here also we are making use of this standard reduction potential, but we are seeing the difference between this is nothing but E 2 and this is nothing but E 1.

So, we are seeing the difference between E 1 and E 2 that is what we are constructing galvanic series. So, this one would stay above and this one would stay below. So, if we have a couple between these two. So, this is the series, so here we mention O2 plus 2 H 2 O plus 4 e is equal to 4 h minus, and here we mention Fe plus plus 2 equal to Fe. So, this is the position of those two. Now, we can have a position of zinc also zinc here. So, there are also we could see that we can have a position. So, we are not mentioning the potential.

We will see a galvanic series in our next lecture. And there we will discuss it more on that, but before that if we see this particular reaction again, this particular reaction again O2 this particular reaction. Now, interestingly E ox, so this is basically ox part this is the red part. So, ox by red equal to E 0 I am not writing those individuals species plus RT by 4 F ln PO2. And if we try to see that the concentration of activity of H2O of course, since it is a pure water we can consider it to be one. And if we maintain this activity of OH minus a same in two situation where in one case PO2 is high, and another case PO2 plus E 0 ox red; so, now if I consider P O 2 1 greater than P O 2 2.

What could be the situation? Now, here the assumptions are activity of H2O is 1, and activity of O H minus in case 1 equal to activity of O H minus in case 2. See if we have this situation this then we have in an interesting situation, which is originated from a concept called concentration cell, and that concentration cell would be able to explain the corrosion of iron if there is one small droplet of water on top of it. So, we will discuss that part in our next lecture. And next lecture, we will also look at the galvanic series in little bit detailed manner.

So, today let us stop here. We will continue our discussion in the next lecture.

Thank you.