

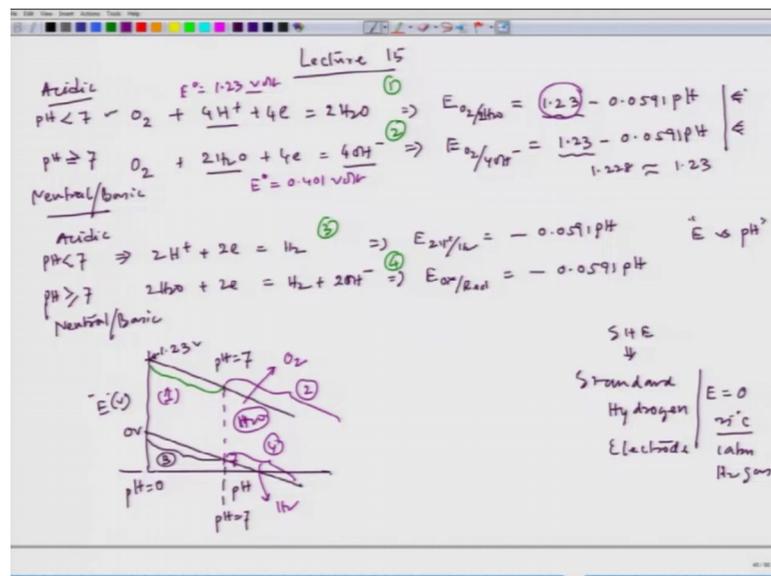
Corrosion – Part I
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Lecture - 15
Nernst Equation in terms of pH.

In lecture 13 and 14, we have discussed standard reduction potential series. And accordingly, we have noticed that hydrogen standard reduction potential is considered as 0 and the potential standard reduction potentials of metals which are greater than 0 are considered to be noble. And if the metals which are having standard reduction potential below 0 value, they are considered as active components.

Now, then we started looking at different reactions that are possible involving oxygen, hydrogen ion, OH ion and H₂O. And then we started looking at how to calculate standard reduction potential for those four major cathodic reactions. And in lecture 15, we will continue our discussion on that on those four reactions. And then we started looking at cathodic reactions, which are possible in water medium considering oxygen, water, as well as hydrogen ion.

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And then we saw that there are four reactions. And those four reactions, one set is oxygen plus 4 H plus 4 e equal to 2 H₂O; another one as O₂ plus 2 H₂O plus 4 e 4 OH minus. And interestingly the Nernst equation in terms of pH, it boils down to E = 0 O₂

H_2O , we can write straight away this value, it is coming close to 1.227, I can write it this one I can write 1.23 minus 0.0591 pH.

Similarly, this Nernst equation for this one also it boils down to 1.23 minus 0.0591 pH. So, I can I am writing 1.23, because the value what we obtained was 1.228, so I can write as 1.23. So, you see the equation, if we try to have a plot between potential and pH, they will fall on the same line. But, the occurrence of first reaction will happen, when we have pH less than 7 and occurrence of second reaction would happen, when pH greater than equal to 7. So that is this is this happen in neutral or basic medium and this happens in acidic medium, because this involves hydrogen ion and this involves water. And then finally, we get to OH minus, so it would increase the basicity of the solution.

Similarly, we had discussed on two more reactions, which is $2H^+ + 2e^- = H_2$ as well as $H_2O + 2e^- = H_2 + 2OH^-$. This is as we have mentioned that the Nernst equation $2H^+ + H_2 = 2e^-$ equal to minus 0.0591 pH. In terms of pH, so this also we saw that, it goes to so, I can write instead of this, I can write E_{ox} by red for this reaction equal to minus 0.0591 pH same equation.

And if we plot them on E versus pH plot, they will lie on the same line, but this will be valid for pH less than 7 and this would be valid when pH greater than equal to 7. So, here also it will be valid in neutral or basic medium or this will be valid in acidic medium.

Now, as we try to draw for pH and E and remember these potential we are measuring with reference to one standard hydrogen reduction standard hydrogen electrode S H E, we call it S H E, which is called Standard Hydrogen Electrode. So, there the potential value is 0 at 25 degree Celsius and 1 atmosphere pressure of hydrogen gas.

So, we will talk about the standard electrode little later. And we will discuss two important or three important standard electrodes; one is standard hydrogen electrode Ag AgCl electrode, and standard calomel electrode. There we will see that how those constructions happened, and what are the benefits for different levels of standard electrodes.

Now, if we try to plot them, so if this is let us say 1.23, when pH equal to 0. So, now if we see these two reaction, they are actually if this is the plot, then if this is the pH equal to 7, so first reaction will be up to this. This is the first reactions, if we consider this is to

be 1, this is to be 2, this is to be 3 and this is to be 4. So, this is the 1st one, because the pH is 7 and the 2nd one if I consider this, the 2nd one starts from this, and then it continues, so this is 7. So, this is 1st reaction, this is 2nd reaction.

Now, if I try to see the variation for these two reactions, so then again we can have another plot let us say this is 0 volt, this is in volt, 1.23 volt is this point. So, now again this will be parallel line to this. And again, this point is pH equal to this line is pH equal to 7. So, the 3rd equation will be valid here and 4th equation will be valid here.

So, this is the plot and in fact, in between we have H_2O , above that we have O_2 , and below that we have H_2 generation. So, we will talk about this again when we talk about stability lines of water, these are basically, two stability lines and in between water is stable.

Now, if I continue our discussion on this on the same line, now we see that even if it is not involving pure metal and also it involves water, hydrogen ion as well as oxygen, then also we get to see a standard reduction potential. This is basically the standard reduction potential values for these two reduction reactions. And sorry for this the standard reduction potential we found out I think if we remember, this value was 0.401 volt and here the standard reduction potential was 1.23 volt. So, we do have standard reduction potential for reactions involving several other constituents other than metal ions.

Now, here also we can constitute standard reduction potential series for other reduction reactions, where hydrogen of course, will be sitting at 0 point. And then above 0, it will be we can call it as strong reduction reactions and below hydrogen we have oxidation reactions, because if in comparison to hydrogen I would say.

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STANDARD REDUCTION POTENTIALS IN AQUEOUS SOLUTION AT 25°C		
Half-reaction		E° (V)
$F_2(g) + 2e^-$	$\rightarrow 2F^-$	2.87
$Co^{3+} + e^-$	$\rightarrow Co^{2+}$	1.82
$Au^{3+} + 3e^-$	$\rightarrow Au(s)$	1.50
$Cl_2(g) + 2e^-$	$\rightarrow 2Cl^-$	1.36
$O_2(g) + 4H^+ + 4e^-$	$\rightarrow 2H_2O(l)$	1.23
$Br_2(l) + 2e^-$	$\rightarrow 2Br^-$	1.07
$2Hg^{2+} + 2e^-$	$\rightarrow Hg_2^{2+}$	0.92
$Hg^{2+} + 2e^-$	$\rightarrow Hg(l)$	0.85
$Ag^+ + e^-$	$\rightarrow Ag(s)$	0.80
$Hg_2^{2+} + 2e^-$	$\rightarrow 2Hg(l)$	0.79
$Fe^{3+} + e^-$	$\rightarrow Fe^{2+}$	0.77
$I_2(s) + 2e^-$	$\rightarrow 2I^-$	0.53
$Cu^+ + e^-$	$\rightarrow Cu(s)$	0.52
$Cu^{2+} + 2e^-$	$\rightarrow Cu(s)$	0.34
$Cu^{2+} + e^-$	$\rightarrow Cu^+$	0.15
$Sn^{4+} + 2e^-$	$\rightarrow Sn^{2+}$	0.15
$S(s) + 2H^+ + 2e^-$	$\rightarrow H_2S(g)$	0.14
$2H^+ + 2e^-$	$\rightarrow H_2(g)$	0.00

Now, if I look the series some of the series for example, one series is let us look at this, this is standard reduction potential series for potential series for metals as well as pure elements. So, now you see gold, this is here, which is 1.50 is of highly positive standard reduction potential. And if I compare hydrogen, hydrogen is here so, if we have a combination between gold and hydrogen, I always get hydrogen evolution. And if there are any gold ions present in the solution, gold will in gold will immediately deposit back.

Similarly, if I compare gold and silver, so gold is standard reduction potential is 1.50, and it is 0.80, so that means, gold is highly noble as compared to silver. So, now if you have gold silver alloy, then if we dip it in acid medium, then gold will remain, silver would dissolve and then we can have a porous gold structure.

And those porosity could be in a nanometric range, so that is what we call it nonporous material. So, this is usual route of making nonporous gold, because once we have a combination of gold and silver, the active component would become silver, so silver would dissolve. And since, gold has got a very high standard reduction potential, so it would try to get reduced or it would try to try to stay back.

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$\text{Ag}^+ + e^-$	\rightarrow	$\text{Ag}(s)$	0.00
$\text{Hg}_2^{2+} + 2e^-$	\rightarrow	$2\text{Hg}(l)$	0.79
$\text{Fe}^{3+} + e^-$	\rightarrow	Fe^{2+}	0.77
$\text{I}_2(s) + 2e^-$	\rightarrow	2I^-	0.53
$\text{Cu}^+ + e^-$	\rightarrow	$\text{Cu}(s)$	0.52
$\text{Cu}^{2+} + 2e^-$	\rightarrow	$\text{Cu}(s)$	0.34
$\text{Cu}^{2+} + e^-$	\rightarrow	Cu^+	0.15
$\text{Sn}^{4+} + 2e^-$	\rightarrow	Sn^{2+}	0.15
$\text{S}(s) + 2\text{H}^+ + 2e^-$	\rightarrow	$\text{H}_2\text{S}(g)$	0.14
$2\text{H}^+ + 2e^-$	\rightarrow	$\text{H}_2(g)$	0.00
$\text{Pb}^{2+} + 2e^-$	\rightarrow	$\text{Pb}(s)$	-0.13
$\text{Sn}^{2+} + 2e^-$	\rightarrow	$\text{Sn}(s)$	-0.14
$\text{Ni}^{2+} + 2e^-$	\rightarrow	$\text{Ni}(s)$	-0.25
$\text{Co}^{2+} + 2e^-$	\rightarrow	$\text{Co}(s)$	-0.28
$\text{Cd}^{2+} + 2e^-$	\rightarrow	$\text{Cd}(s)$	-0.40
$\text{Cr}^{3+} + e^-$	\rightarrow	Cr^{2+}	-0.41
$\text{Fe}^{2+} + 2e^-$	\rightarrow	$\text{Fe}(s)$	-0.44
$\text{Cr}^{3+} + 3e^-$	\rightarrow	$\text{Cr}(s)$	-0.74
$\text{Zn}^{2+} + 2e^-$	\rightarrow	$\text{Zn}(s)$	-0.76
$2\text{H}_2\text{O}(l) + 2e^-$	\rightarrow	$\text{H}_2(g) + 2\text{OH}^-$	-0.83
$\text{Mn}^{2+} + 2e^-$	\rightarrow	$\text{Mn}(s)$	-1.18

Now, if I roll down and then go to whole screen again now, here I have placed hydrogen here now this is hydrogen part. Now, if I try to look at zinc, this is zinc. So, zinc reduction potential is negative, where hydrogen reduction potential is 0, so that is what when you have enough acid medium if you have zinc plate, so that is what you have immediate hydrogen evolution, because the hydrogen ion would get immediately reduced and zinc would dissolve quickly.

Similarly, if we see this and this, so there also we could see that iron would dissolve and hydrogen would hydrogen ion would get reduced, and then form hydrogen gas. There also the iron would dissolve quickly, because iron has got a lower reduction potential as compared to oxy[gen] hydrogen.

Now, if you compare iron and zinc, iron is minus 0.44 and zinc is minus 0.76. So, there also I could see that if we have a couple between iron and zinc, iron has got a higher reduction potential as compared to zinc. So, the possibility would be iron would deposit or stay back, and zinc would dissolve.

So, now you can see that if we choose any of those any of those particular series a series any of those pure elements and then if we club it with another element, where the reduction potential is below the earlier one, then the earlier one will act noble and the bottom one will act active in that particular couple. So that information definitely we can

get from this but, in remember this is for pure metal, we do not have we are not talking about alloys, this is completely 100 percent pure situation.

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Half-Reaction	E° (V)
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	+2.87
$O_2(g) + 2H^+(aq) + 2e^- \rightarrow O_2(g) + H_2O$	+2.07
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O$	+1.70
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O$	+0.96
$2Hg^{2+}(aq) + 2e^- \rightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \rightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- \rightarrow MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \rightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^+(aq) + e^- \rightarrow Cu(s)$	+0.15
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	-0.13
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	-0.14
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	-0.25
$Co^{2+}(aq) + 2e^- \rightarrow Co(s)$	-0.28
$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$	-0.31

Now, if I go back to other cases, like the way I have told you that there could be situation, where you can have reaction, which are not considered in pure elements rather there could be several species. Here also I can have a plot like this if I go to full screen, if you see this, hydrogen again it is staying here hydrogen.

Now, the reaction we what we considered in our in our case was this one. If you see this one, so this is oxygen reduction in neutral or basic medium, the standard reduction potential of was 0.401, so here it is written 0.40 and hydrogen is 00. So, if we have a combination between these two, then definitely this will be preferred as a reduction potential, the other one would be oxidation reactions.

Now, similarly if I try to see 1.23, this reaction sorry, this reaction, which is the oxygen reduction in water medium in acidic condition, it is highly positive as compared to the hydrogen. So, this will be a preferred reduction reaction, if we have acidic medium and dissolve oxygen.

Now, if we compare iron + e and this, so these two if we compare let us say in acidic solution, we have dissolve oxygen. And there we dip in sorry not this one not this one, if I see let us say I have I can put in here itself, it be noted down. If we see iron plus plus 2

e equal to iron, their reduction potential standard reduction potential is 0.44 volt so, it is lying below this below hydrogen. So, there if I have iron in acidic medium, then of course, this is one cathodic reaction and this is another cathodic reaction, both the cathodic reactions can be a possibility. So, iron would dissolve, and these are the cathodic reactions.

So, like that way we can go down. So, like for example, this reactions if I consider this reaction, these are not considering any metal ion metal deposition, rather here we are considering the reduction of ferric iron and it is going to Fe 2 plus. And we see that the reduction potential is 0.77 volt, which is of course, standard reduction potential, because here you see E^0 is mentioned. Now, this is a very strong reduction reaction.

So, now in as we have mentioned in case of zinc dissolution a zinc corrosion in acidic medium, we said that if we have a pure HCl, then reduction reaction is already single one which is hydrogen evolution. But, once we have little bit of ferric iron in it which is considered as impurity, then this reduction reaction can also take place, so which is a very strong reduction reaction. So, then the dissolution rate of zinc would increase.

Now, there was another example, where we consider three reduction reactions. For example, in the acidic medium, we dip zinc and then there we have ferric iron and as well as we have dissolve oxygen, then this reaction can also happen. So, you have three reduction reactions; this one, this one this one, as well as this one, so they would definitely increase the rate of dissolutions.

So, from this an interestingly, whenever we are talking about E^0 , even if the reactions contain only ions like the example what we have given here. Remember, the activities of those ions in that aqueous medium will be will be 1, so that is what that in that Nernst equation.

So, if I write that Nernst equation $E = E^0 + \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}}$. So, in this case, this one and this one will always be 1, when we talk about standard reduction potential. So, there also for example, if I consider this particular situation, the activity of this and activity of this will be 1, then only we can achieve this potential.

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$\text{MnO}_2(s) + 4\text{H}^+(aq) + 2e^- \rightarrow \text{Mn}^{2+}(aq) + 2\text{H}_2\text{O}$	+1.23
$\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightarrow 2\text{H}_2\text{O}$	+1.23
$\text{Br}_2(l) + 2e^- \rightarrow 2\text{Br}^-(aq)$	+1.07
$\text{NO}_3^-(aq) + 4\text{H}^+(aq) + 3e^- \rightarrow \text{NO}(g) + 2\text{H}_2\text{O}$	+0.96
$2\text{Hg}^{2+}(aq) + 2e^- \rightarrow \text{Hg}_2^{2+}(aq)$	+0.92
$\text{Hg}_2^{2+}(aq) + 2e^- \rightarrow 2\text{Hg}(l)$	+0.85
$\text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s)$	+0.80
$\text{Fe}^{3+}(aq) + e^- \rightarrow \text{Fe}^{2+}(aq)$	+0.77
$\text{O}_2(g) + 2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2\text{O}_2(aq)$	+0.68
$\text{MnO}_4^-(aq) + 2\text{H}_2\text{O} + 3e^- \rightarrow \text{MnO}_2(s) + 4\text{OH}^-(aq)$	+0.59
$\text{I}_2(s) + 2e^- \rightarrow 2\text{I}^-(aq)$	+0.53
$\text{O}_2(g) + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-(aq)$	+0.40
$\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s)$	+0.34
$\text{AgCl}(s) + e^- \rightarrow \text{Ag}(s) + \text{Cl}^-(aq)$	+0.22
$\text{SO}_4^{2-}(aq) + 4\text{H}^+(aq) + 2e^- \rightarrow \text{SO}_2(g) + 2\text{H}_2\text{O}$	+0.20
$\text{Cu}^{2+}(aq) + e^- \rightarrow \text{Cu}^+(aq)$	+0.15
$\text{Sn}^{4+}(aq) + 2e^- \rightarrow \text{Sn}^{2+}(aq)$	+0.13
$2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2(g)$	0.00
$\text{Pb}^{2+}(aq) + 2e^- \rightarrow \text{Pb}(s)$	-0.13
$\text{Sn}^{2+}(aq) + 2e^- \rightarrow \text{Sn}(s)$	-0.14
$\text{Ni}^{2+}(aq) + 2e^- \rightarrow \text{Ni}(s)$	-0.25
$\text{Co}^{2+}(aq) + 2e^- \rightarrow \text{Co}(s)$	-0.28
$\text{PbSO}_4(s) + 2e^- \rightarrow \text{Pb}(s) + \text{SO}_4^{2-}(aq)$	-0.31
$\text{Cd}^{2+}(aq) + 2e^- \rightarrow \text{Cd}(s)$	-0.40
$\text{Fe}^{2+}(aq) + 2e^- \rightarrow \text{Fe}(s)$	-0.44
$\text{Cr}^{3+}(aq) + 3e^- \rightarrow \text{Cr}(s)$	-0.74
$\text{Zn}^{2+}(aq) + 2e^- \rightarrow \text{Zn}(s)$	-0.76
$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$	-0.83
$\text{Mn}^{2+}(aq) + 2e^- \rightarrow \text{Mn}(s)$	-1.18
$\text{Al}^{3+}(aq) + 3e^- \rightarrow \text{Al}(s)$	-1.66
$\text{Be}^{2+}(aq) + 2e^- \rightarrow \text{Be}(s)$	-1.85
$\text{Mg}^{2+}(aq) + 2e^- \rightarrow \text{Mg}(s)$	-2.37
$\text{Na}^+(aq) + e^- \rightarrow \text{Na}(s)$	-2.71
$\text{Ca}^{2+}(aq) + 2e^- \rightarrow \text{Ca}(s)$	-2.87
$\text{Sr}^{2+}(aq) + 2e^- \rightarrow \text{Sr}(s)$	-2.89

So these are table for example, if I scroll down and then again go to the full screen. You see now here we have hydrogen here; this is hydrogen. Now, the other reactions if we consider this, so this was the reactions we considered for basic or neutral medium. So, this is pH greater than equal to 7, this happens pH less than 7. So, now this is a very strong reduction oxidation reactions, when we compare with this.

Similarly, we have this, which is minus 0.44 zinc, if I go to zinc, zinc is minus 0.76 even aluminium, it is minus 1.66. And magnesium if you see the magnesium is this so, why I have I am putting importance on aluminium and magnesium as well as zinc, if I say this zinc. So, now these elements zinc, magnesium and aluminium these are very active elements and magnesium of course, is a highly active element.

And you might have a you might come across that magnesium is a very popular sacrificial anode, even zinc and is also used as a very popular sacrificial anode. Aluminium is a problem, though it we can be used, if we maintain the active nature of it. But, the aluminium has got a problem, they has aluminium has got in has got in inherent tendency to get passivated, so it passivates. And when it passivates, so it forms aluminium oxide on the surface so, then it will no longer remain as active component.

So, aluminium has a problem so, we will discuss that thing later also. But, for the time being you see that if I compare the because most of the engineering applications to is still use iron. So, in order to stop this reaction, when we try to stop this reactions or minimise

these reactions, we have to have a counter anodic reactions, so which will supply electrons for this reactions. So, iron dissolution will be minimised, but of course, zinc dissolution would increase. As well as if we club iron and magnesium, magnesium dissolution would increase, so that is what magnesium and zinc they are used as a sacrificial anode for protecting iron object.

So, from this, now we get back to this importance of the series. As we have mentioned that the series are constructed on the basis of thermodynamic values as well as the inherent criteria is they have to be standard state. Those ions and species are to be in standard states, and activities should always be 1 and in case of metals, it is a pure metal condition.

And from this, we can definitely make out that which one would act as noble one and which one would act as active. So, active metal, noble metal can be just from this by looking at this series or active reaction or cathodic reaction can be just from these series. This is the series, where I can see which reaction is going to be cathodic reaction, which reaction is going to be anodic reactions that also we can make out.

But, interestingly this will not be able to tell few things. For example metals, in most of the practical applications, we have alloys, but this table will not be suitable for alloys, because there the activity of ions may not be 1 or activity of metal in the metallic part, since it is an alloy, the activity may not be 1 also. For example, let us say silver zinc, silver is 50, iron is zinc is 50, so that case zinc activity may not be 1 is not 1 in that alloy, so that case this particular series will not come into purpose.

Now, secondly we assume that in that solution we have those species in order to have cathodic or anodic reactions. But, most of the situations, you would see that if there is anodic reactions, then definitely those ions are forming. But, there may not be the cathodic that ions which are there ions of that particular metal available in the system, which we would try to get reduced, rather the reduction reaction would be something different.

So, those information also we cannot make out, so that is what this series is a theoretical series, more practical purpose series is galvanic series. We will continue our discussion on these two series in our next lecture so, let us stop here.

Thank you.