

Corrosion - Part I
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Lecture – 13
Standard Reduction Potential Series for Pure Metals

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Lecture - 13

$ox + ne = red$

$$E_{ox/red} = E^{\circ}_{ox/red} + \frac{RT}{nF} \ln \left[\frac{a_{ox}}{a_{red}} \right]$$

$a = \gamma C$
 ↓
 Activity coefficient = 1 dilute solution ideality is maintained

$E^{\circ}_{ox/red} = E^{\circ}_{ox/red}$ = Standard Reduction potential
 25°C, 1 atm, $a_{ox} = a_{red} = 1$

$4^+ + e = \frac{1}{2} H_2$ $2H^+ + 2e = H_2 \Rightarrow E^{\circ} = 0$
 ↓
 $n=1$ ↓
 $n=2$

$\Delta G^{\circ} = \frac{1}{2} \Delta G^{\circ} - \Delta G^{\circ}$
 $= 0$
 $\Delta G^{\circ} = 0 = -1 \times F \times E^{\circ}$
 $E^{\circ} = 0$

$$E_{H^+/H_2} = E^{\circ}_{H^+/H_2} + \frac{RT}{F} \ln \frac{a_{H^+}}{a_{H_2}^2}$$

$$= E^{\circ}_{2H^+/H_2} + \frac{RT}{2F} \ln \frac{a_{H^+}^2}{a_{H_2}}$$

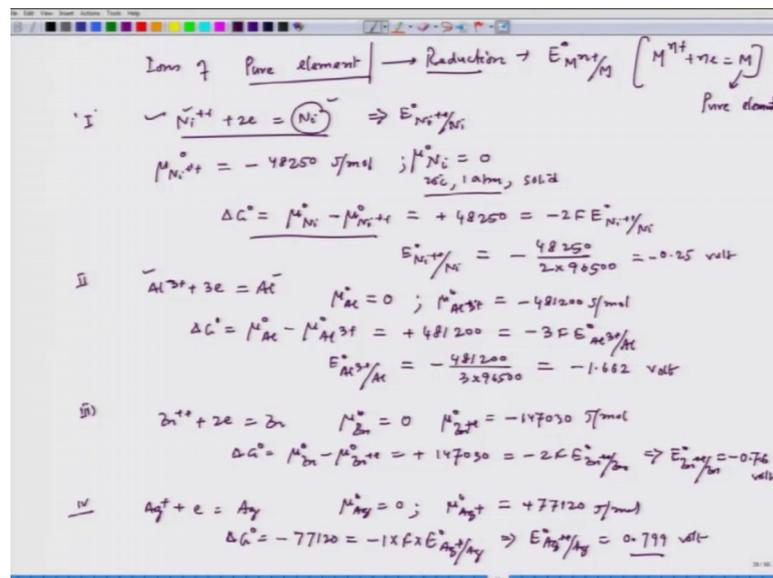
Hello everyone. Let us start lecture 13, in our previous lectures we have come across this triangle where $RT \ln K$ equal to $n F E^{\circ}$ ΔG° equal to minus $n F E^{\circ}$ and ΔG° equal to minus $RT \ln K$. At the same time have come across this Nernst equation where $E_{ox/red}$ equal to $E^{\circ}_{ox/red}$ plus $\frac{RT}{nF} \ln$, activity of ox, activity of red, for this reaction $ox + ne$ equal to red. So, this is the Nernst equation what we have for reduction.

At the same time this activity part can be written in terms of molar concentration ox, red when we considered dilute solution and also the ideally it. Means activity equal to activity coefficient this is the activity coefficient and this is the concentration in molar concentration. Now, this activity coefficient will be 1, when we considered very dilute solution where ideality is maintained, that time I can write this. Now, this particular is called standard reduction potential and when we achieve this standard reduction potential which is 25 degree Celsius 1 atmosphere pressure and activity of ox, activity of red equal to 1 that time we get this equal to red.

Now, once we have this particular knowledge then also we have looked at this hydrogen evolution as well as; and we saw that both these reactions both these reduction reactions are basically same reaction only thing is in the Nernst equation in case of n in this case n equal to 1, in this case n equal to 2. But finally, we would come across this would be equal to $E_H + \frac{1}{2} \ln \frac{p_{H_2}}{a_{H^+}}$ and $\frac{1}{2} \ln \frac{p_{H_2}}{a_{H^+}}$ would be equal to E and you would see that both the cases the equations would remain same.

Now, also we have try to find out the value of this and for example, for this reaction we get ΔG^0 is equal to $\mu^0_{H_2} - \frac{1}{2} \mu^0_{H^+}$ since we are considering half. And then from that this is considered this is the as per convention this is 0, this is also 0 in standard state then we would get 0. So, $\Delta G^0 = 0 = -nFE^0$ equal to 0 equal to minus n equal to 1 $F E^0$, so E^0 it becomes 0. Similarly you would get the same value E^0 equal to 0 this is what we have learnt from our previous lectures. Now, let us see whether this we can find out E^0 for other reduction process.

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And initially we would consider pure element and pure element ions of pure element; that means, in a particular solution we have the ions of that particular atom that particular element and that element is getting that ions are getting reduced.

So, now, for example, if I consider Ni plus plus plus 2 e equal to Ni this reduction process if you consider, we consider the reduction of ions of pure element and then try to

find out E^0 $M^{n+} + M$ so; that means, the reaction would be $n^{+} + ne^{-}$ equal to M . So, M is equal to M is nothing but pure element.

Now, if I consider this as we can also find out E^0 for this process. Now, μ_{Ni}^{+} plus plus 0 it has a value of minus 48250 Joule per mole whereas, μ^0 at standard state that was 25 degree Celsius, 1 atmosphere and solid as we have said that the in case of solid if it is pure and the stable state in this at this particular conditions where we consider; for example, oxygen. At this temperature one atmosphere it is gas, so it is a stable form that for the μ^0 of oxygen gas would be 0. Here also this is solid nickel which is the stable condition at 25 degree Celsius and 1 atmosphere pressure. So, then also it is assigned as 0.

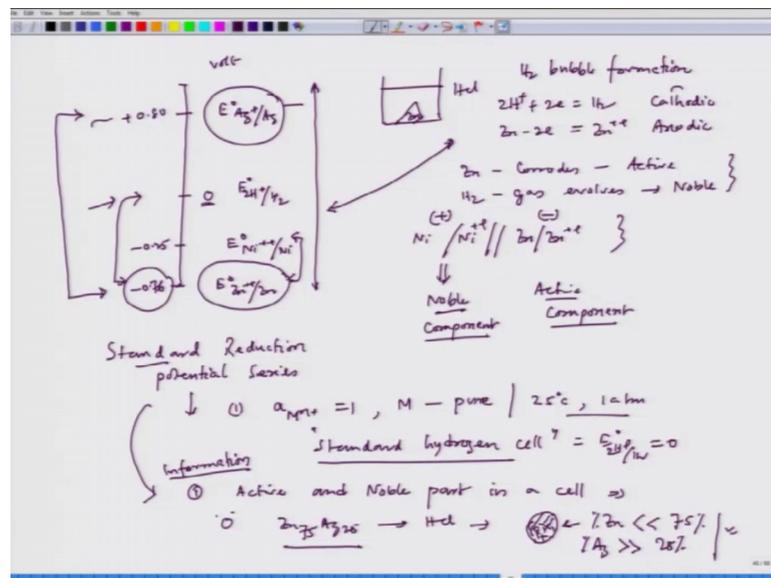
So, now, we can find out ΔG^0 equal to $\mu^0_{Ni} - \mu^0_{Ni^{+}}$ plus plus then it becomes plus 48250 which is nothing, but minus $2 F E^0_{Ni^{+} + Ni}$. Remember since we are considering reduction process that is what we are writing the reduction free energy change, the nickel from this reaction. So, once we have this then we can find out E^0 equal to plus plus $Ni^{+} = 48250$ by 2 into $96500 F$ which is the one faraday it is nothing but 96500 coulomb. So, you know how we get it is basically charge of Avogadro number of electrons. So, if you multiply Avogadro number into the charge of an electron you get this number. It is not going to be exactly this 96500 rather it will be 96488, something around that. So, it is rounded off and then we get 96500 coulomb. So, now, you will get this value to be around 0.25 minus Volt.

Similarly, this is reaction this is one example this let us say example 2. So, we can have example 2 as aluminium let us say aluminium 3 plus plus 3 electron equal to aluminium. Here also $\mu^0_{aluminium}$ in standard state is considered as 0 and $\mu^0_{al} + 3e^{-}$ plus equal to minus 481200 Joule per mole. So, I can again get the same thing $\mu^0_{Al} - \mu^0_{Al^{3+}}$ plus equal to plus 481200 equal to minus $3 F E^0_{aluminium}$.

So, every time I am writing ox by red; that means, this is oxidant this is reductant this is oxidant, this is reductant. So, now, from this we can also get $E^0_{Al^{3+} + aluminium}$ equal to 481200 by 3 into 96500 would be equal to minus 1.662 Volt. So, we can also get like that we can also get for zinc where $\mu^0_{zinc\ solid}$ equal to 0 in standard state and 0 zinc plus plus in solution aqua solution it becomes minus 147030 Joule per mole. So, again we get so this becomes like that we get it.

Now, let us see some other thing. For example, if we consider Ag which is silver plus E equal to Ag again mu 0 Ag solid in standard state equal to 0 and mu 0 Ag plus equal to minus 77120. So, then this is plus, this is plus Joule per mole, so then we get delta 0 is equal to minus 77120 equal to minus 1 into f E 0. So, I get volt; so here I am getting a very positive voltage. Now, we know that hydrogen is E 0 hydrogen is 0 Volt. Now, you see from this calculations that pure metals in case of pure metal the reduction of ions pure metal, we can have reduction potential these are the all standard reduction potential. Now, we can also place them with reference to hydrogen electron.

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Now, if we try to place all those values. Now, if I see that this is a particular line and. Now, hydrogen is here this is in Volt unit this is hydrogen, this is hydrogen. Now, if I try to place nickel in the same scale then it is minus 0.25 which is E 0 nickel plus plus nickel. If I try to place zinc which is minus 0.76 E 0 zinc plus plus zinc and then I can also put Ag which is plus 0.80 around that which is around this is E 0 Ag plus plus Ag. Like that we can calculate for all the other metals and we can distribute in this particular scale scale.

Now, interestingly if we have let us say as we have seen that zinc if you put a zinc plate in Hcl we see that hydrogen bubble hydrogen, bubble formation and that time our reduction is H 2 and oxidation reaction is plus plus. Now, let us see is there any correlation between this reactions, and the kind of scale what we are getting or kind of

distribution of reduction potential and the standard reduction potential in this particular plot, in this particular plot.

Now, see this 0 value is lying on top of this minus 0.76 Volt and here also you are saying that this is cathodic, and this is anodic, that means, if we have a connection between these two I could see that which one is behaving as a noble which one is behaving as a as an active element. Now, in this case zinc corrodes so; that means, it becomes active in HCl solution and hydrogen gas evolves. So, this is acting as a noble part in that particular two half cell reactions and the complete cell reactions.

Similarly, if we connect these two, we could see that nickel reduction will be nickel and reduction would be preferred and zinc would dissolve. So, again I could see that in this particular reaction nickel plus plus nickel zinc zinc plus plus. So, I would say this should be written like this. So, here this would be acting as positive this should be acting as negative, if we have you need activities of those ions of those nickel as well as zinc ions, so then this would be noble this would be active component of that particular cell.

So, now, from this particular and for example, Ag and zinc if I connect Ag and zinc you would also see the similar behaviour; that means, it would deposit because of the reduction process of Ag plus and zinc would dissolve because of this active nature of zinc because its reduction potential is way below the reduction potential of zinc plus Ag plus Ag. Now, like that we when we distribute all the standard reduction potentials we call it as standard reduction potential series and in this we in order to construct is the criteria is activity of metal ion should be one metal should be pure. So, and also since this is a standard reduction potential the temperature 25 degree Celsius and 1 atmosphere. So, this is the criteria to have this series.

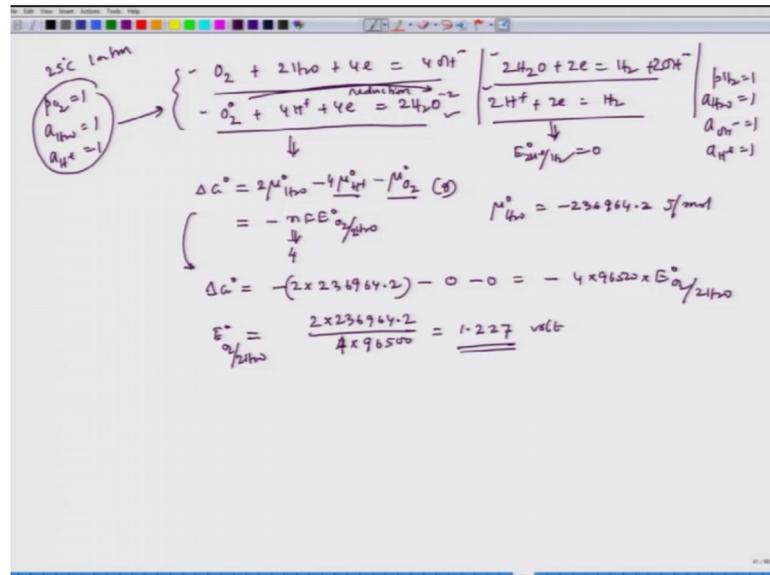
And in fact, we can calculate this potential this is 0 with reference to some with reference to hydrogen standard reduction hydrogen potential rather standard hydrogen cell we can measure this because here the potentially $E^0_{H^+ / H_2}$ is maintained as 0. So, we can calculate this potentials with reference to this. Also we can calculate once we know the thermodynamic data; that means, the chemical potential of ions as well because the chemical potential of the pure component is considered as 0 if it is a standard state; that means, it is in a standard and this is stable state at 25 degree Celsius and 1 atmosphere pressure. So, this is standard reduction potential series.

And this series what information it can give? One information is, one is active and noble part in a cell we can get to know; for example, the example what we have provided this even this even for silver and zinc. For your information if you start with a silver zinc alloy and then expose it to HCl solution then you would see that if you start for example, zinc 75, Ag 25 and if you put it in HCl, dilute HCl solution after sometime you will see that the cell this particle even if you say start with the particle small particle this particle would have several small small pores.

And those pores if we analyze this composition again you would see that zinc has gone down to 75 percent of that composition initial composition, the zinc concentration would be very low in that remaining porous particle and silver concentration would increase more than 25 percent. So, this happens because in this condition this particular standard reduction potential is pretty high as well as this one is pretty low and then if we compare these two reactions then this zinc plus zinc would corrode zinc would dissolved and silver would remain or silver would deposit back if at all there is silver in the system and then we have this kind of situations.

So, silver would act as a cathode and zinc would act as an anode ok. So, the zinc becomes your active component and silver becomes your noble component know. So, that information we can definitely get. Now, let us continue with our discussion. Now, we see that in case of pure metal ion reduction we can calculate the standard reduction potential.

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Now, we have been talking about one reaction which is $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- = 4\text{OH}^-$ or we have also mentioned about another reaction $4\text{H}^+ + 4\text{e}^- = 2\text{H}_2$. So, these two reactions can happen in aqueous medium when we have dissolved oxygen. Now, in addition to that depending on the pH we can have two more reactions in aqueous medium which are these two or we can have $\text{H}^+ + 2\text{e}^- = \text{H}_2$. So, these 4 reactions that are important in aqueous medium or the water medium and we have already talked about these 4 reactions before we just mentioned. Now, this is also a reduction process, this is reduction, this is reduction, this is reduction.

Now, we can also have standard reduction potential for those reduction processes and that case definitely in this case in these two situations we have to consider again 25 degree Celsius, 1 atmosphere pressure p_{O_2} should be 1, activity H_2O should be 1, activity H^+ should be 1, ok. And, here also similarly these free conditions rather in this condition should be prevailing here and here we have p_{H_2} should be 1, H_2 would be 1, activity OH^- should be 1, an activity H^+ should be 1. So, then we can get standard reduction potential for these reactions. We have already seen the standard reduction potential for this we have seen this.

Now, let us calculate one of those oxygen reduction and you will see this is 0 oxidation number and that goes to minus 2. So, it takes basically reduction. So, we have to see this particular situation. Now, in this case definitely we can also calculate ΔG° equal to 0

to $\mu^0_{2H_2O}$ plus minus μ^0_H plus minus $\mu^0_{O_2}$ and then we can equate to minus nFE^0_{oxygen} and I can put it like this. So, this is 2; now here n equal to 4 E equal to 96500.

Now, I can have the value of $\mu^0_{H_2O}$ equal to minus 236964.2 Joule per mole. So, then I get ΔG^0 equal to minus 2 into 236964.2. Now, you see this one is already 0 and this one is also 0 because this is a gas and this is the standard state. So, its value is 0. So, then this is equal to minus 4 into 96500 into E^0_{oxygen} $2H_2O$. So, then we get E^0_{oxygen} $2H_2O$ equal to 2 into 236964.2 divided by 4 into 96500. So, it becomes 2 into 2 (Refer Time: 28:08) so it becomes 1.227 volt. So, we can also calculate the standard reduction potential for this reaction. So, this is the value. So, like that we can calculate for other reactions.

So, let us stop here. So, we will continue our discussion in our next lecture.

Thank you.