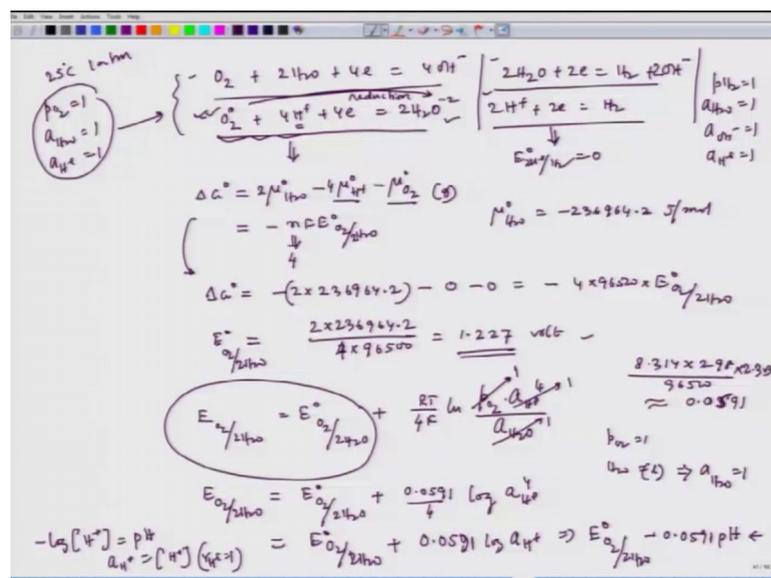


Corrosion – Part I
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Lecture -14
Calculation of Reduction Potential in Acidic and Neutral solution

Let us begin lecture 14. As we have seen in last lecture that we can have a series, which is also called standard reduction potential series for pure metals, where the condition is the ions of pure metals will reduce, and there will be no other elements. Now, at the same time, we have also noticed that some of the reduction processes like oxygen reduction or hydrogen reduction in case of water system aqua system.

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We can also have a concept of standard reduction potential like; what we have calculated in case of this reaction, which is oxygen reduction in acidic medium. Because, you see we have hydrogen ion and there is no OH minus sign that is what it is basically considered to be the reaction happening in acid medium or the PH, when the pH is less than 7 and we got this value.

Now, if we try to write standard this Nernst equation for this reaction, so we can have a Nernst equation plus $\frac{RT}{nF}$ since n is 4 here, so I can write $\frac{4}{n} \ln$ activity of ox. Now, here ox is the entire the top part, so this entire thing becomes my ox. So, this is O_2 or

activity of O_2 , I can write in terms of pressure and activity of H^+ plus 4 to the power 4 and activity of H_2O , which is the reduction reductant.

Now, if we maintain this is to be 1, and this is to be 1 as well as this is to be 1, then we get this standard reduction potential for this reaction. Now, if we keep maintaining P_{O_2} equal to 1 and H_2 if we considered to be pure, and it is in the liquid, so then still we can consider activity H_2 equal to 1, then this equation becomes $E^0_{O_2/H_2O}$ plus and if it is standard state that means, $R T$ by F , it becomes 0.0591.

We have already calculate, because a calculated this 314 into 298 divided 96500, it goes to 0.0591. So, by $4 \ln$, so that time into 2.303. So, we are considering the log conversion so, this becomes my log activity of H^+ plus 4 so, this becomes $E^0_{O_2/H_2O}$ plus 0.0591 into log of activity of H^+ .

Now, I can if it is ideal system, so I can write $E^0_{O_2/H_2O}$ minus 0.0591 pH. So, here log minus H^+ plus equal to pH and we have also considered the dial ideal solution. So, activity of H^+ plus equal to concentration of H^+ plus, where activity coefficient equal to 1, so that case we get this equation. So, similar so this equation will be very critical, when we try to find out the stability of a particular metal in aqueous system.

The stability in the sense that whether in for example, what a metal is dipped in water of certain pH whether that metal would dissolve or it would not at all dissolve or it would dissolve initially and then finally, it will passive it. All three conditions can be judged from a diagram, which is called pourbaix diagram that while drawing that pourbaix diagram, this equation would be very critical.

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$\mu_{OH^-}^0 = -157147.1 \text{ J/mol}$
 $\Delta G^0 = 4\mu_{OH^-}^0 - 2\mu_{H_2O}^0 - \mu_{O_2}^0 = 4 \times (-157147.1) - 2(-236964.2)$
 $= -628588.4 + 473928.4$
 $= -154660 = -nFE_{O_2/OH^-}^0$
 $E_{O_2/OH^-}^0 = \frac{154660}{4 \times 96500} = 0.401 \text{ volt}$
 $E_{O_2/OH^-} = E_{O_2/OH^-}^0 + \frac{RT}{4F} \ln \frac{a_{O_2} \cdot a_{H_2O}^2}{a_{OH^-}^4}$
 $\Rightarrow \frac{0.0591}{4} \cdot \log \frac{1}{[OH^-]^4} \Rightarrow \frac{0.0591}{4} \times 4 \log \frac{1}{[OH^-]}$
 $\Rightarrow -0.0591 \log [OH^-] \Rightarrow +0.0591 \text{ pH}$
 $E_{O_2/OH^-} = E_{O_2/OH^-}^0 + 0.0591 \text{ pH}$
 $\frac{-\text{pH}}{\log [H^+]} + \frac{-\text{pH}}{\log [OH^-]} = -14 \Rightarrow -\text{pH} + \text{pH} = -14$
 $\Rightarrow \text{pH} = 14 - \text{pH}$
 $H_2O \rightleftharpoons H^+ + OH^-$
 $K = 10^{-14}$
 $\Delta G^0 = -RT \ln K$
 $(H^+)(OH^-) = 10^{-14}$

Now, coming to so now if we try to see the other reaction, $O_2 + 2H_2O + 4e^- = 4OH^-$, this is another reduction reaction. Here also we can calculate $\Delta G^0 = \mu_{OH^-}^0 - \mu_{O_2}^0$. So, this is 0 as per our convention, because standard state oxygen chemical potential of pure oxygen is 0. So, this we can calculate $4 \mu_{OH^-}^0 = -157147.1 \text{ joule per mole}$.

And we know $\mu_{H_2O}^0 = -236964.2 \text{ joule per mole}$. So, then this becomes $-157147.1 - 2(-236964.2)$. So, this becomes if I try to find out those values, $2 \times 236964.2 = 473928.4$ minus $4 \times 157147.1 = 628588.4$, so this minus 628588.4 equal to minus 154660 . So, this is equal to nothing but $-nFE_{O_2/OH^-}^0$.

So, $E_{O_2/OH^-}^0 = 0.401$ here, so, $E_{O_2/OH^-} = 0.401$ equal to 154660 divided by 4×96500 equal to 0.401 volt. So, this is $4OH^-$ minus, because this is my reductant, this is my oxidant. So, we get this and also if we try to write the Nernst equation, so we can write $\frac{RT}{4F} \ln$ activity instead of activity in case of oxygen we can write P_{O_2} , then we can write activity of H_2O divided by activity of OH^- to the power 4.

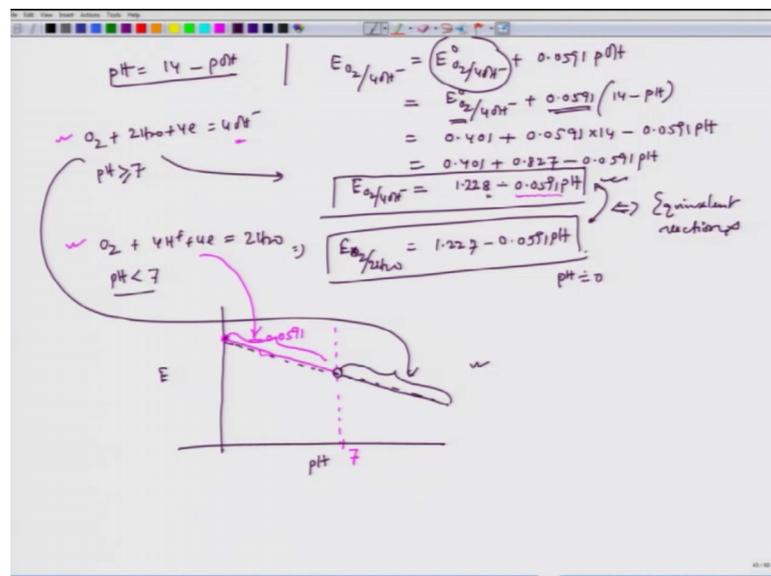
So, this we can simplify, if we simplify this part only, so this part becomes 0.0591 by 4 . So, this is 1, this is we keep it 1 and when this activity of OH^- is all 1, then this becomes this. This potential of the cell becomes half-cell becomes the potential-standard reduction potential. So, now if this is not equal to 1, then we can have and if it

is a dilute solution, because in the dilute solution ideality can be maintained, so then log 1 by 4. So, this we can write it as 0.0591 by 4 into 4 log 1 by OH minus. So, I can still write it like 0.0591 minus log of OH minus or I can write pOH.

Since, the definition of pOH equal to minus log of OH minus this is the definition. So, I can write this, so this equation becomes $E_{O_2/O_2^{2-}} = E_{O_2/O_2^{2-}} + 0.0591 \text{ pOH}$ minus plus 0.0591 pOH. Now, if I consider H_2O the water, I can write this the dissociation of water and in that case, we can write the dissociation constant is nothing but 10^{-14} . So that case I can write $\Delta G = -RT \ln K$ ok. So, I can write this, when the system reaches equilibrium and since K is 10^{-14} .

So, I can write activity in terms of concentration if I would like to write, $H^+ + OH^- = \text{divided by } H_2O = 10^{-14}$. Now, if I take logarithm of this, so $\log H^+ + \log OH^- = -14$, which I can write in the form of $\text{pH} + \text{pOH} = 14$. Since, this is nothing but $-\log H^+$, this is nothing but $-\log OH^-$. So, this pOH becomes $14 - \text{pH}$.

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So, we have this reacti[on]- equation so, I can start with this since $\text{pH} = 14 - \text{pOH}$. And also we know $O_2 + 4H^+ + 4e^- = 2H_2O$ would be equal to $E_{O_2/O_2^{2-}} + 0.0591 \text{ pOH}$ minus plus 0.0591 pOH. So, if I try to find out this we have calculated $0.401 + 0.0591 \times 14 - 0.0591 \text{ pH}$. So, if I try to find out this

value, so 0.0591 into 14 equal to 401 plus 0.827 minus 591 pH equal to 8212 minus. So, we get this which is if we try to compare the value, what we have obtained here in this case. So, this is the reaction number where acidic media, so which I can write it as 1.227 minus 0.0591 pH, so that means, I can see that this is for this reaction. .

And if I try to see, now you could see that these two reactions are almost similar with a little bit difference on the third digit after decimal, but this difference is not going to be there. If we take exact value of all the parameters for calculating this quantity or this quantity ok, so finally we can say that these are equivalent reactions, I can say equivalent reactions.

For example, let us say I would like to plot them on pH versus E^0 sorry, E potential is a reduction potential, now when pH is equal to 0, both the potentials are almost on the same point. This is this, and this is this so, thus both are one the same point. In the slope of the reaction is nothing but this is the slope minus 0.0591. So, and if this is my 7, so if I try to extend this 7 pH so, I know that this reaction happens, when pH is less than 7. So, then up to that we extend this, this is the slope is minus 0.0591 with the pH so, this reaction happen over this plot.

Now, in the basic medium, because it involves OH minus and also in the neutral case this reactions happens, so that time the plot would be and if you see this particular region. Where we can also see that this reaction, this particular plot for this reactions, it is also on the same line because, this would be lying on the same plot, and then it will be extending.

So, this reaction happens in this zone, but actually they are lying on the same line. Only difference is oxygen reduction in acidic medium happens, when pH is less than 7. And oxygen reduction in basic or neutral medium happens, when pH equal to 7 or greater than 7. So, these happens, when pH 7 and these happens pH, less than 7. So, this is only difference, but they are falling on the same plot.

Now, my interest is now you see that here also, we can find a reduction standard reduction potential. And in the previous case also, we could find the standard reduction potential here is this one. This is the standard reduction potential for the oxygen reduction in acidic medium. So, this particular diagram will you will come again for

discussion, when we start talking about probe diagram, but from this at least we are clear that both the reactions are falling on the same slope line.

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The image shows a handwritten derivation on a whiteboard. At the top, it states $\mu_{OH^-}^0 = -157147.1 \text{ J/mol}$. The main reaction is $2H_2O + 2e^- = H_2 + 2OH^-$. The standard Gibbs free energy change is calculated as $\Delta G^0 = \mu_{H_2}^0 + 2\mu_{OH^-}^0 - 2\mu_{H_2O}^0 = 0 + 2(-157147.1) + 2 \times 236964.2 = +159634.2 = -nFE_{2H_2O/H_2}^0$. This leads to $E_{2H_2O/H_2}^0 = -\frac{159634.2}{2 \times 96500} = -0.827 \text{ V}$. The Nernst equation is then used: $E_{2H_2O/H_2} = E_{2H_2O/H_2}^0 + \frac{RT}{2F} \ln \frac{a_{H_2}}{a_{OH^-}^2}$. For $a_{H_2} = 1$ and $a_{OH^-} = 10^{-pOH}$, it simplifies to $E_{2H_2O/H_2} = -0.827 - \frac{0.0591}{2} \log(10^{-2pOH}) = -0.827 + 0.0591 pOH$. A note indicates $pOH = 14 - pH$. The final boxed result is $E_{2H_2O/H_2} = -0.0591 pH$.

Now, if we have to see the another reaction, which is $2 H_2 O$ plus $2 e$ equal to H_2 plus $2 OH$ minus, this is also a reaction in aqueous medium. Here also, we can calculate E^0 that time this would be I can say that this is H_2 . So, this is the reduction process, because this is reduction I can calculate this. So, how do I calculate, again I have to find out ΔG^0 equal to $\mu^0 H_2$ plus $2 \mu^0 OH$ minus $\mu^0 2 H_2 O$.

So, I can put those values, this is 0 plus 2 minus 157147.1 plus 2 into 236964.2 . So, I can calculate this value, this becomes 236964.2 minus so this becomes minus plus 159634.2 , which is equal to minus $n F E^0 H_2$ n equal to here 4 , so this is the 2 electrons. So, E^0 equal to 159634.2 by 2 into 96500 equal to minus 0.827 volt.

Now, if I write it in terms of Nernst equation, now here this particular part we can simplify, so this becomes 0.0591 by 2 . So, this is 1 , this is 1 over atmosphere, if we maintain that and if this goes to OH minus square, so that means it is a dilute solution. And also ideality is maintained, then this goes to $\log OH$ minus O_2 , which is 0.0591 pOH with a minus sign with minus sign definitely yes, so, this is becomes this becomes 0.0591 by 2 into $\log OH$ minus ion, so this pOH .

And now again, I can have pOH equal to 14 minus pH so, then I can write ok, so here we see that we have committed a mistake, because here we have put ox here. Actually, ox should be here and this part should be here. So, in order to write it again, so I can cancel it I can cancel this part, and write $\frac{RT}{2F} \ln a_{H_2O} pH^2$. So, now this 1 this goes to 1 and this I can write it as OH minus square.

So, everything is all right, only thing is I have to put a minus sign here. So, then it becomes plus, because this was done with reference to this numerator and denominator would be exchanged, so this becomes minus. And finally, it becomes plus pOH. So, then I can write 14 minus pH, so $E = \frac{RT}{2F} \ln a_{H_2O} pH^2 + 0.0591$ into 14 minus 0.0591 pH, so this is minus 0.827. We have also calculated before this is 0.827 minus 0.0591 pH. So, this so finally this becomes minus 0.0591 pH, so need not this.

Now, you see this relation and for this what was the relation, so these are also similar. So, it means that this reaction and this reaction, they will also fall on the same line with the same slope. But, one equation would be valid for in case of the acidic medium, another equation would be valid for basic medium. This should be basic or neutral, this would be valid, when pH greater than equal to 7. And this would be valid, when pH less than equal to this then 7. So we stop here, we will continue our discussion on these equations, and then standard reduction potentials in our next lecture.

Thank you.