# Corrosion – Part I
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## Lecture - 18
## Examples of Concentration Cell and Spontaneity of Corrosion Process

Let us begin lecture 18.

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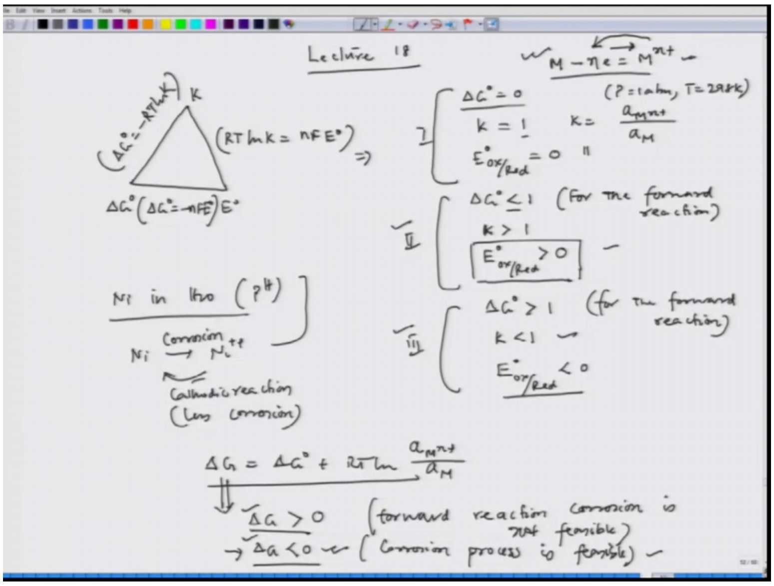

Lecture 18

$M - ne = M^{n+}$

$K$

$(\Delta G^\circ = -RT\ln K)$

$(RT\ln K = nFE^\circ)$ ⇒

$\Delta G^\circ (\Delta G^\circ = -nFE) E^\circ$

I $\Delta G^\circ = 0$, $K = 1$, $E^\circ_{ox/Red} = 0$ $(P = 1 atm, T = 298 K)$ $K = \frac{a_{M^{n+}}}{a_M}$

II $\Delta G^\circ \le 1$ (For the forward reaction), $K > 1$, $\boxed{E^\circ_{ox/Red} > 0}$

III $\Delta G^\circ > 1$ (for the forward reaction), $K < 1$, $E^\circ_{ox/Red} < 0$

Ni in $H_2O$ (pH)

$Ni \xrightarrow{Corrosion} Ni^{++}$

Cathodic reaction (Less corrosion)

$\Delta G = \Delta G^\circ + RT\ln\frac{a_{M^{n+}}}{a_M}$

⇓ $\Delta G > 0$ (forward reaction corrosion is not feasible)

→ $\Delta G < 0$ (Corrosion process is feasible)

We discussed concentration cell in brief and then we attacked a problem on corrosion under rain water droplet. And then we explained that at the centre position after sometime at the centre position becomes preferentially anode and the annular portion becomes preferentially cathode because we have more oxygen there.

So, there cathodic reaction should happen and they would act as cathode in the centre portion anodic reactions that iron would go into iron plus bus as well as iron plus 3. And those iron plus 3 as well as plus 2, they will combine with OH which minus that is the product for this product in the reduction reactions of oxygen in play in combination with water. So, they will form ferric hydroxide or ferrous hydroxide and they will deposit around that centre positions.

Now, you might have seen that in some cases if let us say some handle the a metallic handle is fixed on a wooden block on the door or some places in the window. And you might see that if you after sometime after some years; if you take that particular block particular the metal block out, the portion where screwing has been done. And if you watch the screw carefully or the nail carefully, you would see a nice observation if you are if you have observed before.

I have brought 2 samples let us see whether we can see something and then we can have a direct correlation on this concentration cell and that differential aeration cell that develops due to the difference in oxygen concentration. Now first example I am showing this one if you see this is a broken wood then it was nailed here; this was fixed on a particular, this particular broken wood was fixed on a another block with this nail this was a nail or rather it is a screw this is a screw if you see this cut you can see this cut.

So, let me put (Refer Time: 03:03) put a pen and then if you see this cut. So, this is the cut so; that means, it is a screw it is a screw and see the top part top part of the screw its corroded there are red rust is the signature of red rest. But once you see this the rest of the part which are going inside the wood; let us say this part if I see this part; this part if I carefully see let me put light on this; so, then you will it will be clear, if you see this let us see this you can see it carefully can you please zoom it little more, is it possible to zoom?

So, I am talking about this nail this nail this nail part, this is the nail I am talking about the rest of the screw part it is seriously corroded. But top part which is exposed to the atmosphere is corroded, but that not serious; this also can be explained from difference in oxygen content. Now, let us see another one; if we see this one this is more severe this is the metal object and there are screws here, there are 2 screws here and one screw here.

So, almost similar type of screw one screw is missing because when I pulled it up and then once screw got missing. But if you see this particular segment this screw top there are corrosions I am not saying that there are not no corrosion, there are corrosion, but interestingly if you see the other part, if you see this you see it is a kind of exfoliation this screw the rest of the screw has swelled. And this swelling has happened because of this iron hydroxide and iron hydroxide formation these are rust these are basically the red rust.

And if you see this one some part has vanished because the corrosion was so severe the some part has vanished because it got lost into the atmosphere not into that particular remain in that particular wooden part because it was fixed like this on the on a wood. So, this is a wood and this was fixed like this. So, now, why there is a little bit of corrosion on top, but the part which has entered into the wood there we see lot of corrosions. So why? So, this can also be explained by using this concentration cell.

Now, if I see this top part, if I see this top part the top part is exposed to the environment. Yes there are moisture there are oxygen, but the bottom part which has entered into the wood; though we assume that the wood also the wood is of pervious because there are fibres that fibres can have moisture or even the moisture can enter into the wood over the time.

And, but the oxygen content on top and the so; that means, we have electrolyte that the they are basically electrically connected. Because here also we have moisture here also we have moisture because the wood contains moisture all over the time the moisture can sweep in and this part of course, we have moisture. At the same time we have oxygen here, but the oxygen content in this zone will be very less. So, here we have a maximum oxygen, but as we go towards depth the oxygen content would reduce drastically.

So; that means, these zone the at the extreme part wood be anode, but the top part where we have more oxygen; so, cathodic reaction which is oxygen reduction in neutral media. So, that reaction would happen onto this entire surface, but the bottom part where we do not have oxygen that becomes my anode. And since iron dissolution, iron goes into iron ions they are strong anodic reactions those reactions would happen here. And then those iron ions that are forming they will combine with this OH minus that are forming and they form red rust or hydroxide or a hydrated oxides of iron.

So, this is again can be explained from the point of concentration difference of oxygen. So, this is a classic example you might also see at several location such kind of things happen. So, now this is what I wanted to say that concentration cell is a serious consequence even crevice or pitting corrosions. These two are very serious forms of corrosion as we have explained before because they are localised extremely localised and they are also related to the concentration difference of oxygen.

So, in the creviced part there would be oxygen depletion and the away from the creviced part; we have still oxygen. So, the creviced part becomes preferentially anode and the crevice section away from the crevice section, they will act as cathode. So, the creviced part would corrode; the cathodic part the rest of the part would corrode less. Similarly pitting also, in the pitting zone we have preferentially anode and preferentially anodic reactions or iron dissolution and then formation of iron oxide or iron hydroxide they would form and the rest of the part would remain as cathode because there we have more oxygen. So, these are the kind of examples what we find in our day to day corrosion phenomenon.

Now in lecture 18; we will look at that see this corrosions are taking place because of the ions formation. And then we have a concentration cell development and oxygen effect (Refer Time: 09:21) oxygen content, it can change in a short region and then we can have cathode and anode all those examples we have put. Now final we have to see that when a metal oxidizes or corrodes in a particular aqueous medium.

Now, when we talk about aqueous medium; in the beginning we concentrate on a presence of moisture or water. And when we talk about moisture or water we have to talk about pH level or p OH level. So, now, we will consider the presence of metal ions, metal, pH and water. So, when we have this kind of system which are commonly observed. So, there we have to see at what condition we have corrosion of that particular metal. Now when we talk about this what condition that initially we talk about the thermodynamics part; that means, initially we have to see whether the free energy change for that corrosion process is negative or not.

When the corrosion process free energy change is negative, we say that the corrosion is spontaneous. Otherwise if we see that the free energy change becomes positive then we may say that we have we will say that the corrosion process is not spontaneous rather it is difficult; rather thermodynamically we will say that it is not feasible. So, let us have some examples for before that we see this particular plot.

This particular plot is a serious plot and I want you to understand this plot and time to time this plot has come in this particular set of lectures. So, we see delta G 0; E 0 and K, K is the basically equilibrium constant. So, now, relation between these arms basically l n K equal to n F E 0 and here it will be delta G 0 equal to minus R T l n K and here delta G 0 equal to minus n F E 0; so, these are the relations between the arms.

Now, if we try to see let us say delta G 0 equal to 0; now for a particular equilibrium reaction let us say this is my equilibrium reaction, I am considering M n e equal to M n plus; so, this is the reaction what we talk about. Then if we consider the standard free energy change delta G 0; that means, P equal to 1 atmosphere T equal to 298 Kelvin; then K would be 1; so, K is nothing, but activity of M n plus by activity of M.

Now, when we have this one to be 0; then we see E 0 ox red equal to 0; now if delta G 0 less than 1 so; that means, there is a quite a lot of spontaneity in this particular reaction; that means, by that time we consider this reaction; that means, the forward reaction is taking place. So for a forward reaction; for the forward reaction; so that case K becomes greater than 0; that means, K becomes positive. So, more amount of product will form and that time E 0 ox red also greater than 0; sorry here we made a mistake because when it is 0 that time 1. So, it is more than 1 and when this is equal to this is less than 1; so, this becomes greater than 0.

Now, K greater than 1 and K equal to 1 means; so both forward and backward reactions they are equally possible, but when K greater than 1; it means that the preferentially forward reaction is taking place. And that is what when this becomes less than delta G 0 is less than 1; so, this condition holds true; so, there is a positive potential gradient; so current would flow.

Now, if delta G 0 greater than 1 then for forward reaction. So, that case K less than 1 and E 0 less than 0; so that means, the forward reaction would be less probable and the backward reaction; that means, this reaction becomes more probable if we have this situation and that time we have this so; that means, the potential would go towards negative. That means, the cathodic so, we so; that means, we have less amount of this reaction so; that means, metal ion would not be formed rather metal ion would get reduced.

So, when we say that metal ion would get reduced; it means that the corrosion process that mean ion formation process would not be a probability, rather deposition becomes my probability that case we might say that the corrosion is controlled or corrosion is minimised. But in this case corrosion is maximized and in this case its equilibrium. So, the corrosion as well as metal deposition they are happening at a same rate. So, these 3 situations this is situation I, this is situation II and this is situation III. In fact, situation II and III would guide us whether the corrosion would take place or not.

Now, when we talk about normal system; that means, let us say nickel in H 2 O of certain pH. So, nickel might get oxidized; that means, nickel can form nickel ion so; that means, it is a corrosion or it can go back and form nickel. So, that becomes my cathodic reaction or less corrosion and that time; since these are all the standard states; that means, E 0 as well as G 0, we are talking about standard state and in the actual system we may not maintain standard state.

So, the nickel concentration in water may not be 1 that activity of nickel ion may not be 1; so, that times we have to consider non standard situation. In the non standard situation, we have the similar kind of analysis. So, that time we have to consider this equation it is Q or the activity quotient. So, Q can be written in the form of activity of n plus activity of M; so, we are talking with reference to this reaction. So, there we are having a non standard free energy change and then we have to consider this value. We have to if we see this goes to is greater than 0; that means, the forward reaction or corrosion reaction is not feasible.

And if delta G less than 0; that means, corrosion process is and here we are considering with reference to the corrosion; so, that case this would be a feasible process. Now our interest would be to find out with the data set what we can generate from this to see whether this is greater than 0 or this is less than 0 at that particular condition. So, in order to know this we have to have a numerical problem and then we would be really clear that yes if we have this condition; that means, this is the pH level, this is the temperature, this is the pressure level; then we can decide that whether a particular metal would corrode in that particular solution.

And when we talk about corrode in that particular solution; that means, the corrosion process becomes spontaneous. And when we talk about spontaneity we have to consider free energy change and we have to say this condition is met.

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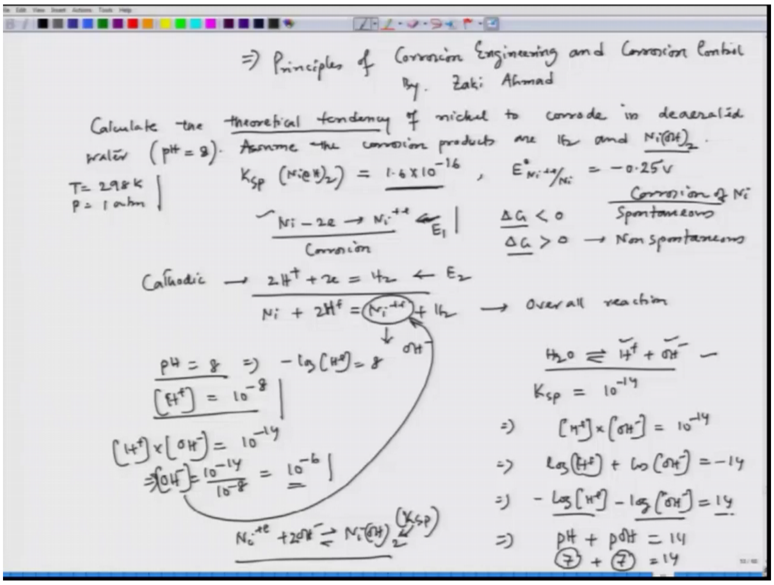

$\Rightarrow$ Principles of Corrosion Engineering and Corrosion Control
By. Zaki Ahmad

Calculate the theoretical tendency of nickel to corrode in deaerated water ($pH = 8$). Assume the corrosion products are $H_2$ and $Ni(OH)_2$.

$T = 298\,K$
$P = 1\,atm$

$K_{sp}\,(Ni(OH)_2) = 1.6 \times 10^{-16}$, $E^0_{Ni^{++}/Ni} = -0.25\,V$

$Ni - 2e \rightarrow Ni^{++} \leftarrow E_1$
Corrosion

$\Delta G < 0$ Corrosion of Ni Spontaneous
$\Delta G > 0 \rightarrow$ Non spontaneous

Cathodic $\rightarrow 2H^+ + 2e = H_2 \leftarrow E_2$

$Ni + 2H^+ = Ni^{++} + H_2 \rightarrow$ Overall reaction

$OH^-$

$pH = 8 \Rightarrow -\log[H^+] = 8$
$[H^+] = 10^{-8}$

$[H^+] \times [OH^-] = 10^{-14}$
$\Rightarrow [OH^-] = \frac{10^{-14}}{10^{-8}} = 10^{-6}$

$Ni^{++} + 2OH^- \rightleftharpoons Ni(OH)_2$ ($K_{sp}$)

$H_2O \rightleftharpoons H^+ + OH^-$
$K_{sp} = 10^{-14}$
$\Rightarrow [H^+] \times [OH^-] = 10^{-14}$
$\Rightarrow \log[H^+] + \log[OH^-] = -14$
$\Rightarrow -\log[H^+] - \log[OH^-] = 14$
$\Rightarrow pH + pOH = 14$
$\boxed{7} + \boxed{7} = 14$

Now, in order to do that we will take up a problem; that problem I am taking from a book which is a very good book Principles of Corrosion Engineering and Corrosion Control by Zaki Ahmad; you can read this book this is a fantastic book, I will just take one problem from that.

So, the problem statement says that calculate the theoretical tendency of nickel to corrode in deaerated solution, deaerated water where pH equal to 8. And I assume the corrosion potential; corrosion products are H 2 and Ni OH whole 2. Data given K SP for Ni OH whole 2 equal to 1.6 into 10 to the power minus 16, E 0 Ni plus Ni equal to minus 0.25 volt. Temperature of course, is 298 Kelvin, pressure equal to 1 atmosphere.

So, now it is saying theoretical tendency; so, theoretical tendency whenever we are talking about theoretical tendency; we first consider that nickel is corroding. So, nickel 2 e equal to nickel plus plus this reaction is taking place. And then we will see that if this reaction happens then we have to find delta G 0 for the entire system should be less than 0.

So, then we would say that the nickel corrosion is spontaneous; so this is corrosion. But if we find delta G 0 delta G greater than 0; then we will say that this is non spontaneous and this is spontaneous, we are talking about corrosion of nickel. Now, we are talking about; so when we say that entire system; so not for this particular reaction. So, we have to see the another reaction which takes place because this is my anodic reaction; so, we have to have a cathodic reaction.

So, cathodic reaction is this; so now, if I 2 this; so, if I add them. So, then it becomes Ni plus 2 H plus it goes to Ni plus plus H 2. So, this is my the total this is my overall system reaction; that means, there is a equivalent cathodic as well as anodic reactions; so this is my cathodic reaction.

But in addition to this we see that Ni OH 2 is forming and it has got a very low solubility product. So; that means, these Ni plus plus; this Ni plus plus will react with OH minus that is there in the water system already. Because water we can also dissociate H 2 O; it goes to H plus plus OH minus; so this reaction we can consider. So, when we consider this reaction then we have to also take care of K SP of this H 2 O. So, the K SP of a (Refer Time: 24:54) 10 to the power minus 14. So, this 10 to the power minus 14 we can write H plus into OH minus equal to 10 to the power minus 14.

So, if we take log; so log of H plus plus log of OH minus equal to minus 14. So, if we take minus log of H plus and minus of log of OH minus equal to 14; since we have one more, one H plus and one OH minus. So, we can assume that the number of H plus and number of OH minus should be equal. So, then this and this they would have equal contribution to this 14. So, I can say that and this is nothing, but pH plus this is nothing, but p OH equal to 14.

Now, if we have 7 and 7; then it becomes 14 and we have if we have a neutral solution that time the pH is 7. So, that is what we have p OH is also 7; now here we have pH; pH equal to 8. So; that means, H plus concentration is nothing, but 10 to the power minus 8; since minus log of H plus equal to 8 and that is what the concentration of H plus I can find out.

So, now if I find out H plus then I can find out OH minus into H plus equal to 10 to the power minus 14. So, I know what is the concentration of H plus ion; so, I can find 10 to the power minus 14 equal to 10 to the power minus 8 in to 10 to the power minus 6; so, I know the concentration of OH minus. Now, once we find out OH minus now these OH is available to react with; this OH is available to react with Ni plus plus and when they react; they form whole 2.

So, now it will also have its own equilibrium; now there the amount of nickel plus plus that is available in the system would be decided by the K SP of Ni OH whole 2. Because once Ni OH whole 2 forms, the limited solubility of Ni OH whole 2 would allow little bit of nickel plus plus ion to be present in the solution and once we know the concentration of nickel plus plus in the solution; then we can find out what is the potential that would generate for this particular reaction, for this particular reaction in that particular solution and also we know pH.

So, we also can find out E 1 and E 2 and then we can have a difference between these 2 potentials and that would lead to finding out these 2 situations. So, we will discuss this same problem in our next lecture; for the time being we know that we have to go through this route to find out the nickel concentration, nickel ion concentration in the solution. Let us stop here; we will continue this lecture in our next class.

Thank you.