Corrosion - Part I
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Lecture - 23
Construction of Pourbaix diagram for Ni – H 2 O system – III

Welcome back to the course corrosion, today we are going to have our lecture number 23.

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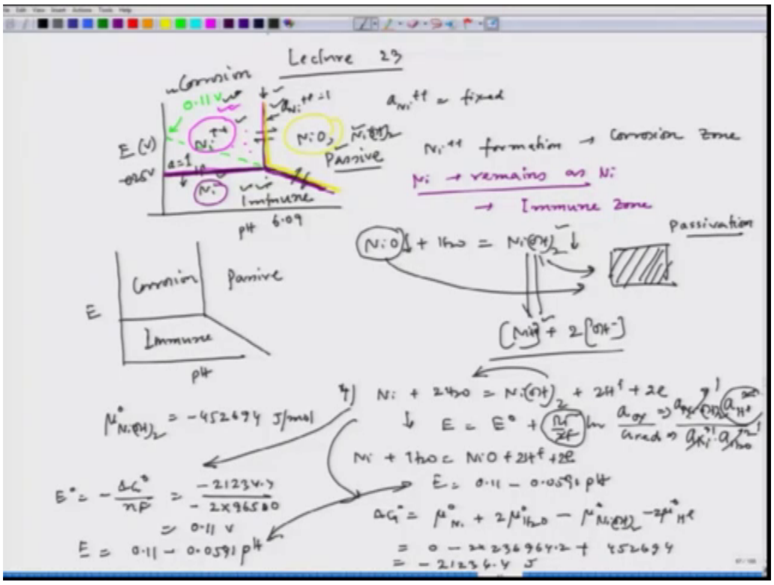

So, in last lecture we started discussing, we discussing on nickel H 2 O system and then we could draw a pourbaix diagram involving nickel; nickel plus plus and an Ni O and the diagram look like. So, this is pH axis this is E in volt unit this is un verse nickel this was nickel plus plus and this region was this was Ni O where if we extend this line; this line if we extend.

The point would be 0.11 volt and this was minus 25 0 point volt and this pH was 6.09 and we could also see why different regions how can we make sure that this region belongs to nickel, this region belongs to Ni O and this region belongs to Ni plus plus. And this also talks about the stability of those phases in those regions in that E verses PH diagram, moreover each line indicates the equilibrium between N i plus plus. For example, this line indicates Ni plus plus and Ni, this line indicates Ni and Ni O and this line indicates Ni plus plus and Ni O; moreover we could also see that some lines are potential independent.

For example, this line belongs to potential independent then we have one line which is parallel to the PH axis that means, it becomes potential a pH independent, but potential dependent. As we have seen that this was drawn as a when nickel ion concentration was 1 this is also belong to Ni plus plus activity equal to 1 then only we could get 0.25 volt and we would see that if we change the activity of nickel plus plus from 1 to 10 to the power minus 1 10 to the power minus 2 like that.

So, these line would go down an interestingly another important aspect is when we draw these lines according to the reactions what we have stated earlier, we have to fix a nickel ion concentration. Now, if we fix this activity to be 1 then for this line we have to also see the activity of nickel ion concentration should be 1. Now if we change it to 10 to the power minus 6 then this line also needs to be change to 10 to the power minus 6. So, it will be valid for a particular nickel ion concentration, so this has to be fixed first and then we need to draw all free lines.

Now, here if we could see that if we put it in a red colour, let us say let me choose a colour let us say this red colour, if we choose that colour. So, this region I could see nickel plus plus we could or we can get nickel plus plus if we remain any potential and voltage potential and pH coordinate in this particular section; this particular section covered by this particular boundary.

We would at any coordinates for example, any coordinate Ni plus plus and Ni plus plus formation this nothing, but corrosion. That means ions, if we get ions of that particular metal then it is actually dissolving in the solution water base solution because its containing H 2 O and that means, corrosion. Now if we consider a boundary let us say if we have this boundary there we get nickel and as per our convention in this region we have least presence of Ni plus plus that means, nickel remains as nickel.

So, we call this particular zone as immune zone and now the earlier zone we used to call it corrosion zone. Now there is one more zone which is covered by this zone where we have a Ni O and interestingly we had a problem where we tried to see what is the, what is basically the tendency of nickel to get corroded in the water system, there we considered Ni O h, but here it is Ni O. Now interestingly Ni O if we take Ni O and H 2 O Ni O plus H 2 O equal to Ni O H whole 2.

This also settles down, this also settles down because they have very low solubility product. Now when it settles down that time if that if it settles down on the nickel substrate then we have a covering of the nickel surface for the time being let us put in this fashion that if you have a nickel substrate on that substrate you we have this particular phase formation or this particular phase formation we get a covering of that particular nickel surface. And then the nickel surface exposed to the water system, water or electrolyte will be limited. So, the corrosion tendency of nickel will be sluggish.

Though nickel corrosion is taking place depending on the solubility of nickel plus plus ion and 2 O H minus sign. So, depending on that the solubility will decide how much nickel plus plus ion exist in the solution, but that solubility would be so low so the nickel ion presence should be so low. So, that time we call it as passivation, so we call it passivation. So, this zone we call it passive zone. So, this is immune and this zone is corrosion, so we have three zones specified according to the calculations what we have, in this zone we have immune.

That means, nickel remains as nickel no corrosion would take place in this zone we have that means, we could say from this diagram that the corrosion of nickel would be a spontaneous process that means, more and more nickel ion would form. And here Ni O or Ni O H when it forms that time they try to make a deposit on the nickel substrate and the solubility of that particular deposit we will decide the nickel ion dissolution rate, nickel dissolution rate and that dissolution rate would be much lower than the dissolution rate what we can experience in this particular zone.

So, we call it a passive zone, so we decide three zones immune corrosion and passive. In fact, we can have such diagrams for many other metals when coming to this particular phase since we have done the calculation on the basis of chemical potential of Ni O we can have also the same plot if we consider Ni O H. So, that time you have to take two more equations that time we will not consider Ni O formation Ni plus 2 H 2 O equal to Ni O H whole 2 plus 2 H plus plus 2 E 1 reaction.

And if we do the calculation we would see that the calculation would generate the same line what we see here, the same line it will generate the same line if we fix the concentration of nickel ion, now here the nickel ion is not coming into picture. So, only thing is it will be decided by potential which will be E 0 plus RT 2 f l n ox by red. So, this is activity of ox activity or red and here ox is nothing, but Ni O H whole 2 activity and activity of H plus square and this one would be equal to activity of Ni activity of H 2 O square.

And if you do the same calculations because if you take the chemical potential value of Ni O H whole 2 which is nothing, but minus 452694 joule per mole you will generate the same equation what we had for this reaction. So, they here we had if we go back you will see that this value would be 0.11 minus 0.0591 pH here also you will get the same value let us do that calculation. So, that time delta G 0 would be mu 0 because we have to consider this way.

Because we have to write ox plus E equal to red mu 0 Ni plus 2 mu 0 H 2 O minus mu 0 Ni O H whole 2 minus mu 0 H plus and 2 electrons are involved. So, this is 0 this is minus 2 into 236 964.2 this is this will become plus 452694 this going to be; this is going to be minus. So, E 0 would be equal to so here this is minus 212234.4 N is equal 2 and F equal to 96400 and with a minus sign so this becomes 0.111 forth.

So, you for this reaction you get E 0 like this and E would become 0.11 minus if you do the simplification these goes to 1, these goes to 1 these goes to 1 so you are left with this quantity, so these 2 2 will get cancelled. So, finally, you would get the same pH same equation. So, these 2 are getting the same equation so that means, this line would be similar to Ni O H whole 2, if we form Ni O H whole 2 instead of Ni O and if we you want to do calculation for the vertical line.

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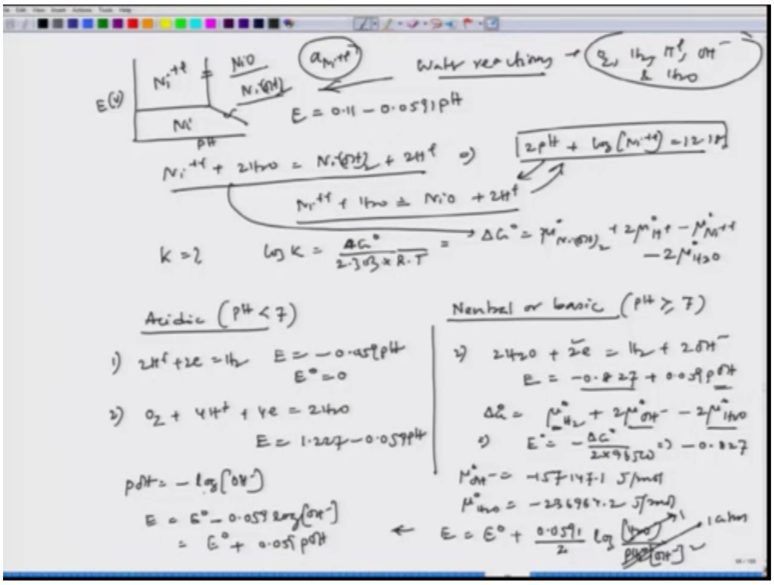

$\boxed{a_{Ni^{++}}}$

Water reaching → O_2, H_2, H^+, OH^- & H_2O

$E = 0.11 - 0.0591\,pH$

$Ni^{++} + 2H_2O = Ni(OH)_2 + 2H^+ \Rightarrow \boxed{2pH + \log[Ni^{++}] = 12.18}$

$Ni^{++} + H_2O = NiO + 2H^+$

$K = ?$ $\quad \log K = \frac{\Delta G^\circ}{2.303 \times R \cdot T}$ $\quad \Delta G^\circ = \mu^\circ_{Ni(OH)_2} + 2\mu^\circ_{H^+} - \mu^\circ_{Ni^{++}} - 2\mu^\circ_{H_2O}$

Acidic $(pH < 7)$

1) $2H^+ + 2e = H_2$ $\quad E = -0.059\,pH$, $E^\circ = 0$

2) $O_2 + 4H^+ + 4e = 2H_2O$ $\quad E = 1.227 - 0.059\,pH$

$pOH = -\log[OH^-]$

$E = E^\circ - 0.059\log[OH^-]$

$= E^\circ + 0.059\,pOH$ ←

Neutral or basic $(pH \geq 7)$

1) $2H_2O + 2e^- = H_2 + 2OH^-$

$E = \underline{-0.827} + 0.059\,p\underline{OH}$

$\Delta G = \mu^\circ_{H_2} + 2\mu^\circ_{OH^-} - 2\mu^\circ_{H_2O}$

$\Rightarrow E^\circ = -\frac{\Delta G^\circ}{2 \times 96500} \Rightarrow -0.827$

$\mu^\circ_{OH^-} = -157147.1$ J/mol

$\mu^\circ_{H_2O} = -236967.2$ J/mol

$E = E^\circ + \frac{0.0591}{2}\log\frac{\cancel{[H_2O]}}{\cancel{P_{H_2}}[OH^-]^2}$ 1 atm

So, if you draw the, if you try to see the vertical line also this is Ni O H whole 2 and Ni this line gives the E equal to 0.11 minus 0.0591 pH and this line would be same as for this reaction. So, if you try to d try to see the vertical line.

So, the new reaction would be Ni plus plus plus 2 H 2 O equal to Ni O H whole 2 plus 2 H plus it will give you the same equations. Let us get back to the equation you will get the same equation like this minus 2 pH 2 pH plus log a Ni plus plus, you will get the same equation what we gotten for this reaction for this reaction we got the same equation.

I want you to try it out from the K so you have to find out k k value. So, the log k equal to 0 delta G 0 by 2.303 into R into T. So, if you follow that and you have to find out delta G 0 for this reaction. So, delta d 0 you find out from mu 0 Ni O H whole 2 plus 2 mu 0 H plus minus mu 0 Ni plus plus minus 2 mu 0 H 2 O you would get the same equation.

So that means, whether you write Ni O or Ni O H these lines would be same because provided you are fixing the Ni plus plus and concentration you have to fix that. So, that is what you are getting main cruxes, you are trying to plot the corrosion zone, immunity zone and passive zone, but this pourbiax diagram is not complete if you do not put the equations or the reactions which involve no metals rather than oxygen, dissolve oxygen, hydrogen evolution, hydrogen H 2 H plus and O H minus of course, there will be water.

So, I mean to say that this particular phase this diagram this E verses PH diagram this should be complete once we include water reaction involving O 2, H 2, H plus O H minus and H 2 O so let us do that. In fact, we have seen before if you see the earlier lectures we have done it, now we will just mention those equations and then accordingly we try to plot them.

Now, if we write down those equations first is acidic and then neutral or basic, so this is pH less than 7 and here pH greater than equal to 7. So, there are two types of reactions one is an in that two types we have two reactions each one is H plus plus 2 e equal to H 2 where the real equation would be minus 0.059 p H where E 0 equal to 0, 2 O 2 plus 4 H plus plus 4 e equal to 2 H 2 O and here you see that only H plus ions are involved. So, there E equal to 1.227 minus 0.059 p H and on the other side we have 2 H 2 O plus 2 e equal to H 2 plus 2 O H minus and for this E equal to minus 0.827 minus plus 0.059 p O H.

Why this term is coming for this reaction if you do the calculation delta G 0 would be mu 0 H 2 plus 2 mu 0 O H minus minus 2 mu 0 H 2 O and then here to electrons are involved. So, E 0 would be delta G 0 minus 2 into 96500, if you do that calculation because already you know the values of this you just go back earlier lectures and then find out what is the values. So, let me iterate the same value once again.

So, mu 0 O H minus equal to minus 157147.1 joule and mu 0 H 2 O equal to minus 236964.2 joule per mole and of course, this quantity is 0 and you get minus 0.827. Now interestingly here it is p O H because E equal to E 0 plus 0.0591 by 2 and then activity of that log H 2 O, if we put it in concentration term p H 2 O and O H minus whole 2.

So, this is maintain at one atmosphere the pressure of hydrogen gas is one atmosphere this is one a pure substance. And so it becomes E equal to E 0 plus 059 minus log of O H minus is nothing, but E 0 plus 059 p O H. Where p O H equal to minus log of O H minus ion, then if you do the simplification then you would get E equal to E 0 minus 0.0591 14 minus p H.

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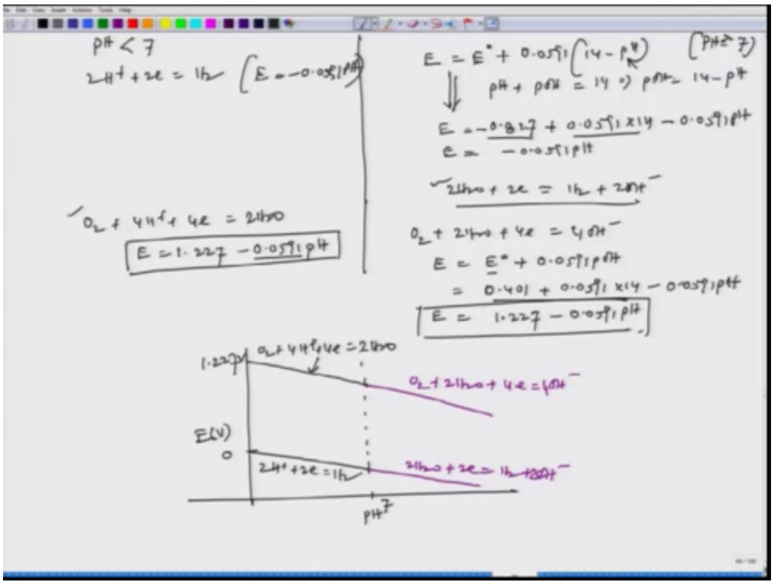

$pH < 7$

$2H^+ + 2e = H_2$ $\left(E = -0.0591 pH \right)$

$O_2 + 4H^+ + 4e = 2H_2O$

$\boxed{E = 1.227 - \underline{0.0591} pH}$

$E = E^\circ + 0.0591 (14 - pH)$ $(pH \geq 7)$

$\Downarrow$ $pH + pOH = 14 \Rightarrow pOH = 14 - pH$

$E = -\underline{0.827} + \underline{0.0591 \times 14} - 0.0591 pH$

$E = -0.0591 pH$

$2H_2O + 2e = H_2 + 2OH^-$

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

$E = \underline{E}^\circ + 0.0591 pOH$

$= 0.401 + 0.0591 \times 14 - 0.0591 pH$

$\boxed{E = 1.227 - 0.0591 pH}$

So, where p H plus p O H equal to 14 so E equal to 0.827 minus sorry this was plus, this should be class because plus 0.0591 p O H, so p O H equal to 14 minus pH. So, that is what you have put here this becomes plus 0.0591 into 14 minus 0.0591 pH you will see that these two quantities could cancel so it become 0.0591 pH. So, now, this acidic side, basic side this was a basic side where p H equal to greater than 7, but on the basics acid side this is the basic and neutral side less than 7 for the first reaction we had the same equation.

So that means, they will be lying on the same line, but one starts from 7 on the right side in the pH axis, one starts one this reaction would start below 7 pH and this reaction come involving H 2 O this reaction would start when pH is equal to or greater than 7. Now we had another reaction which is O 2 plus four H plus plus 4 e equal to 2 H 2 O there a equation 1.227 minus 0.0591 pH. And here this side also here another reaction involving oxygen plus 2 H 2 O plus 4 e equal to 4 O H minus.

In this case the equation would become E 0 minus plus 0.0591 P O H if you follow the same philosophy what we have done for this equation then you convert this we have this particular value would be 0.401 and then 0.0591 into 14 minus 0.0591 pH. So, if you add them you would get the value which is 227 roughly minus 0.0591 pH. So, you have the same equation what we had for the acidic reactions now if you would like to plot all those two reactions.

So, in this pourbiax diagram E verses pH this value is 0 and then up to 7 pH we have H 2, and then if we extend it that time it will be 2 H 2 O plus 2 E equal to H 2 plus O H minus 2. Similarly if we consider this reaction this is 7 pH they will be parallel because both the cases the slope is 0.0591. So, 1.227 volt and then on the right side they should be turned equation for this would be O 2 plus 2 H 2 O plus 4 e equal to O H 4 O H minus and on this side it will be 2 H 2 O. Now, this particular 4 lines are to be clubed with the nickel pourbiax diagram, nickel those lines then it will be a.