Corrosion – Part I
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Lecture - 19
Spontaneity of Corrosion Process and Introduction to Pourbaix Diagram

Let us begin lectures 19.

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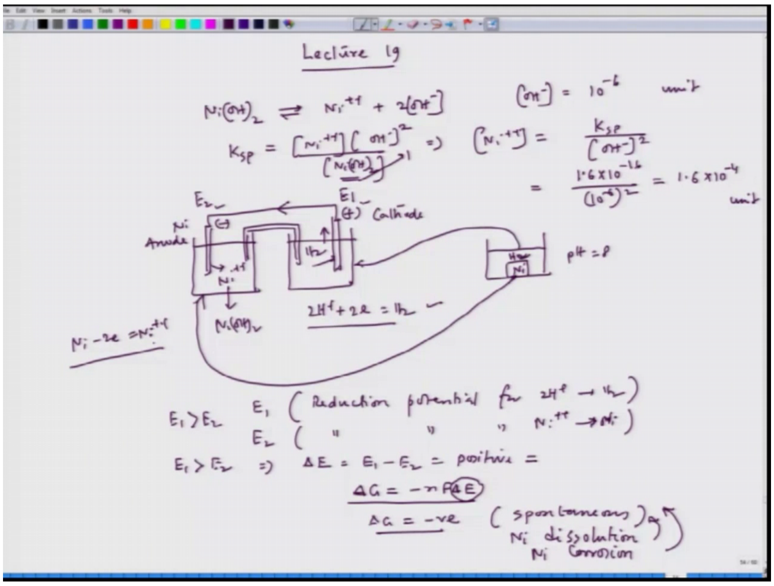

Lecture 19

$Ni(OH)_2 \rightleftharpoons Ni^{++} + 2[OH^-]$ $[OH^-] = 10^{-6}$ unit

$K_{sp} = \frac{[Ni^{++}][OH^-]^2}{[Ni(OH)_2] \to 1} \Rightarrow [Ni^{++}] = \frac{K_{sp}}{[OH^-]^2}$

$= \frac{1.6\times10^{-16}}{(10^{-6})^2} = 1.6\times10^{-4}$ unit

$2H^+ + 2e = H_2$

$Ni - 2e = Ni^{++}$

$E_1 > E_2$ E_1 (Reduction potential for $2H^+ \to H_2$)

E_2 (" " " $Ni^{++} \to Ni$)

$E_1 > E_2 \Rightarrow \Delta E = E_1 - E_2 =$ positive =

$\Delta G = -nF\Delta E$

$\Delta G = -ve$ (spontaneous) (Ni dissolution, Ni corrosion)

So, in last lecture the end we started discussing nickel corrosion; I we would like to say that it is whether that nickel would corrode in a particular solution.

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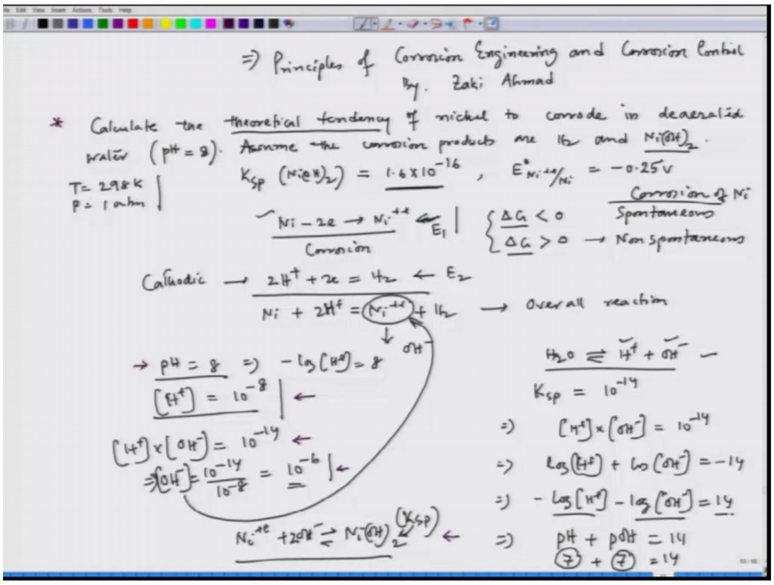

⇒ Principles of Corrosion Engineering and Corrosion Control
By. Zaki Ahmad

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

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

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

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

Corrosion of Ni
$\Delta G < 0$ 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^-

$\rightarrow pH = 8 \Rightarrow -\log[H^+] = 8$

$[H^+] = 10^{-8} \leftarrow$

$[H^+] \times [OH^-] = 10^{-14} \leftarrow$

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

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

$H_2O \rightleftharpoons H^+ + OH^-$

$K_{sp} = 10^{-14}$

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

$\Rightarrow \log[H^+] + \log[OH^-] = -14$

$\Rightarrow -\log[H^+] - \log[OH^-] = 14$

$\Rightarrow pH + pOH = 14$

⑦ + ⑦ = 14

And the problem statement was; if you see the problem statement, this was the problem statement. We need to calculate theoretical tendency of nickel to corrode in deaerated water pH 8. Assume that the corrosion products are H 2 and Ni OH whole 2 and we have the data temperature pressure 298 Kelvin and 1 atmosphere. Solubility product of nickel hydroxide is 1.6 into 10 to the power minus 16 and standard reduction potential of nickel is minus 0.25 volt.

And we did these calculations, you can just go back and then see these calculations; we just wanted to see what is the concentration of nickel ion that could be present in the solution, when we have this Ni OH whole 2 product formation. And when we have Ni OH whole 2 and this Ni OH whole 2 would dissociate into Ni plus plus and OH minus ions. And we know the pH of the solution and from the pH we can calculate what is the concentration of hydrogen ion and then accordingly we can also calculate the concentration of OH minus ion. And that concentration will be in equilibrium as set by the solubility product of Ni OH whole 2. Now if you see that since the pH is 8; so, you know the hydrogen ion concentration is 10 to the power minus 8.

And since hydrogen ion concentration the product of H plus and OH minus ion concentration is 10 to the power minus 14. So, we get OH minus concentration was OH minus ion concentration to be 10 to the power minus 6. And now we have to look at this particular equation which talks about the equilibrium between Ni plus plus and OH minus. And it is forming Ni OH whole 2 and this Ni OH whole 2 has got its own dissociation constant; so, we start from here. Now if we see this Ni OH whole 2, it can have equilibrium between Ni plus plus plus 2 OH minus. Now we know that OH minus ion concentration in the solution is 10 to the power minus 6.

Now, from K SP consideration would be equal to concentration of Ni OH 2 OH whole 2 divided by whole 2. So, now, this is a solid product which is precipitating out. So, we can consider to be 1 and then we get to Ni plus plus ion concentration which is K SP divided by OH ion whole 2. So, here it should be we made a mistake; so, this 2 should be here square because we are considering the dissociation constant.

So, now, if we know this we know K SP 1.6 into 10 to the power minus 16 and here 10 to the power minus 6 square. So, it ends of 1.6 into 10 to the power minus 4. So, I am just putting unit concentration unit which could be mole per centimeter cube. Now, once we have this then initially we are assuming that nickel is corroding. So, if we have an electrode, if we see this 2 electrode; one side is hydrogen electrode and one side is nickel electrode.

And when nickel is dissolving and that is of course, forming Ni OH whole 2. Now since nickel is dissolving and hydrogen is evolving; so, this is H 2 is evolving. So, hydrogen plus plus plus 2e equal to H 2; this cathodic reaction is taking place on this particular electrode. Now if we have a connection like this with the solve bridge; then if we connect them the current should flow from this way to this way. So, this is positive end this is my negative end; so, this would be my cathode and this will be my anode.

So, this cell is also replicating the situation here; how it is replicating? Because in this case I have a solution with a pH 8 and in that we have a nickel piece. So, this nickel piece is forming a half cell which is similar like this and hydrogen evolution on the surface of the nickel piece is mimicking the hydrogen electrode on the other side. So, this is the solution and this is the solution; here these are these 2 half electrodes have been electrodes have been broken. So, the entire reaction is broken into 2 halves; that means, 2 half cell reactions which is one side is Ni minus 2 equal to Ni plus plus another side is this one.

Now, when we have this situation because we are assuming there is a nickel is corroding. So, then this side should be always positive; this side should be always negative. So, now, the potential E 1 which is setup on this right side should be greater than the potential on the left side and this potential of course, for our convention is we will take reduction potential.

So, E 1 which is a reduction potential for H plus going to H 2 and E 2 reduction potential for Ni plus plus going to Ni. And in order to have nickel going into Ni plus plus; so this E 1 should be E 2 and if E 1 is greater than E 2; so, the cell potential which is del E is nothing, but E 1 minus E 2 should be positive. And if it is positive then we see that since we know del G for the reaction is equal to nothing, but minus n F del E over the cell potential.

And if this is positive, so del G would be negative and once we get del G to be negative then we can say that the reaction is spontaneous. And since we are considering nickel is dissolving; so, nickel dissolution is spontaneous or corrosion is nickel corrosion is spontaneous. Now then our main interest should be to find out the reduction potential on this side and the reduction potential on that side; so, let us find out.

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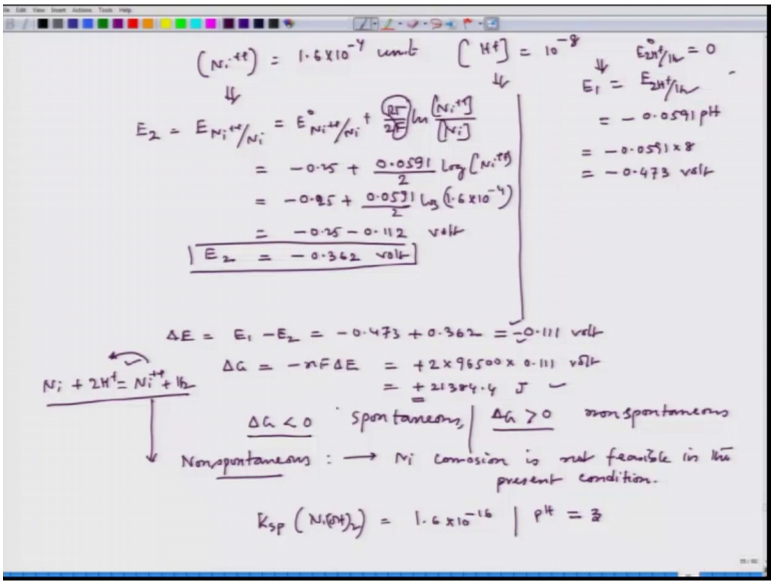

$(Ni^{++}) = 1.6 \times 10^{-4}$ unit $\quad [H^+] = 10^{-8} \quad E^\circ_{2H^+/H_2} = 0$

$$E_2 = E_{Ni^{++}/Ni} = E^\circ_{Ni^{++}/Ni} + \frac{RT}{2F} \ln \frac{[Ni^{++}]}{[Ni]}$$
$$= -0.25 + \frac{0.0591}{2} \log [Ni^{++}]$$
$$= -0.25 + \frac{0.0591}{2} \log (1.6 \times 10^{-4})$$
$$= -0.25 - 0.112 \text{ volt}$$
$$\boxed{E_2 = -0.362 \text{ volt}}$$

$$E_1 = E_{2H^+/H_2}$$
$$= -0.0591\,pH$$
$$= -0.0591 \times 8$$
$$= -0.473 \text{ volt}$$

$$\Delta E = E_1 - E_2 = -0.473 + 0.362 = -0.111 \text{ volt}$$
$$\Delta G = -nF\Delta E = +2 \times 96500 \times 0.111 \text{ volt}$$
$$= +21384.4 \text{ J}$$

$Ni + 2H^+ = Ni^{++} + H_2$

$\Delta G < 0$ spontaneous, | $\Delta G > 0$ nonspontaneous

Nonspontaneous : $\longrightarrow$ Ni corrosion is not feasible in the present condition.

$K_{sp}(Ni(OH)_2) = 1.6 \times 10^{-16}$ | pH = 3

Now, we have all the ideas all the data because nickel ion concentration we know which is 1.6 into 10 to the power minus 4 unit; we can consider mole molar unit sorry, we can consider molar unit. So, now, H plus is equal to 10 to the power minus 8; now let us see what potential it would get.

So, E 2 equal to nothing, but E Ni plus plus Ni equal to E 0 Ni plus plus Ni plus RT by 2 F; since 2 electrons are involved for this reduction reaction ln Ni plus plus ion concentration which is oxidant and nickel ion concentration nickel concentration which is the nickel metal.

So, this we know minus 0.25 volt and if it is 298 Kelvin and 1 atmosphere pressure. So, then this particular quantity becomes 0.0591; we have calculated before, 2 and this becomes then log because when we take log say 2.303 that conversion factor from lon to log need to be multiplied with RT by F factor. So, this becomes minus 0.25 plus 0.0591 by 2 log 1.6 into 10 to the power minus 4. So, we get the value; so the value becomes; so this becomes divided by 2 into 0.0591 by 2 minus 0.25 minus 0.112 volt equal to minus 0.362 volt; so, E 2 is nothing, but this much.

Now, we can calculate E 1 which is this side nothing, but E H 2 equal to minus 0.0591 pH. We have done it this particular calculation before because E 0 H plus H 2 equal to 0. So, E 1 becomes minus 0.0591 into 8; so this becomes minus 0.473 volt. So, del E would be equal to E 1 minus E 2 which is minus 0.473 minus 0.362 plus would be equal to 0.111 volt with a minus sign, this is a minus sign here.

So, del G for the overall free energy change for the system and the overall reaction is Ni plus 2 H plus equal to Ni plus plus plus H 2; this is the overall reaction. So, for that the change would be minus n F del E and here n is equal to 2; so 2 into 96500 into 0.111 volt and since there is a minus sign here. So, it becomes plus into equal to plus 21384.4 joule and remember this is a plus sign.

So, for a spontaneous process del G should have been less than 0; as we have seen before if we see this part you see this is the section I am talking about. So, del G negative means spontaneous del G positive is non spontaneous. So, now here we are getting spontaneous and del G positive non spontaneous and here we are getting del G positive. So, it becomes definitely the; this particular process becomes non spontaneous; means the assumption we had that the nickel would corrode that assumption does not hold true.

So, if this particular process is non-spontaneous then the reverse process should be spontaneous. So, the nickel ion rather would get reduced; so nickel corrosion is not feasible in the present condition. Now let us see; so this is the in order to find out whether the nickel would corrode or not; we are doing the calculations and all those consideration starting from here.

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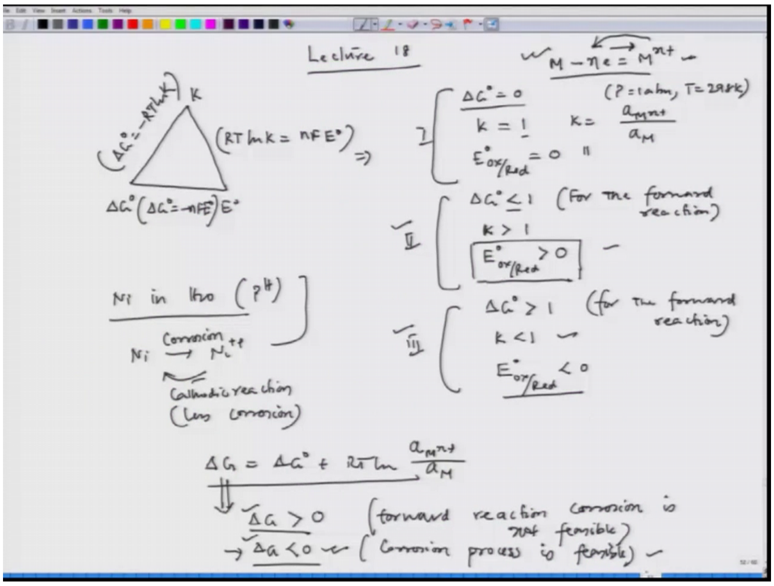

Lecture 18

$M - ne \rightleftharpoons M^{n+}$

$(P = 1\text{atm}, T = 298K)$

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

$(RT\ln K = nFE^\circ)$ $\Rightarrow$

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

I $\Delta G^\circ = 0$

$K = 1$ $\quad K = \frac{a_{M^{n+}}}{a_M}$

$E^\circ_{ox/Red} = 0$

II $\Delta G^\circ \leq 1$ (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)

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

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)

If you see this section this particular slide we see that entire lot of calculations and finally, our primary interest is to find whether del G is negative for the process or del G is positive for the process.

Now, let us see if we maintain all other this particular Ni OH whole 2 that is forming and if the temperature is fix. So, if we maintain this particular K SP constant of Ni OH whole 2 is not changing. So, it still 1.6 into 10 to the power minus 16 and if we change pH; let us say pH becomes 3, let us see what happens.

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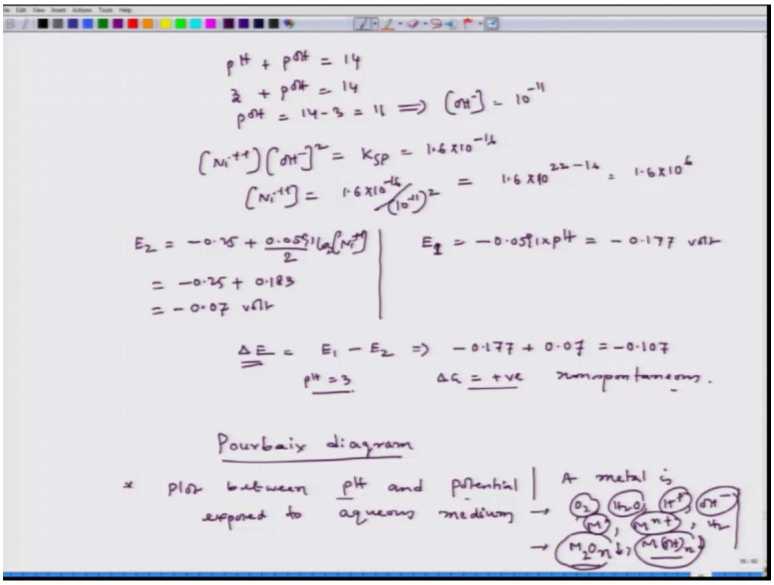

$pH + pOH = 14$

$3 + pOH = 14$

$pOH = 14 - 3 = 11 \Rightarrow [OH^-] = 10^{-11}$

$[Ni^{++}][OH^-]^2 = K_{SP} = 1.6 \times 10^{-16}$

$[Ni^{++}] = 1.6 \times 10^{-16} / (10^{-11})^2 = 1.6 \times 10^{22-16} = 1.6 \times 10^{6}$

$E_2 = -0.25 + \frac{0.0591}{2} \log [Ni^{++}]$

$= -0.25 + 0.183$

$= -0.07$ volt

$E_1 = -0.0591 \times pH = -0.177$ volt

$\underline{\underline{\Delta E}} = E_1 - E_2 \Rightarrow -0.177 + 0.07 = -0.107$

$\underline{pH = 3}$ $\Delta G \underline{= +ve}$ nonspontaneous.

Pourbaix diagram

- Plot between pH and potential exposed to aqueous medium

A metal is → O_2, H_2O, H^+, OH^-, M, M^{n+}, H_2

→ $M_2O_n \downarrow$, $M(OH)_n$

So, if pH becomes 3; then I can find out H plus ion concentration or I can do a different route. Since we have seen pH plus p OH equal to 14; so, pH is equal to 3 plus p OH equal to 14. So, p OH equal to fourteen minus 3 equal to 11.

So, this can give me the concentration of p OH minus ion is equal to 10 to the power minus 11. Now K SP remains same; so Ni plus plus OH minus whole 2 equal to K SP equal to 1.6 into 10 to the power minus 16. So, that time nickel ion concentration becomes 1.6 into 10 to the power minus 16 divided by 10 to the power minus 11 ; 2 is going to be 1.6 into 10 to the power minus 22 minus 16 equal to 1.6 into 10 to the power 6; this is the concentration level of nickel ion concentration in that solution.

So, we can have again calculate E 2; E 0 which is minus 0.25 plus 0.0591 by 2 log Ni plus plus ion concentration and this side becomes into pH is a pH is equal to 3. So, I would get 0.0591 into 3; it goes to minus 0.1773 or I can just simply say 0.1 volt and this side becomes plus. So, that consultation becomes 1.6 into 6; 0.183; so this becomes minus 0.25; 0.07 volt.

Now, if I try to find out del E is equal to E 1 minus E 2. So, that becomes ok; so, we can find out del E again and then del beco[mes]- del E becomes 0.177 minus or which will become 0.07 which goes to 0.107. So, I still see that I get a negative del E value. So, even at a pH of 3; which is highly acidic I could see if this data other data holds; other data hold other data are just like the way we have considered, still we could see that the del E becomes negative. So, del E becomes negative means del G becomes positive. So, then again it becomes non spontaneous non spontaneous.

So; that means, we have to do a entire lot of calculations in order to see whether del G becomes negative or positive. Just like that we can have other calculations, but instead of doing this; this entire calculations to see whether the del G becomes negative for a particular corrosion process, we can also have another route to understand whether the system or the metal would corrode in the water system or not; when it is dipped in atmosphere with certain pH level. So, that information can be obtained from a particular diagram which is called pourbaix diagram.

So, this pourbaix diagram is nothing, but plot between pH and potential. When a metal is exposed to aqueous medium and whenever we are talking about a metal is exposed to aqueous medium; we take following species, oxygen, H 2 O, H plus ion, OH minus ion and of course, metal and metal plus plus ion or rather if we do not know what is the oxidation number; we can consider n plus ion. So, M n plus this M is nothing, but the metal; now whenever we have existence of metal ion then there could be possibility of formation of m oxygen n this oxide can form or M OH whole n, this hydroxide can form.

So, generally these oxides or hydroxides they have very low solubility product and that is what they tend to settle down. So, now, whenever we expose a metal in this particular system containing such ions; there could be possibility that oxygen is not present, but hydrogen ion would always be there. Now there could be possibility of presence of oxygen and of course, you once you have a metal there could be possibility of formation of metal ion and if the system situation permits we can have oxide or hydroxide.

So, that time we can have the stability of different phases for example, this phase this phase or this phase and this phase even this one. All those phases we can have some information from that diagram and we are also we are forgetting another important species which is hydrogen H 2. So, there could be possibility of hydrogen evolution also when a metal is dipped in an aqueous medium; just like zinc when it is exposed to dilute HCL, where we have pH less than 7 its acidic then we see that hydrogen bubble forms and of course, Ni plus plus ion also forms. So, this is a stability diagram between pH and potential.

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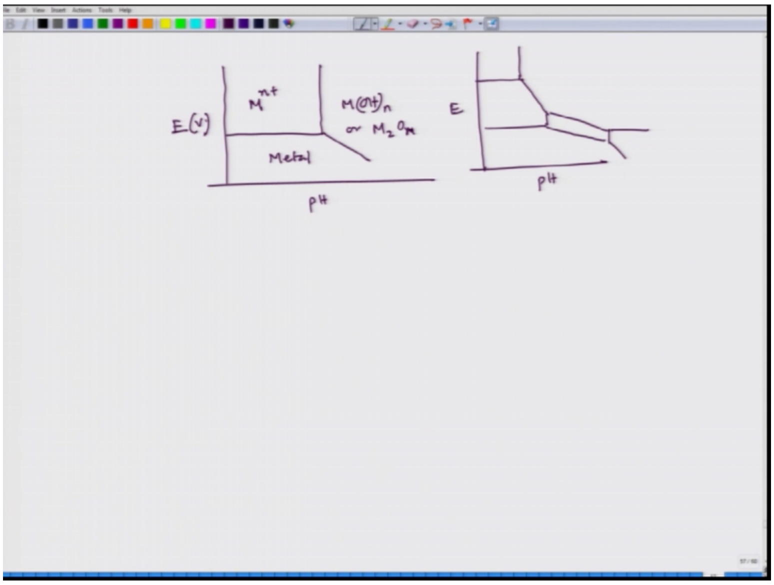

So, these diagram has 2 axis one axis becomes this pH, another axis becomes potential which is in volt and this is in pH which is a number.

Now, there we can have a kind of if you see a pourbaix diagram of certain metal; we can see certain kind of this kind of diagram or we can have a diagram like this, we can have a diagram like this is E versus pH also. So, this diagram if we see carefully, then we will see that this is metal, this is metal ion and this is metal hydroxide n or M 2 o N; so, this kind of boundary we can have.

Now from this diagram without going for that calculation; detail calculations that whether del G becomes negative or not to understand whether the corrosion would take place or not. If we look at this diagram, then immediately we can make out that whether the metal would corrode or not; so, this is the benefit of this diagram.

So, the our next level of understanding would be how to construct this diagram and what are the informations we can snatch out of this diagram? And remember this diagram place a very very important role in electrochemistry and specially in corrosion because in corrosion sometimes you will hear that the metal is passivating and this diagram can also tell you whether the metal would actually passivate or not.

So, those information definitely we can we can snatch out from this diagram and it would also enable us to find out the tendency of the metal to remain as metal or metal ion; that means, corrosion or passivating state; without going for detailed calculation the way we have done for nickel. So, our next topic would be pourbaix diagram; let us stop here, we will continue our discussion in our next lecture.

Thank you.