Corrosion - Part I
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Lecture – 20
Construction of Pourbaix Diagram

Let us begin lecture 20.

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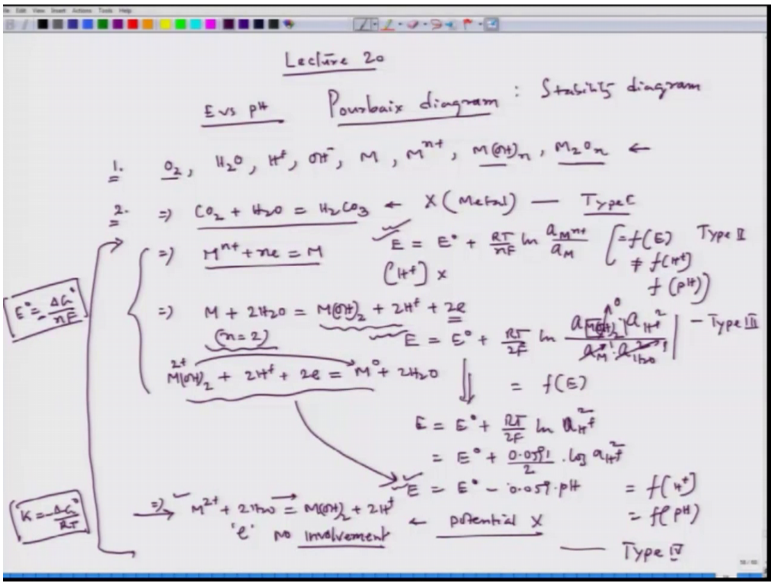

Lecture 20

E vs pH Pourbaix diagram : Stability diagram

1. O_2, H_2O, H^+, OH^-, M, M^{n+}, $M(OH)_n$, M_2O_n ←

2. ⇒ $CO_2 + H_2O = H_2CO_3$ ← X (Metal) — Type I

⇒ $M^{n+} + ne = M$ $E = E^\circ + \frac{RT}{nF} \ln \frac{a_{M^{n+}}}{a_M}$ $\left[= f(E) \quad \text{Type II} \; \neq f(H^+) \; f(pH) \right)$

(H^+) X

⇒ $M + 2H_2O = M(OH)_2 + 2H^+ + 2e$ (n = 2)

$E = E^\circ + \frac{RT}{2F} \ln \frac{a_{M(OH)_2} \cdot a_{H^+}^2}{a_M \cdot a_{H_2O}^2}$ — Type III

$M(OH)_2 + 2H^+ + 2e = M^\circ + 2H_2O$ = f(E)

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

$= E^\circ + \frac{0.0591}{2} \cdot \log a_{H^+}^2$

$E = E^\circ - 0.059 \cdot pH$ $= f(H^+)$ $= f(pH)$

⇒ $M^{2+} + 2H_2O = M(OH)_2 + 2H^+$ ← potential X

'e' no involvement — Type IV

$E^\circ = -\frac{\Delta G^\circ}{nF}$

$K = -\frac{\Delta G^\circ}{RT}$

See in next couple of lectures we will be discussing Pourbaix diagram, we have already started looking at Pourbaix diagram because it is an important aspect important feature in electrochemistry. And when you look at the corrosion then this understanding of Pourbaix diagram is very very essential. Now, as we have told that the Pourbaix diagram is nothing, but the stability plot between of different phases between in the plot of E versus p H, this is the Pourbaix diagram, this is basically stability diagram.

Now, whenever we talk about Pourbaix diagram we must understand certain facts, and what are those facts? 1, we would only consider reactions involving oxygen, H 2 O, H plus, OH minus, metal ion, metal-metal ion, metal hydroxide or metal oxide. So, here we are talking about only this kind that would be several complex oxides involving these many species and remember we will not considered any other species.

Second part, we would consider reactions and those reactions can be categorised into 4 major reaction stages one reaction of course, will not consider, but that indirectly affects the p H of the system, but that will not be plotted on the Pourbaix diagram. And certain reaction only involve metal and metal ion, certain reaction would involve hydrogen ion, H 2 O; that means, what a metal, metal ion or an hydroxide metal hydroxide on metal oxide. And certain reactions would involve metal, H 2 O, hydrogen ion and metal hydroxide or metal oxide, but between these two last two cases one case we would see that there is no electrons involve for those particular reaction, but other case we have electrons involvement of electron.

So, let us categorised those reaction, let us categorise those reactions one reaction for example, in water we sometime we have dissolve of carbon dioxide that can react with H 2 O and form H 2 CO 3. So, as I have told that this reaction cannot be plotted in Pourbaix diagram of a metal, but actually whenever we have this is an acid, this acid would have this is the weak acid, but still it would lead to set certain p H of the system that can affect the corrosion stage. And, this is a typical acid that affects the corrosion of rebar; that means, reinforce bar in the which is basically embedded in concrete mixture.

But this particular reaction if you see, it does not involve any metal, no involvement of metal. So, this is kind of type-I I can say this is type-I reaction. Now type - II reaction for example, metal I can have n plus plus ne equal to M, M is the metal and now since I do not know what is the oxidation number then n plus for example, if it is a copper copper plus plus going to copper n becomes 2 Fe plus 3 going to Fe n becomes 3 like that way we can have the value of n. So, n is basically nothing, but the oxidation number.

So, this is this particular reaction if you see carefully it depends on potential why because this reaction can be expressed with in terms of Nernst equation, but this particular reaction does not involve any H plus ion. So, this H plus ion is not involved so, then the p H of this particular for this particular reaction would have no effect. So, it we can say that this is function of potential, but it is not a function of hydrogen ion concentration. So, this is the function of e, but not a function of hydrogen ion or not a function of p H. So, whenever we have hydrogen ion presence we can express in terms of p H this we call it type- II.

We can have another reaction for example, let us say I can have M which can react with 2 H 2 O it can go to M OH whole 2 plus 2 H plus plus 2 e and that time n is basically 2, this is another reaction we can consider that can happen in water when a metal is expose to moisture or water atmospheric. So, now, here we see that it is we have it here also we can express this particular reaction in terms of Nernst equation RT 2F since number of electrons involve for this reduction processes 2F 2 ln activity of oxidant.

Now here the oxidant part is this part and reductant part is this part so, I can write this particular reaction in reverse; so, M OH whole 2 plus 2 H plus plus 2 e equal to M plus 2 H 2 O. So, now, here M has got 2 plus so, the 2 plus going to 0. So, it is a reduction so, this reduction process we can express in terms of a M OH whole 2 a H plus to the power 2, a M a H 2 O this a is nothing, but the activity I can express this in this form.

Now, interestingly this particular equation once we express in terms of Nernst equation it becomes a function of potential. But here if we consider these this particular hydroxide to deposit back to or to settle down that may because of it is very low solubility product solubility constant. So, this particular thing if it is we consider to be pure and solid. So, I can consider activity to be 1 and if we considered it is a pure water we comes activity 1 metal of course, it is pure an activity 1.

So, then this equation we can write in terms of E 0 plus RT 2F ln activity of H plus we can write. So, we can express this reaction through this Nernst equation. So, you see that it is function of potential at the same time it a it is a function of H plus ion presents or function of p H. So, this reaction becomes the type - III category. Now we have one more reaction that is also possible where let us say this is 1, this is 2, this is 3, now we have one more, which is M 2 plus plus 2 H 2 O it can go to M OH whole 2 plus 2 H plus.

So, this reaction we can also have, where you see that it does not involve any electron. So, if there is no involvement of electrons we cannot express the equilibrium for this particular reaction in terms of potential we cannot express, but this is the chemical reaction.

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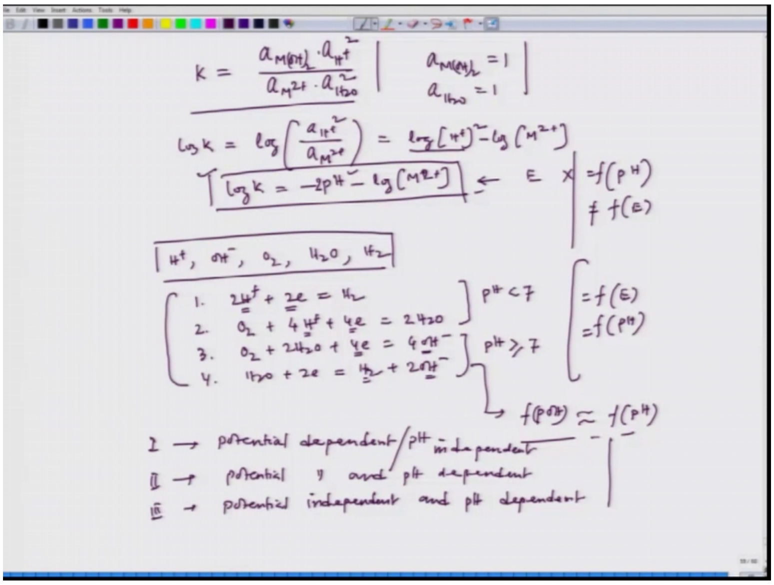

$$K = \frac{a_{M(OH)_2} \cdot a_{H^+}^2}{a_{M^{2+}} \cdot a_{H_2O}^2} \quad \Big| \quad a_{M(OH)_2} = 1, \; a_{H_2O} = 1$$

$$\log K = \log\left(\frac{a_{H^+}^2}{a_{M^{2+}}}\right) = \log[H^+]^2 - \log[M^{2+}]$$

$$\boxed{\log K = -2pH - \log[M^{2+}]} \leftarrow E \times \; = f(pH), \; \neq f(E)$$

$$\boxed{H^+, OH^-, O_2, H_2O, H_2}$$

1. $2H^+ + 2e = H_2$
2. $O_2 + 4H^+ + 4e = 2H_2O$
3. $O_2 + 2H_2O + 4e = 4OH^-$
4. $H_2O + 2e = H_2 + 2OH^-$

1, 2: $pH < 7$; 3, 4: $pH \geq 7$; $= f(E)$, $= f(pH)$

$\rightarrow f(pOH) \simeq f(pH)$

I → potential dependent/pH independent

II → potential " and pH dependent

III → potential independent and pH dependent

So, this chemical reaction can be expressed in terms of equilibrium constant which is nothing, but activity of product; so, activities M OH whole 2 H plus square activity of M 2 plus an activity of H 2 O square. So, if we see this reaction, this reaction so, if we consider the forward reaction. So, I can express K to be like this whether forward or backward it does not matter because it is a equilibrium constant so, I can write this.

Now once we write this then we can also simplify this equation, this equation can be written log K equal to as we have mentioned M OH settle down. So, it is a solid and that too pure. So, M OH whole 2 we can consider 1, a H 2 O still we can consider 1 because it is a pure water, then it goes to the equation boils to log activity of H plus, activity of M 2 plus this.

So, I can write if I convert activity into concentration assuming that it is maintaining ideal solution. So, in case of ideal solution activity becomes concentration so, that case I can write log 2 minus log 2 plus. Now we see that in this final equation becomes I can put it as p H because this is nothing, but minus of p H with a 2 sign because 2 would come here minus log of M plus 2 plus concentration. So, this is an equation which can decide the stability of M 2 plus and stability of M OH whole 2.

But this particular reaction does not contain potential. So, the potential cannot decide this particular reaction, potential cannot tell me the stability of this particular reaction because it does not involve any electron acceptance or electron if the system is not also giving away electrons. So, no cathodic or anodic reactions are taking place in this entire reaction. So, it is p H dependent function of p H because here we have p H, but it is not a function of potential. So, this is type – IV. So, this equation becomes type – IV. So, the type- IV equation can be expressed with this.

Now, whenever we are having this equations for example, equations like this, equation like this and finally, we are boiling with 2 we are getting to this particular equations or equations like this, these equations would enable us to plot Pourbaix diagram and also enable us to find out the stability of M 2 plus M or M hydroxide because here we are only considering hydroxide we can also have set of reactions involving oxides also metal oxides.

Now, as I told you that the first one was this many species are considered depending on the possibility of formation of this species or this species and the possibility of having dissolve oxygen or deaerated and then second part was we can have 4 types of reactions, but mainly we are considering type - III to type – IV. So, these reactions we are considering to happen in the aqueous system and that would lead to the plotting of e versus p H and that too that would give us the Pourbaix diagram. Now interestingly the Pourbaix diagram will not be complete, if we do not consider 4 reactions involving only oxygen, dissolve oxygen of course, hydrogen, hydrogen ion and 2 other species which are O H minus and H 2 O.

So, now, we can have 4 more reactions involving H plus, O H minus, O 2, H 2 O, H 2. So, this 5 species can have following reactions: 1. H plus plus 2 e equal to H 2, 2. O 2 plus 4 H plus plus 4 e equal to 2 H 2 O, 3. O 2 plus 2 H 2 O plus 4 e equal 4 OH minus and 4. H 2 O plus 2 e equal to H 2 plus 2 H minus. Now you see all 4 reactions we have already discussed before these 2 reactions are possible in p H less than 7; that means, acidic medium and these 2 reactions are possible when p H is greater than equal to 7 neutral or basic medium.

Now, all 4 reactions you see that the electrons are involved and all 4 reactions we have H plus ion presence in this 2 cases and OH minus ion presence. Now whether we have H plus or OH minus we can express Nernst equation in terms of potential as well as p H. So, now, all 4 reactions are function of potential and function of p H. So, in these 2 cases it is a function of p OH which can be written in the form of p H now this calculations we have done it before you just go back. And, then see some of the earlier lectures you will see that all 4 reactions we have try to find out the reduction potential as a function of standard reduction potential and the p H of the solution and also we have try to plot those reactions as a function of p H we if you go back you can have a look at it again.

So, but this 4 reactions also R function of potential and function of H so; that means, logically we have 2 types of reactions one which involves 3 types, one which involve potential so; that means, 3 type, type-I only potential dependent, but p H independent, second type potential dependent and p H dependent and third type potential independent and p H dependent. So, this 3 would allow us to find out a Pourbaix diagram.

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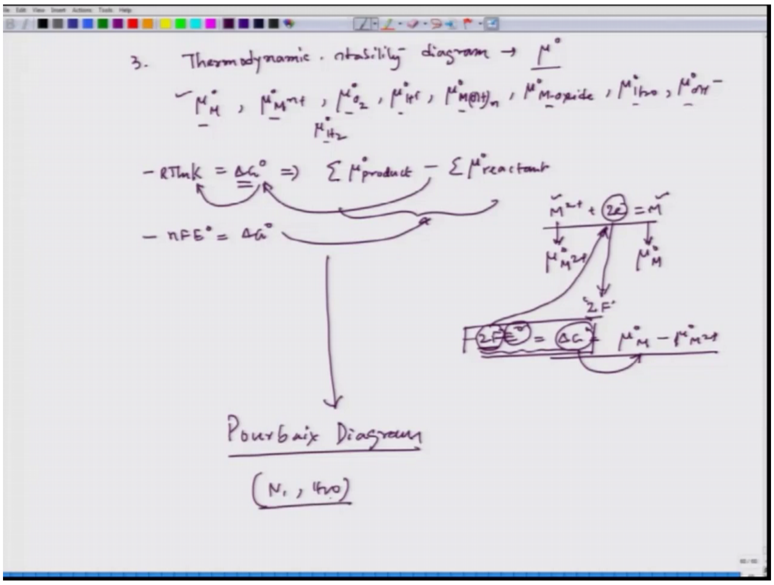

3. Thermodynamic stability diagram → μ°

μ°_M, $\mu^\circ_{M^{n+}}$, $\mu^\circ_{O_2}$, $\mu^\circ_{H^+}$, $\mu^\circ_{M(OH)_n}$, $\mu^\circ_{M\text{-oxide}}$, $\mu^\circ_{H_2O}$, $\mu^\circ_{OH^-}$

$\mu^\circ_{H_2}$

$-RT\ln K = \Delta G^\circ \Rightarrow \sum \mu^\circ_{product} - \sum \mu^\circ_{reactant}$

$-nFE^\circ = \Delta G^\circ$

$M^{2+} + 2e = M$

$\mu^\circ_{M^{2+}}$ μ°_M

$2F$

$-2FE^\circ = \Delta G^\circ = \mu^\circ_M - \mu^\circ_{M^{2+}}$

Pourbaix Diagram

(Ni, H_2O)

Now in addition to that we can have the third criteria condition. So, these Pourbaix diagrams are basically a thermodynamic stability diagram, it does not involve any kinetics.

Now, from this diagram we will not be able to tell at what rate if there is any corrosion of a metal in the aqueous medium, what rate it is going we cannot be able to tell from this Pourbaix diagram, because it is a thermodynamic stability diagram why. In order to find a Pourbaix diagram we have to find out those equations the equations like what we have shown. So, this equation like this one or this one or this one and then finally, of course, this equation and the equations related to all 4 reactions involving hydrogen and oxygen, water, hydroxide and hydrogen we have to get the information about standard chemical potential. And whenever we talk about standard chemical potential of a species that indicates that there in their activity- 1 and whenever we talking about activity- 1 we assume that they are pure state.

So, since we have understood that what are the species that are possible in combination of course, we have chemical potential of metal, chemical potential of metal ion, chemical potential of oxygen, chemical potential of hydrogen, chemical potential of metal hydroxide, chemical potential of metal oxide, H 2 O OH minus are we missing anything. So, metal ion oxygen, hydrogen plus, metal hydroxide, metal oxide, H 2 O, OH minus and of course, H 2. We have to make use of the standard chemical potentials of all the species in a particular reactions, particular set of reactions we have to consider those chemical potentials.

Now, how do we get it for example, K if I consider the activity this equilibrium constant is nothing, but delta G 0 with the negative sign here. Now delta G 0 we can write as we have done it before the summation of chemical potential of standard chemical potential of product minus summation of chemical potential of reactant. So, this will give us free energy change from that we can calculate activity this equilibrium constant.

And similarly we have another reaction nFE 0 equal to delta G 0 which is similar like this, we can have product minus summation of product of this chemical potential standard chemical potential of all the species that are involved in the reaction and the summation of chemical standard chemical potential of reactance in that particular reactions.

For example M 2 plus plus ne equal to M, here we have this chemical species this species and of course, sorry here we are considering 2; that means, instead of n we can put 2 e. So, here this is we have to consider chemical potential of 2 plus we have to consider chemical potential of M and of course, we can consider the chemical potential of electron also that chemical potential will be used up in 2F. So, you have a relation for this we are not getting the detail of that relation, but this one contributes to this 2F delta G 0 comes from chemical potential of M minus chemical potential of M 2 plus. So, this is delta G 0 minus 2 FE0.

So, this 2F is related to this 2 electron and of course, that is also related to chemical potential of electron as we have said that we are not going detail derivation of this particular election for reaction relation from the chemical potential of all the species involving electron also. But, for our understanding we can see that this one this electron is contributing this part and this one is can be found out from this relation and this comes from this.

So, we see that these are all thermodynamic data, these are all thermodynamic data and this thermodynamic data will be used up to find out reaction equilibrium constant or the chemical or the standard reduction potential and this equilibrium constant will be used for type - IV type of this particular reactions. And in this case K equal to delta G 0 RT and in this case E 0 equal to delta G 0 nF minus. So, there we have application of delta G 0 or the application of standard chemical potential of the species.

In addition to that so, we have to calculate this K or E 0 from standard chemical potential data, but sometimes we do experience ion activity to be not to be 1. So, that case we have to make use of Nernst equation where we also have contribution from the ions of metals. So, then finally, we would construct Pourbaix diagram. So, these are the basic consideration on which this diagram will be better.

So, in our next lecture, we will try to find out one example in the nickel system nickel H 2 O system we will try to see the Pourbaix diagram. And, we will start from the chemical potential of different species and we will end up getting the diagram and then we will see that yes, in this position if I am then I will get metal remaining as metal. In this position if I go I will get metal ion formation or corrosion or at certain region you might get metal hydroxide which will settle down. So, we considered it to be a passivating zone. So, let us stop here, we will continue our discussion in our next lecture while we start with the Pourbaix diagram calculation in case of nickel H 2 O system.

Thank you.