Corrosion – Part I
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Lecture – 21
Construction of Pourbaix diagram for Ni-H_2O System-I

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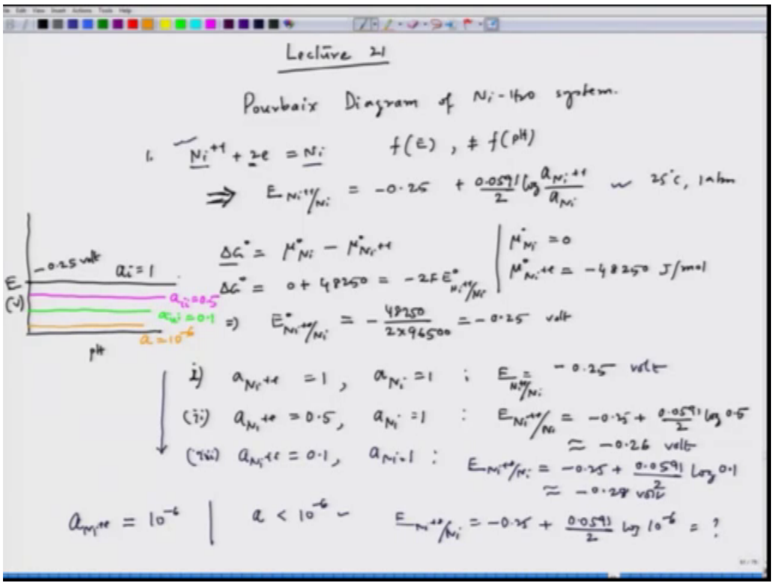

Let us start lecture 21, as we have ended lecture 20 saying that we would construct a simple Pourbaix diagram and we will take an example with nickel H2O system. So, our job today is to find diagram of nickel or nickel H2O system. So, for that we have to see what are the reactions that are possible for nickel in H2O system and we can see that all the reactions can be categorised in terms of type 1 type 2 type 3 as we have discussed in our last lecture. So, the first type what we can think of is basically the type 1 reaction, which is nickel plus plus 2e nickel this reaction which is function of potential.

But not a function of pH since there is no hydrogen ion formed in this reaction and in order to find an equation which will give an idea about this reaction which is a Nernst equation E Ni equal to E0 Ni plus RT by 2 F ln activity of Ni plus plus activity of Ni; see it we will follow ox by slash red and we will consider 25 degree Celsius 1 atmosphere pressure. So, this quantity and then if we convert this one to log, then we will get following factor log of 0.0591 by 2. Here 2 is coming from 2 electron that is involved in this reduction reaction.

Now the next step is we have to find out this quantity and in order to find out we have to find out delta G0, which is nothing but chemical potential where the standard chemical potential of product minus standard chemical potential of Ni plus plus. And, we can we have the knowledge of chemical potential of standard chemical potential of nickel as well as Ni plus plus ion and Ni equal to 0 mu 0 Ni plus plus is equal to 48250 joule per mole.

So, we get so there is a minus sign 0 minus, so minus and this minus should become plus 48250. So, which is to be equated to minus 2 FE0 and in this case E 0 is this. So, we get E 0 equal to 48250 2 into 96500 equal to 0.25 volt and then we can modify this equation instead of this quantity we can put this 0 point with a minus sign 0.25. So, we can have a plot for this equation, for this equation on E versus pH, so here unit is volt now this is minus 0.25 volt.

When activity of when the conditions let us say let us put several condition, condition 1 activity of Ni plus plus equal to 1 and since activity of Ni is 1, then E equal to this condition E equal to minus 0.25. So, it will be a parallel line parallel to pH axis so we get this line. So, at all the pH values we can have we can plot this equation E equal to minus 0.25 and that time condition is activity of activity is equal to 1. So, here I am putting activity or a 1 the condition 1 I would say condition 1, so a i equal to 1.

Now let us see what happens if we have a Ni plus plus equal to 0.5 and of course a Ni equal to 1 since it is a solid pure solid. So, E Ni plus plus Ni would become minus 0.25 minus plus 0.0591 by 2 log of 0.5 which eventually becomes minus 0.26. So, if I give it a colour so this becomes my a 2 equal to 0.5. Now we can have another set a Ni plus plus equal to 0.1 and that time a Ni equal to 1, so that case E Ni plus plus Ni equal to minus 0.25 plus 0.0591 by 2 log of 0.1 so it becomes minus 0.28 volt. So, this is also volt so here also we will have a plot which is a 3 equal to 0.1.

So, for each activity of nickel ion in the solution, we see that we can construct a line to indicate this reaction, this reaction on E verses pH plot and this line will be parallel to pH axis because, since there is no pH term in this equation. So, now question is whenever we have this line we have to also see the stability of 2 spaces, the here the stability means this one and this one this 2 spaces are there. Now, question is which side would be my nickel and which side would be Ni plus plus, for that let us assume that for a particular solution we can measure the concentration of ions because, once we have nickel in water we will see that nickel plus plus ion is forming.

Now, let us say 10 to the power minus 6 that is the concentration of 6, that is a limit up to which we can measure the activity of Ni plus plus. But once the activity of nickel ion is less than 10 to the power minus 6, then we will not be able to detect anything what does it mean. So, if we if we cannot detect anything so you would say that as if there is no nickel ion. So, then if there is no nickel ion, that means the nickel is present only no ion base present this is one part, second part is we see that as the activity of nickel ion concentration is decreasing.

That means as we see that it is decreasing we are saying that this lines these 1 2 3 lines you see the lines are dropping down, so they are going down so. That means, if we go for 10 to the power minus 6 it will it will go further down, so you can also calculate what could be that potential. So, that potential would be definitely E Ni plus plus Ni equal to 0.25 plus 0.0591 by 2 log of activity of nickel ion is 10 to the power minus 6 we can find out some value. So, it will be further down so for that we can have another plot, so this could be let us say here where a is equal to 10 to the power minus 6.

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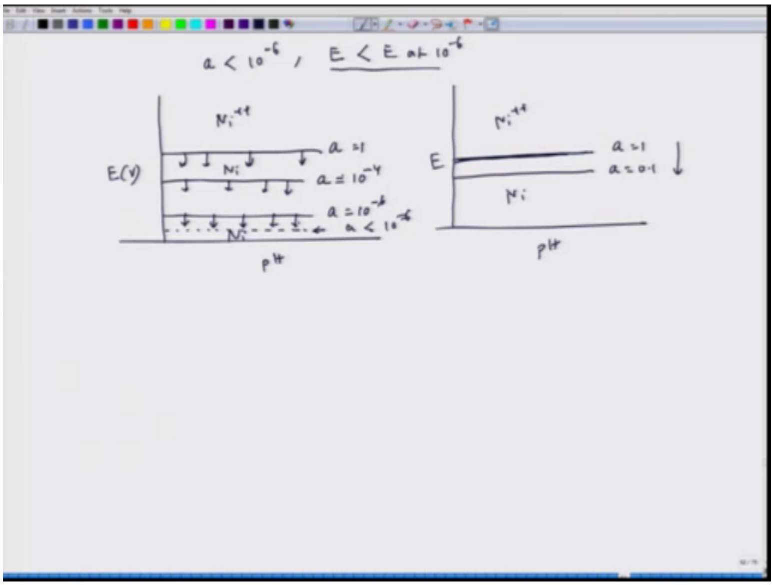

So, that means, but question is if we go further down if let us say activity is less than 10 to the power minus 6. So, what could be the potential, so that potential would be less than the potential at 10 to the power minus 6. Now we see that 10 to the power minus 6 is my limit to measure nickel ion concentration, then of course when we achieve this situation we would only see nickel. Now if I redraw that particular diagram this is pH this is E volt, so we get this is a equal to 1 this is a equal to 10 to the power minus 6 and now some a less than 10 to the power minus 6.

How do we measure this concentration? We would have potential here at this point, but here we are not able to measure nickel ion so that means nickel is only there. What does it mean, that below this line we have nickel because, we are not able to detect any concentration below 10 to the power minus 6. Now let us say we assume that we cannot measure our concentration a if it is 10 to the power minus 4, if we say that activity below this we will now we are not able to detect any nickel ion. So, we would definitely say the below this activity 10 to the power minus 4 there would be all the things will be nickel. So, what does it mean, that means line below this only nickel is present.

So, what happens on top of it? So, on top of it definitely we have nickel ion, so this is nickel ion and here it is nickel. So, if I try to see again so any line which indicates that reduction reaction for nickel ion reduction, which is parallel to pH axis below that line we have nickel and above that line we have nickel plus plus. Now interestingly as we increase decrease the activity we are actually pushing, we are actually extending the nickel ion stability. So, this is activity equal to 1 and then if this is the activity equal to 0.1.

Like that way as we are decreasing activity of nickel ion or detectable nickel ion we are extending the nickel ion region and contracting the nickel region. So then of course, the bottom part would be a bottom part of this line would be bottom part of this line would be definitely nickel and top part would definitely be Ni plus plus. So, now we are clear that which side is nickel and which side is nickel plus plus.

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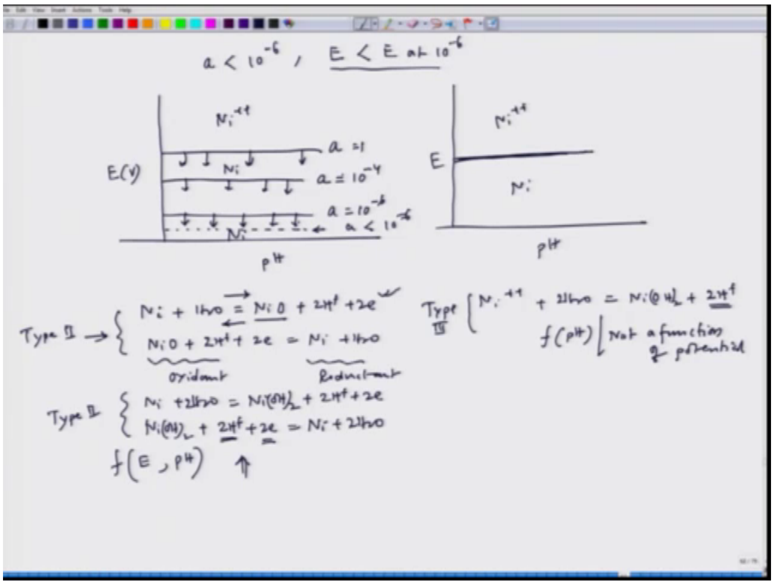

So, this is the situation for the first reaction which is type 1 type where we have potential dependency but it is pH independent, we can now we have 2 spaces one is nickel, one is nickel plus plus. So, the nickel ion can react with H2O and then form NiO these reaction is possible and these reactions you see that whenever nickel is forming nickel ion is first forming and then that would again react with H2O to form NiO. Interestingly if we see the forward reaction it is an oxidation reaction, but if you see the backward reaction it is a reduction reaction.

So, since we always consider the reduction reaction in order to find out potential, so we can write this entire reaction reverse. So, it becomes nickel oxide 2H plus plus 2 e equal to Ni plus H2O, so this side is oxidant and this side becomes reductant and similarly for nickel ion we can also react with H2O and then form nickel OH whole 2 plus 2 H plus we can have this reaction. Now, interestingly you see that these reaction is type II and this reaction is type III, now we can also construct another nickel plus H2O it can form NiO H whole 2 plus 2H plus plus 2 e or we can reverse we can write reverse NiO H whole 2 plus 2H plus plus 2 e equal to Ni plus 2 H2O, this is also type II.

So that means, we see that we again have 2 types of reaction one is type II another is type III, these reaction is pH as well as potential dependent, this is only function of pH and no not a function of potential. Since here only we have H plus ion presents but no electrons are involved in this reaction and but here we have electron involvement as well as hydrogen ion involvement. Now first look at this type of reaction, so first consider this is a simple type let us consider that.

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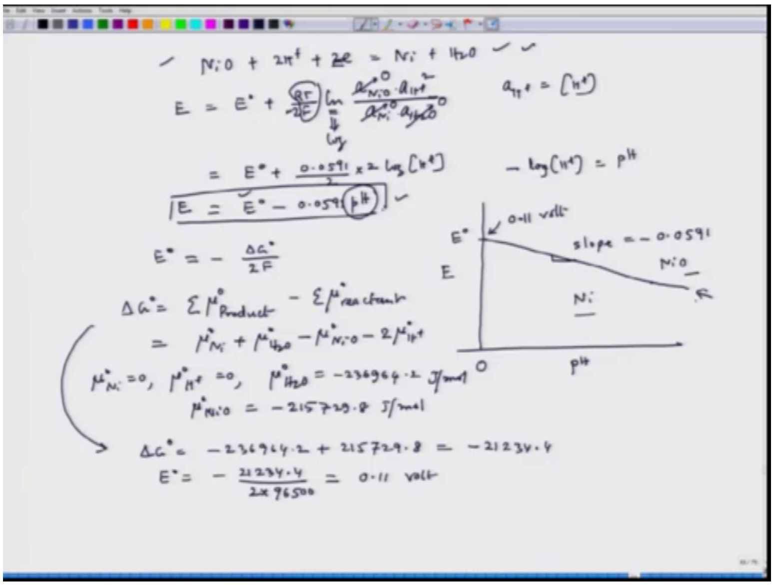

So, when I consider that so NiO plus 2 H plus plus 2 e equal to Ni plus H2O, now we have to find out a Nernst equation for this. So, Nernst equation so I am not writing ox and reduct like that, so this is the oxidation the left side is oxidation part and right side is basically the redactor part; so, E 0 plus RT 2 F ln activity of NiO activity of H plus square activity of Ni and activity of H2O.

Now, since this is a solid and it is a pure solid so it is 0 this is 0 this is also pure 0, so we are left with a H plus; now if we assume that the system is maintaining ideality. So, a H plus we can consider with the concentration and then if we convert ln to log, so we can write the entire this particular stuff in addition to this we can write E 0 plus 0.0591 by 2 into 2 log of H plus or E 0 minus 0.0591 pH since minus log of H plus equal to pH.

So, we can plot this reaction this equation on a E versus pH plot. Now, definitely these are a negative slope see if I try to see E versus pH, so that pH 0 I would get E 0 and then as the pH is changing. So, the there would be a straight line this is a plot of a straight line with a slope minus 0.0591. So, we have to find out E 0, so E 0 is nothing but n F and here n F is 2 F because, there are 2 electrons involved delta G 0 is equal to summation of chemical potential it should be product reactant then mu of nickel mu 0 mu 0 of H2O minus mu 0 of NiO minus 2 mu 0 of H plus.

So, again we know that mu 0 Ni equal to 0 mu 0 H plus equal to 0 these are convention, now mu 0 H2O is equal to minus 236964.2 joule per mole and mu 0 NiO equal to minus 215729.8 joule per mole. Then minus 236964.2 plus 215729.8 is equal to minus 21234.4. Therefore, E 0 be equal to minus 21234.4 divided by 2 into 96500 is equal to 0.11 volt.

So, for this line this point would be 0.11 volt; since when pH is equal to this equal to 0 then E equal to E 0. So, you do get a plot, now which side would be nickel and which side would be NiO, definitely this side would be nickel and this side would be NiO. Now we see that this side we have said that this side is nickel and this side is nickel oxide, in our next lecture we will understand why the below this line we have nickel and above this line we have nickel oxide.

So, let us stop here, we will continue our discussion on Pourbaix diagram of nickel in our next lecture.

Thank you.