Corrosion – Part I
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Lecture - 24
Construction of Pourbaix diagram for Ni-H2O system and AI-H2O system

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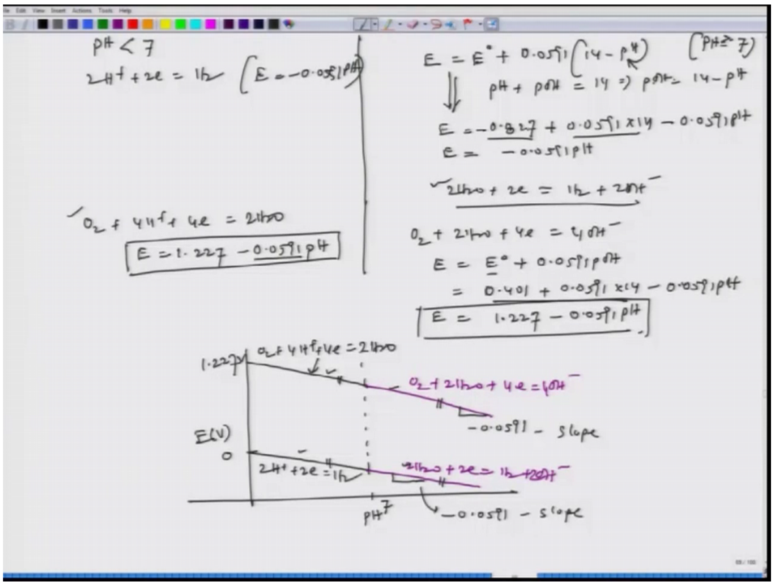

Let us start lecture 24. In the last lecture we ended with that discussion on plotting water lines, if we go back to our last lecture we saw 2 lines one belongs to lines involving O 2 and one involved H 2 rather evolution of H 2. Now, we see that this is one line, this is second line, third, fourth and both the lines all 4 lines for example, this 2 line are merging because they have the same slope minus 0.0591, here also they are merging in the same line this one as well as this one.

So, here also slope was minus 0591 is basically slope this is also slope. Now as we have said that these 4 lines are equally important and these 4 lines are to be merged with nickel those 3 lines what we have drawn as well as the stability regions of those phases, here what will do?

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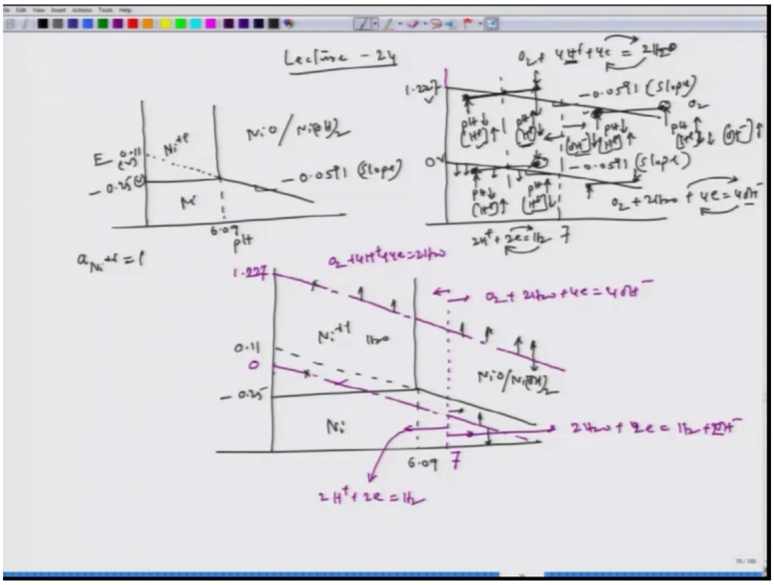

We will try to merge them. So, this was nickel this is p H and we are trying with. So, we saw that the slope was also minus 0.0591 slope this is N i O or N i OH whole 2. Rather I put it like this because they are have they are basically belonging to the same family. So, H this is N i plus plus region and this is N i, this is 0.25 and if we extend this line, this will be 0.114. This is one set the another set is reactions involving this is 0, let us say this is 0 slope was 0.0591. Of course, we have a p H 7 and here the p H is 6.09 when activity of nickel plus plus equal to 1 and there is one more line which is the slope 0.0591 with a minus sign.

Of course we have seen that below this line acidic reactions, those are reactions for the acidic part would happen and on the right side basic reactions would happen and then if we club them. So, let me draw the water lines this is 0 let us say this is 0, this region is N i plus plus this is N i and now before this beyond this, and then here also we get this reaction, on the left side this line H 2. Now we know the regions in nickel system N i plus plus N i N i O or N i OH whole 2.

But we have to also see the regions this is 1.227 volt, this is 0 volt this is 0 volt. We have also see that on the right side for example, if we consider this particular p H, right side of it and left side of it what are the phases that could be stable or that would be the continuity. Similarly, here also if we see the right side and left side we have to see for example, if we reach to this position and this position what are the phases is that could be possible, that would be decided by the reaction equilibrium at that point because this particular diagram also talks about the equilibrium between different phases.

So, let us consider and that is what we once we finalize what are the phases that are possible, then we can also finalize what are the phases that would be existing between this line and this line as well as what could be possible above this line and below this line as well as here above this line or below this. So, in order to do that we have to see the reactions; first for example, consider what reactions is possible at this point, which is the equilibrium point. Now, the reaction that is possible is O 2 plus 4 H plus plus 4 e equal to 2 H 2 O.

Now once it reaches equilibrium. So, since I am not changing the potential I am changing the p H. So, if we are here and if we are here both the cases the p H values are different. Now if I consider that oxygen partial pressure remains 1 atmosphere and H 2 O definitely it will be always considered to be pure and then it does not its activity is considered to be 1, then depending on O H values this p H values I can get different concentration of H plus ion. So, left side p H is less, but which OH and sorry this should be H plus ion; H plus ion concentration is more.

And here we have p H is more. So, H plus ion concentration is less. So, they are inversely proportional because there is a minus minus log of H plus ion concentration is nothing, but the p H. So, now, at this position if we have high amount of H plus in order to maintain equilibrium, the reaction should move this way. So, if we move this way. So, left side of this particular point will always have H 2 O and similarly on the right side since p H is more. So, H plus ion concentration is less, in order to maintain equilibrium the reaction should move this way.

So, beyond at this point we have oxygen evolution ok. So, more amount of oxygen would generate. Similarly if we have if we consider this; so, at this point similarly on the neutral or basic region also depending on the p H for example, here we have p H more, H plus ion concentration is less here p H less H plus ion concentration is more; now here is a problem. The problem is we cannot though we see that this particular situation holding true, but here when the p H is more than 7 we do not have the existence of H plus ion.

So, we have the existence of O H minus ion. So, if we have H plus ion to be less. So, O H mine ion concentration would be more and here H plus ion concentration is more. So, O H minus ion concentration would be less and when the p H is more than 7, the reaction is H plus plus 2 H 2 O plus 4 e equal to 4 O H minus. Now at this point, we see that the O H minus ion concentration is less sorry we put a wrong connotation here. So, p H is less the H plus ion concentration is more.

So, we see that this point we have higher O H minus ion concentration compared to this point. So, if you have higher O H minus the reaction would move this way so, will have oxygen generation oxygen generation. And so, the oxygen generation would be always on top of this line, this line and below that we have H 2 O ok. So, now, let us see what happens for the reactions which are not involving oxygen rather H plus and O H minus. And of course, on the line right side of 7 we have H 2 O involved.

But interesting if we consider this point again just I forgot to mention that, we have less amount of O H minus. So, then the reaction should go this way; so, would which would increase the p H level of the system. So; that means, it will also increase the O H minus ion concentration trying to increase the O H minus ion concentration. Now let us come back to these 2 points, now here p H is more and p H is less here. So, H plus ion concentration is more and H plus ion concentration is less here. So, now, we consider this reaction.

So, then at this position since the H plus ion concentration is more. So, the reaction would this way go turn the right side. So, gaseous hydrogen would generate below this line. Now if I consider this point there H plus ion concentration is less. So, the reaction would try to go this way. So, we have more and more H plus ion concentration, and then it will increase the acidity of the water system. Now, similarly we can have similar argument here this.

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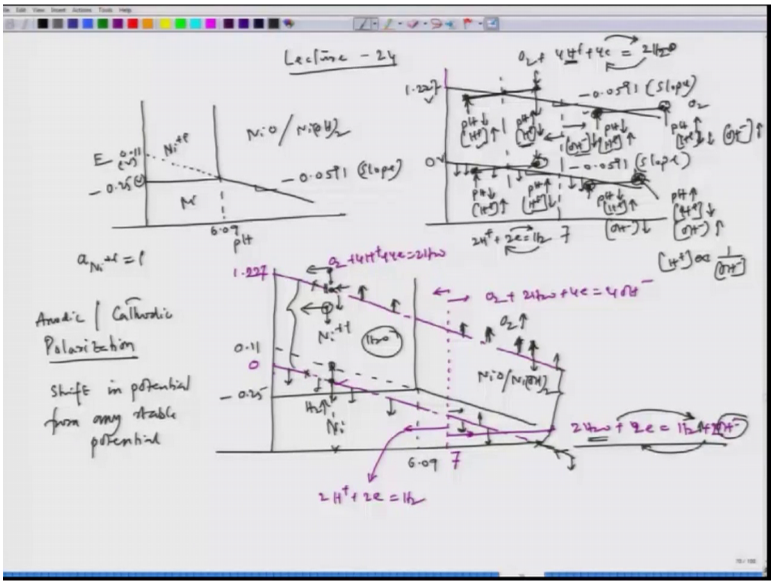

And this point we can have p H high sorry p H is less H plus ion concentration is more, O H mine ion concentration is less and here p H is high H plus ion concentration is less and O H minus ion concentration is more because p H and p O H are inversely proportional. So, I can say sorry not p H and p O H rather H plus ion concentration is inversely proportional to 1 minus. So, this is the relation we have so, that is what we have this particular correlations. Now if I take these things in these particular equations, if we consider at this point first their H plus O H minus concentration is less. So, this concentration is less.

So, the in order to maintain that concentration, the reaction should go on the right side. So, hydrogen evolution again starts. So, below this line we have hydrogen evolution and at this point, we have H plus O H minus concentration is more. So, this concentration is more. So, the reaction should go this way. So, water we will get water so; that means, below this line we have H 2 gas and above this point above this line, this water line we have O 2 evolution and within this zone we have H 2 O.

So, this is the basic mode of constructing this Pourbaix diagram, now what is the importance of specifying that which one would be O 2 and which one would be where would we get O 2 gas evolution and where would we get hydrogen gas evolution, that would be decided by the potential p H coordinate during polarization. So, will talk about polarization later on, polarization for the time being let us understand this polarization.

Polarization is nothing, but the shift in potential from any stable potential. Now here we are talking about equilibrium so, it is basically the equilibrium potential.

Now, if we somehow I am here and I am here, now at this point my potential p H is this and at this point my potential p H is this. Now here once since the p H I am not changing. So, I am changing the potential once I go from lower to higher potential, once I cross this particular line then we would get oxygen evolution and we do get bubbling when we do experiment during polarization. Polarization means if this is my stable potential, this point is stable potential or the equilibrium potential if I go to positive side we call it anodic anodic polarization, if we go to negative side we get cathodic polarization.

So, during cathodic polarization, in this case we get water and if we do anodic polarization from the equilibrium polar potential, we get oxygen evolution. Similarly here if you see this is the equilibrium potential at that p H value, this is the p H value. So, now, if we go anodic polarization; that means, the polarization is taking place from the positive side from the on the positive side from the equilibrium potential. So, then we get water and if we go below that then we get hydrogen evolution that is what happened during polarization.

So, will talk about that later on; so, for the time being that is what we have to make sure that which region is water lined water and which region is gas. So, on top of this particular line where it involves oxygen, we have oxygen evolution and that these line which involves H 2 evolution. So, below this line we get H 2 or the gas evolution H 2 gas evolution.

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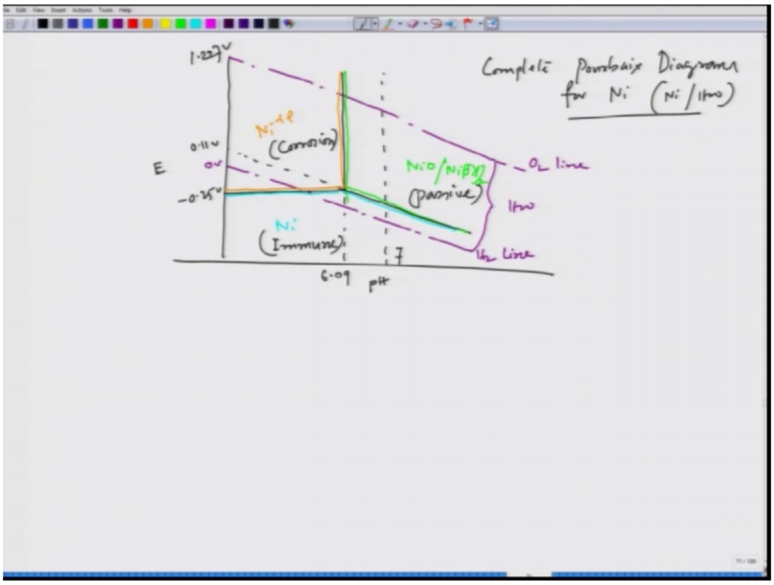

So, the final diagram we have to do it this way, this is p H this is E. Let me do the hydrogen line, this is basically hydrogen line. So, below this line we have hydrogen evolution and this we call it oxygen line, above that we have oxygen evolution and between this. So, let me draw it with between this we get H 2 O and this zone this zone is N i O N i O H whole 2, this zone is N i plus plus and this 1 is N i. So, this is my complete Pourbiax diagram for or we can say for nickel. So, it is basically indicating H 2 O system fine. So, we have done this is basically the simplified version.

In nickel there are other reactions involved, and we can call it as corrosion zone this is immune this is passive. Now let us take one more example. So, here I will not draw the diagrams, I will not to the do the calculations I leave it to you to the, to do the calculation, but there is a small cracks here. So, I will discuss that cracks here. Because whenever we do take equilibrium we have to club it into 2 segments is basically we have to see those equations the reactions, and accordingly will choose we block them actually we will segregate them into according to the reaction species that are involved in those reactions. So, best example is aluminium.

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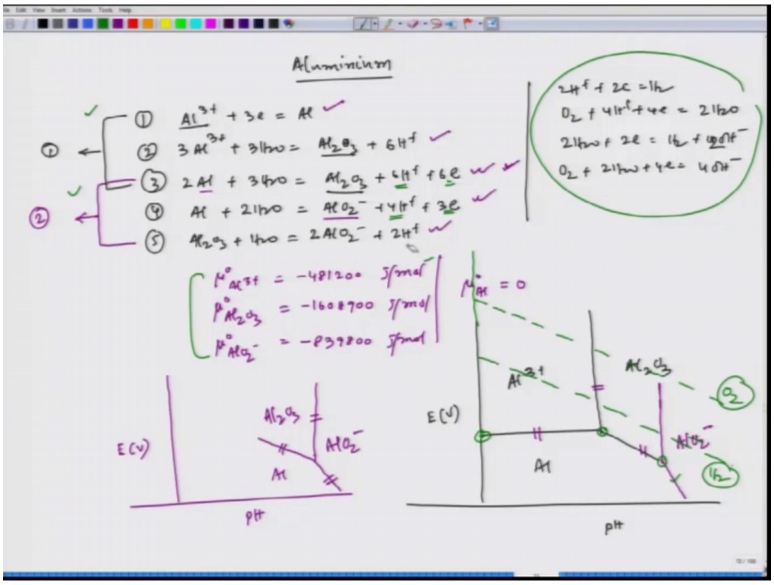

So, in aluminium system we can have following reactions and here I am taking one extra species, then you will understand why I am saying that, that reactions after looking at the reactions you have to block them you have to segregate them in segments. So, aluminium these are the reactions you can consider, then 3 Al I am just writing the equations first and then of course, we have water equations.

So, we have written all those equations, now you see that this 1 2 3 this 3 equations that be can be clubbed together, because here we see 3 products 1 3 species rather 1 2 and then 3. So, this H plus and H 2 we are not considering the species here, because we have to see the metal reactions first the way we have seen in case of nickel and then will talk about water reactions. These 3 can be clubbed. This is club number 1 and the another clubbing that is possible if we see 4 5 the clubbing could be this 2.

Now, first we see that aluminium and Al plus 3 and Al 2 O 3 are the reactants or the products that involve aluminium. And in the second set we see aluminium Al 2 O 3 and Al O 2 minus these 3 species are involved involving aluminium. So, second set we do not have Al plus 3 and the first set we do not have Al O 2 minus. So that means, the first set whenever we see those phase boundaries or rather stability diagrams, then that will involve only those equilibrium between all 3 phases like Al 3 plus Al and Al 2 O 3.

And the second set would involve equilibrium between Al, Al 2 O 3 and a l O 2 minus. And then you can have those data you already have the water data then all you need to have mu of Al 3 plus equal to minus 481200 joule per mole then mu 0 0 Al 2 O 3 equal to minus 1608900 joule per mole and mu 0 Al O 2 minus equal to minus 839800 joule per mole and remember mu 0 Al would be 0.

So, once we have data and then H 2 O mu 0 H 2 O you can find out from previous lectures, mu 0 H plus as well as mu 0 O H minus you can find it out from the previous lectures. Now, if we draw the Pourbiax diagram, you will see that the first 3 set will have diagram like this. So, here it is Al 3 plus A l and A l 2 O 3 and the second set we will have diagram.

You will have this diagram. So, you see that this indicates this line this one indicates this line and this one indicates this line. And, here this one is nothing, but this one is nothing, but this and this one is nothing, but this. So, if we club them you will see that the plot will come here minus and of course, you will have diagram for this 4 reactions. So, those diagrams in this will be much below, this is a very highly negative from this value you can find out; we will see the this would be hydrogen line and then oxygen line would be above that this would be oxygen line.

So, this is the complete Pourbiax diagram for aluminium H 2 O system. Only thing is you need to find out these values from these data and then plot it by doing this clubbing this 2 clubbing, you should get it. And another important aspect is here you will see the slope is decided by the number of electrons and number of hydrogen that are participating in the reaction, which involves up potential and p H.

So, let us stop here, we will continue our discussion in our next lecture.

Thank you.