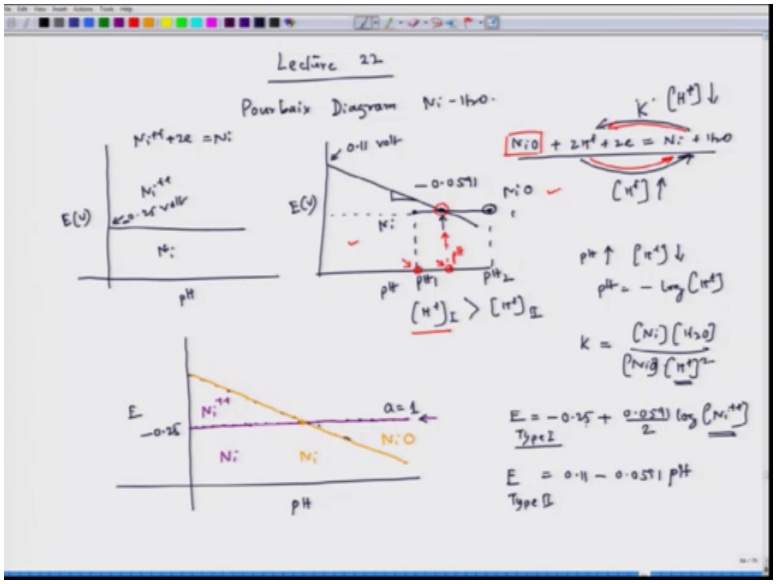
Corrosion – Part I
Prof. Kallol Mondal
Material Science Engineering
Indian Institute of Technology, Kanpur

Lecture - 22
Construction of Pourbaix diagram for Ni-H_2O system-II

Let us start the lecture 22.

(Refer Slide Time: 00:19)



So, we will continue our discussion on pourbaix diagram of nickel hydroxide nickel H 2 O system. Now we have plotted nickel plus plus this we have 10 calculations for simple nickel ion reduction to nickel and then we have gotten another plot this is type 1 and then another plot was like this with a slope 0.591. And here it was 0.11 volt and here it was 0.25 volt with a minus sign. See this two, type 1 and type 2 one of the type two reactions we have considered and then try to plot them.

Now, we have seen we have told that this side is nickel and this side is nickel oxide and here the reaction is nickel oxide plus 2 plus 2 equal to Ni plus H 2 O and this is Ni plus plus 2 e equal to Ni. Now let us see whether this side right side would be Ni oxide Ni O. So, let us have a parallel line and I am changing the PH; this is PH 1, this is PH 2 and the potential remains same and this is the so we see that left side let us see that when it is PH 1 what is the hydrogen ion concentration. So, the PH 1 hydrogen ion concentration is this let us say 1 and here H plus 2.

Now, if we increase PH concentration of H plus ion decreases, since PH is equal to negative log of H plus ion concentration. Now for this reaction, we can consider reaction equilibrium constant which is K, so this K can be written as Ni or in terms of concentration so we can write this what this chemical reaction. Now we will see that K is constant at this point K is constant, because we have attained equilibrium. Now if we increase H plus ion concentration, then the system should go this way in order to maintain the reaction equilibrium constant.

And if we decrease H plus ion concentration the system should go this way. So, this is H plus ion concentration increasing and on this side is decreasing. So, now, if we increase PH if we have this point if we increase PH, so if we go to this point I am reducing H plus ion concentration.

So, here H plus ion concentration if I try to have a relation between these two, so this should be this and now once we have this situation then if I go from this point to this point because at this point this equilibrium has set up. So, H plus ion concentration is decreasing so then of course, then reverse reaction so this reverse reaction should take place reverse reactions should take place. So, that time nickel should get oxidised to form nickel oxidize nickel oxide so that means, this side definitely should then be Ni O.

Now, if I go to PH 1, then I see that H plus ion concentration is decreasing in comparison to of course, this one this was also having some PH level. So, this PH at this point is more than the PH at this point, so at this point PH plus ion concentration would be more than the H plus ion concentration what is there at this point. So, which is indicating the PH level at on the line of that e verses PH plot, so once we see the hydrogen ion concentration is increasing. So, in order to maintain this equilibrium constant we have to go to the other side that means this side. So, then this region definitely should be nickel and this region should definitely be Ni O.

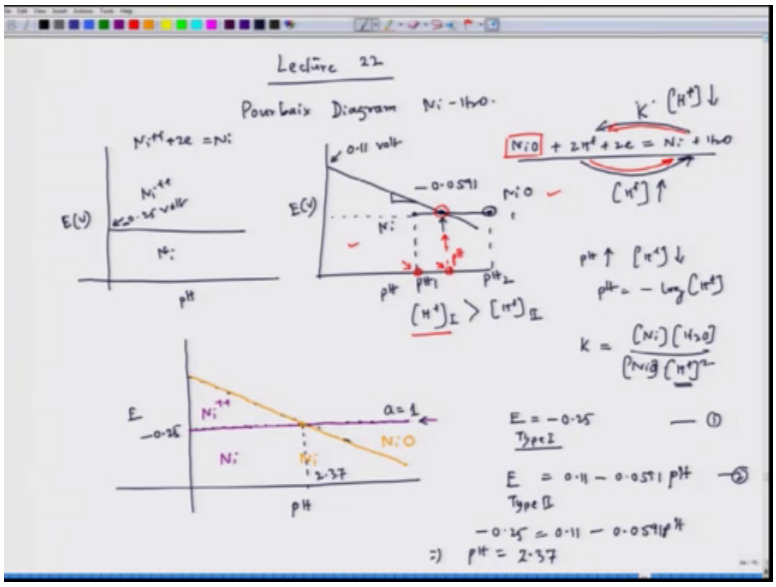
Now, can we combine these two? So definitely we can combine. Now once we combine let us see what situation is arising. So, this is E, this is PH, so first draw dotted line and then we have this. So, now, we can have two different colours this is for type one reaction this is for type two reactions.

Now for type one we know this is nickel side this is nickel plus plus side and for type two this is nickel side this is nickel oxide side. Now already we know if we consider this

is the connection between these two this connection point can be found out by simply solving two equations what we have already found out one equation is for the type 1 is minus 0.25 plus 0.591 by 2 log of Ni plus plus. So, instead of activity we are writing in the form of a Ni plus plus and this is type 1 and E type two is equal to 0.11 minus 0591 PH.

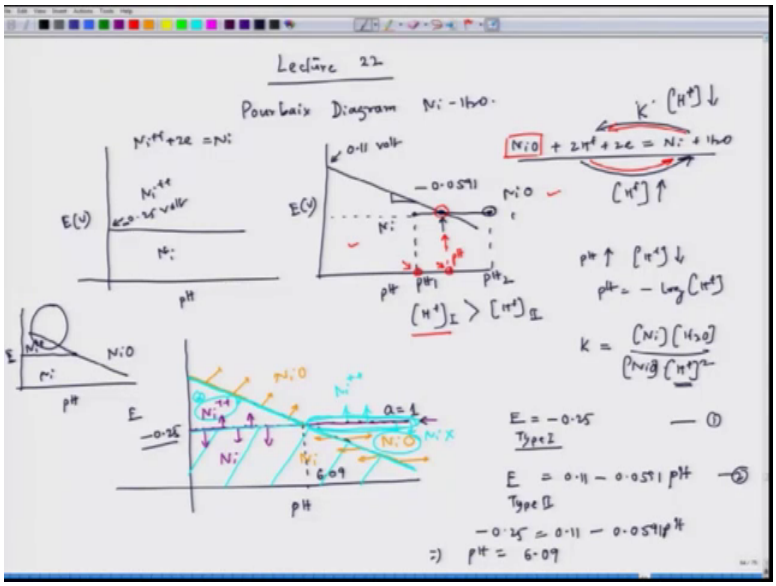
So, these two equations if you solve for a particular nickel ion activity or concentration we can get to know the potential as well as PH value. Remember for that case we have to fix certain concentration of nickel ion or activity of nickel ion let us say we fix this nickel ion activity to be 10 to be one let us say. So, then this point would definitely by would be minus 0.25 now that case this equation this type one equation would simply be this.

(Refer Slide Time: 09:40)



This is type one this is two so then we can get at this point these two equations are equal so minus 2.5 equal to 0.11 minus 0.0591 PH. So, we get PH is equal to 2.37 is so the PH this PH value is nothing, but 2.37 if we solve this we can definitely get to a sorry I think we made a mistake in the calculation. So, it should be 0.25 plus 0.11 equal to divided by 0.0591 equal to 6.09.

(Refer Slide Time: 10:35)



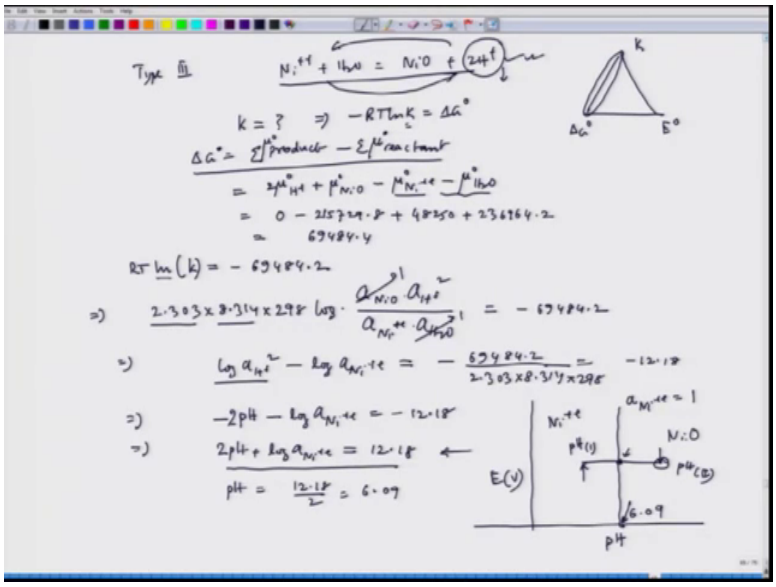
So, this is this value is 6.09 this is the PH level and potential of course, it will be minus 0.25 if we consider activity to be 1. Now, we have to decide whether some of the parts of these 09 lines can be possible on the stability region of three species. Now where we are having stability of Ni plus plus as well as Ni and Ni O. Now we know this region is this left to this is Ni right to this is Ni O below this is Ni above this is Ni plus plus so right to this Ni O.

Now we see that in this zone we have no confusion because here we are not having any Ni plus plus or Ni O, but if we consider this zone on top of this particular line we see that Ni plus plus is stable and below this line we should see Ni, but actually Ni Ni plus plus stability line indicates that this region should be Ni plus plus.

So, this particular line this particular line we cannot definitely say that it should exist completely because we do not know what is the relation between Ni plus plus and Ni O for that reason we have to go for the type three reaction. And similarly if we see this part right top of it should be Ni O Ni plus plus and bottom side it should be nickel, but already we know that on the right side of this line it should be Ni O. So, nickel should not be present on the on top of this line. So, this particular region of the line it should not exist because that line indicating the equilibrium between Ni and Ni plus plus, but we see that in this zone we have in this particular zone we have Ni O after seeing the type two reaction.

Finally, if we club it if we see the clubbing, so it should be it should be like this. So, we know this is Ni this is Ni O this is Ni plus plus, but we have no idea what is going on here in order to do that we have to consider another reaction which is type 3 type.

(Refer Slide Time: 14:46)



It indicates equilibrium between Ni plus plus and Ni O. Now from this reaction we see that there is no involvement of electron if we don't have no involvement of electron. So, as per this triangle we see only this region we can work with see if we work with that particular region then we can find out K value. In order to find that we have to find out a relation between we know the relation between delta G 0 and where K is the equilibrium constant for this reaction.

So, delta G 0 would be again then summation of product minus summation of sorry mu 0 mu 0 of reactant. Now we can see from this reaction mu 0 of product is this is the reaction equation we are getting we have already known this value this is 0 this is 0 point this is this value becomes minus 257, 215729.8 this value is it will become plus because this value is minus 48250. This would also become plus because the value of mu 0 H 2 O is 2 3 6 minus 236964.2 so 236964.2.

So, if we get this value this becomes 69484.4 so k becomes or rather RT ln k is equal to minus 69484.2 we can do little bit of juggling with this k. So, instead of RT ln k I can write 2.303 into 8.314 into 298 Kelvin since we are considering 25 degree Celsius this is

r value universal gas constant and log since we are converting log ln to a log. So, that is what this multiplication factor 2.303 is coming up.

And then so far this k case if we consider in terms of concentration Ni O or we can write since we are writing in terms of activity; activity of Ni O and activity of H plus activity of Ni plus plus H 2 O. So, these two goes to one because these are pure substance and now this equal to minus 69484.2. So, log of minus log of equal to minus 69484.2 by 2.303 into 8.314 so this value becomes of course, into 298 it becomes minus 12.18 therefore, this is nothing, but minus if I consider activity to be concentration of H plus ion considering that the interaction parameter is one or activity coefficient is one rather.

So, this becomes minus PH minus log of a Ni plus plus equal to minus 12.18. So, I can simplify PH plus log of a Ni plus plus equal to 12.18 this is the equation we are getting to indicate the equilibrium for this particular reaction. Now once we know this equation then we can also plot this on E verses PH for a particular concentration of or activity of Ni plus plus ion. So, this is PH axis this is potential since here we are not having any potential value definitely this particular reaction would be parallel to potential axis because it is becoming potential independent reaction. So, it will be like a parallel line parallel to potential axis and where of course, the activity of nickel plus plus ion is to be mentioned.

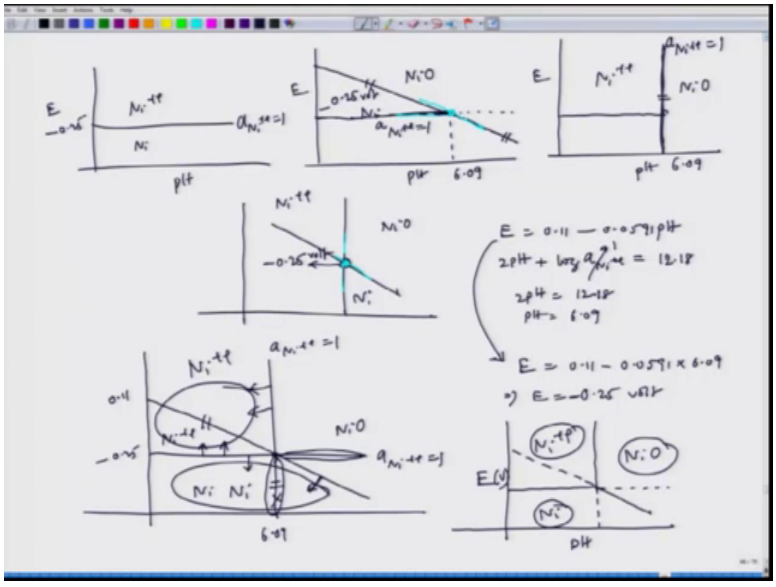
Now, if we mention that I think we made a small mistake here so there should be two here 2 PH because this power 2 would come. So, now, if we consider this is to be one then the PH value at which this particular equation would be valid PH would be 12.18 by 2 equal to 6.09, so this PH would be 6.09 this is the point. Now here we can definitely say which side is nickel plus plus and which side is nickel oxide because this is reaction which is equilibrium between nickel plus plus and Ni O. So, if we draw a parallel line to PH axis this is the PH where the system has reached equilibrium. Now if I go to PH level PH 1 the PH 1 the concentration of H plus ion is definitely more than the value what is there when the PH is 6.09.

Because if we have decrease in PH value the activity of H plus ion increases or the concentration of H plus ion increases, so that time since I am increasing this H plus ion concentration. So, in order to maintain the equilibrium constant the system should go this way reverse way. So, the Ni plus plus ion should form so this side is Ni plus plus. Now if

I go at this point which is PH 2 where the hydrogen ion concentration should be definitely less than a the PH at this point which is the equilibrium PH.

So, in order to maintain the equilibrium since the hydrogen ion concentration has decreases at this point. So, system should go forward direction in order to maintain the hydrogen ion concentration and that is what the, if it goes to forward direction Ni O should form, so this side would be definitely Ni O. Now, interestingly we have three plots.

(Refer Slide Time: 24:32)



One is type one another one is type two another one is type three which is this; this is PH this is PH and here we see that this is Ni this is Ni plus plus this is Ni Ni O Ni plus plus Ni O. If activity of nickel plus plus equal to 1 this is 0.25 and that time this value goes to as we have calculated before 60.9, when activity is Ni plus plus equal to 1 and this is also 6.09 when activity of Ni plus plus equal to 1.

Now we can club these two now here we can club these two lines since we have seen that this particular extended line should not exist because it is the region of Ni O. But we are not sure whether this particular line would exist because we are not sure whether it is a nickel plus plus it is a mixture of nickel plus plus and Ni O zone.

So, now if we try to solve equation this one and this one let us see what happens what is the point we can achieve. So, if we this is line and this line rather I would say that this is

nickel plus plus Ni O Ni now I would like to find out this point. So, we can definitely find this point by solving E equal to 0.11 minus 0.0591 PH and 2 PH plus log of activity of Ni plus plus equal to 12.18 and since we are considering this to be 1. So, then 2 PH equal to 12.18 so PH equal to 6.09 so if I put this here E is equal to minus volt.

So, you see that this point the potential also becoming minus 0.25 and here also it was minus 0.25 volt the connection between this line this line and this line was this and when I try to see the connection between this and this. So, there are also the same point we are getting the same co-ordinate we are getting on E verses PH plot. So, we would get a plot like this now we combine all three reactions, this is reaction 1. Now we see that this reaction also should go through the same coordinate which is minus 0.25 and PH equal to 6.09 and also this line should also continue like this; this is 0.11 0.25 6.09 this is activity of Ni plus plus equal to 1 activity of Ni plus plus equal to 1 this side is nickel nickel plus plus nickel oxide.

Now, interestingly last time we saw that this particular portion of the line should not exist we were not sure about this particular line. Now once we get to this particular line for the type three we know the left of this line should be Ni plus plus then if it is done on on top of this we should have Ni Ni plus plus. So, this entire zone should be Ni plus plus and what about this line now we know below this line its Ni left to this particular line is Ni, so this entire zone should be Ni so this portion should not exist.

So, if I draw the final region whatever is not able to exist whatever line that portion we will draw with a dotted line and then we can plot the regions Ni plus plus Ni and this is E this is PH. So, we see that we can distinctively specify the stability regions of three species this species this one and this one. So, in nickel H 2 O system we have consider three simple reactions and then, try to see the stability regions in E verses PH plot. So, we will have more on this pourbaix diagram we will stop here for the time being and next class we will start with four important reactions which are PH as well as potential dependent that involves those involve no metal or metalize rather those involve oxygen H plus O H minus and H 2 O let us stop here.

Thank you.