Indian Institute of Technology Kanpur

Present

NPTEL

NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING

Environmental Degradation of Materials

Module Lecture 08

Broad Subject: Pourbaix diagram

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Let us start here we have ended in last lecture. We have already plotted for this diagram for nickel and that diagram like this. So it should connect here. So this is the diagram for and this is coming at pH equal to 6. If the concentration of all the species, ionic species are 1 and this is Ni^{++} region. This is Ni and this is Ni which whole two NiO We have seen that. Now we are left with the reaction which involves hydrogen ion, water and oxygen. We have already seen and this coming and touching at 0.11 volt this is -0.24 volt it's not exactly according to the scale but this should come like this. Now we have already seen if this is my zero volt, zero volt we have already seen the equation H+C going to H_2 that case we have seen this can be related to $E=-0.059\ pH$. So this is -- this can be again this equation can be again plotted in this E versus pH diagram which is nothing but from zero it will start because when it is zero volt that time the pH should be zero because if you extend this relay then it could come $E= E_0 -0.059\ pH$. This is nothing but RT by F you just put that value 8.314 into 2.303 it would become -- so this would become if you take R equal to 8.314 into T which is at 25 degree Celsius, 298 Kelvin and F is close to 96500 coulomb per gram equivalent then you will see that this equal to this close to 0.059 then there will be other parts also. So we are taking it as 0.059. So if pH is zero then this would become E equal to zero for this reaction and already we know that E0 for hydrogen reaction is zero. So this value, pH value should be zero.

Now we have started with the next relation. Next equation which is H_2O+2e going to H_2+2OH^- this is another reduction process. So we have started calculating now we have already seen that this becomes which is ox/red would be equal to E0ox/red minus if you simplify it then it would become 0.059. Now you can also use one or you can even omit this one because it's in three decimal part if you keep it. So then this is become OH^-. Now the same relation we have to find out what is the value of E0 and for the value of E0 would be equal to the delG 0 for this reaction with a minus sign because delG0 equal to -NFE0 and N is 2 here. So this should be 2 into F which is 1 Faraday. Now this del0 we can also find out -2 of 157147.1 now plus because this would come in the form of reactant. So this would be 2 into 236964.2. This would be by 2 into 96500. They should become if you do this calculation then this value would become -0.8 it would become 0. – just let me let me find it out 0.8 -- just hold on let me find it out. It would become 0. --- 0.827 volt.

Now let me put this value here. So let me remove this part. Let me also remove this part. So 0.827 minus sign. Now OH- can also be converted into H+. It can be – the same thing can be written in terms of H+ sign concentration. How would we do it?

Now similarly for H2O, H++OH- can dissociate into H++OH- sign for this reaction we can also calculate what is equilibrium constant, K, would be equal to an if you have this situation let's say an equilibrium and it's a neutral condition, then K would be equal to H+ concentration, OH- concentration, H2O and this is in pure H2O form. So this should become one. So the K would be equal to this. Now K is also related to delG0. So K, Lnk would be equal to delGO minus RT. Now if you write in the form of log so the same thing you just change it to log and here you put 2.303. And now if you put this delG0 which is nothing but Mu of OH- plus Mu of H+ - Mu of H2O. There is a minus sign RT into 2.303 and at 25 degrees Celsius you put all these values we would get which is close to -14.01.

So now log is nothing but -14.01. let me remove all this part now. So this would be equal to 14.01 into 10 to the power minus 14.01 they should be 10 to the power minus 14.01 because we have seen log of K will be equal to in a neutral condition -10 to the -14.01 which you can write as 14. So K would be equal to 10 to the power -14. So I am just removing the decimal parts, and then I am writing 10 to the power -14 and again for H2O when it dissociates it forms if it forms 1H+ ion similarly it would also form 1OH-ion so number of H+ ion would be equal to number of OH- ion. At the same time the concentration of H+ ion would be equal to OH- ion in the neutral condition.

So then it can – you can write it as H+ square equal to 10 to the power -14 in the neutral condition, so it becomes H+ ion concentration in the neutral condition would be 10 to the power -7. Now what would be the pH of neutral solution? So pH would be -log of concentration of H+ would be equal to 7. So neutral condition the pH of the solution or H2O water would be 7.

Now from this relation we can write OH- ion concentration in the form of OH- ion concentration let us say let me - equal to 10 to the power -14 by H+. So I replace this OH- concentration in the form of, replace this in this place. So if I replace this we would get equal to -0.827, -0.059 log of 10 to the power -14 H+. So this should become -0.827 -+ 059 into log of 10 to the power -14+ so there will be minus sign because I have not taken this minus out, + log of 0.059 log of H+ and it would be minus sign, sorry there would be a plus sign because this minus and here would be a minus sign so that minus minus would become plus.

Now if you take this if you make it 0.827+ you will see that though we have taken 0.059 actually this value is coming from 2.303 RT by F and if you put the values at 25 degree Celsius you would see that this is actually 0.0591. So if you multiply this to 14 because this 14 will come out, you will see that it becomes 827 and if you take minus out then it would be -0.059 log of H+, sorry 0.059 into pH. So because -log of H+ ion concentration is pH. So this becomes E ox/red would become 0-0.059 pH. Now this is the equation for this relation basically this reaction and for this reaction also we have seen E equal to -0.059 pH. So the both the relations final relation is same, both the relations are same. So that means practically these two lines if you plot this line from this equation in the pH versus E versus pH diagram as well as this reaction in the form of this both should merge. So that means they should merge and this line, this dotted line indicates the equation H++E= H2 and this also indicate H2O+ 2e equal to H2+OH- 2 but we have to see where we would get this relation, this reaction where you would get this reaction because this relation is pH as well as potential dependent. Now if you see this here we have H+ ion. So reaction which involves H+ that means it's happens in acidic medium. Now this relation you see there is one OH- there are two OH- ion so that means if the solution has excess OH- ions that means that should be happening in basic medium and also from the pH factor if you see the 7, 7 is the neutral solution and the basic medium where we have excess OH- ion that should be pH should be greater than 7. So this is basic and less than 7 would be acidic where you have excess H+ that suggests that this relation this reaction would happen in acidic medium. This reaction would happen in basic medium as well as in neutral solution because up to neutral solution this reaction is possible and from neutral to basic this reaction is possible.

So we can have a clear-cut decision which is basically nothing but pH 7. pH= 7 so the right side of this, this reaction would happen, left side of this reaction would happen. So and what would be the value of the potential at pH 7? if it is pH 7 so instead of 10 to the power 14 here you just put 10 to the power -7 so then you would see that this would become around 0 and 413. So we can have two reactions on the E versus pH diagram now if you see this reaction again you can understand that above this line H2O is stable, below this line H+ or OH- are stable.

Now that means this is stability line for H2 because we have H2 and this beyond this, above this line would be H2O stability region. Now we have this is, this reaction does not involve O2, this reaction does not involve O2 but we have come to know that there will be two other reactions which would be involving O2. Let us see those two reactions.

So one is same way. One would be happening in acidic media because the relay reaction would be O2 which is dissolved oxygen plus 4H+ + 4e this is also a reduction process going to 2H2O. Now the same relation you can also write in the form of last equation E0+ RT/4F because here we have four electron ln O2 or now here we consider PO2 because this is in gaseous form. PO2 H+ ion concentration to the power 4 because there are four H+ ions. Now H2O2 this should be 1 because it's in the pure H2O medium. This – let's say this is considered to be one atmosphere, then the same relation we can write it as E0 minus if you put all those values RT at 25 degree Celsius as well as F and convert this ln to log then you will say this becomes 0.059 pH and this E0 would be around 1.223, 1.227 something. Yes 1.227 or it would be close to 1.23. This must hold. This also you can find out from this relation E0 equal to -delG0 by and nF and here n is 4 and put the value of F and delG0 find out from Mu 0 of all those species you would get this value. So this is another relation and at pH0 this potential would be 1.227. So here the potential would be 1.23 volt and from that this straight line equation with a negative slope of 0.059 would start if the pH is zero and it would also move like this which would be parallel to this line and here also this is acidic. So this should again have a demarcation line which is pH 7. This is pH 7 so below this pH we have this reaction and again if you see below this H2O would be stable, beyond this O2 would be stable and now we have one more reaction that is O2 + 2H2O+4e would be equal to 4OH- ion so this is again just like H2O+ 2H2O+2e equal to H2+2HOH- same way this relation this reaction is also happening in basic or neutral medium and this should start from pH 7 and the way I have done the calculations for this earlier two reaction hydrogen ion reduction and H2O reduction same way if you do this operation you would see that for these if you write the Nernst equation equation you would get the same relation 1.227- 0.059 pH. You would get the same relation. So that means this reaction on this reaction if you draw that reaction on the potential pH diagram it would have the same line. Both the reaction would be falling on the same line with the same slope. So beyond this pH 7 we will have this reaction. This reaction below this we will have this reaction.

So now we see that there – this two from this four reactions which are involving H+ O2 and H2O we can pinpoint what is the stability zone for water and that is called the water stability line or H2O stability region and these are two water stability lines. So now if you want to draw a Pourbaix diagram for Ni H2O system then this should be my complete diagram. This should be my complete diagram with the reactions which are available in our hand. So now we come to know the complete Pourbaix diagram for Nickel H2O system.

Now from this you can see that if we are in this zone, let's say I am sitting in this portion with the potential of this much, let's say 0.8 volt and pH of 2 if I am sitting here let's say within the solution if I can maintain the potential at 0.0 volt and the Nickel, if the Nickel plate that could potentially is maintained at -0.8 volt and the pH of the solution is 2 then the phase I would be getting at 25 degree Celsius would be Nickel. So Nickel will not go to Nickel plus plus that suggests that there would be no dissolution and if there is no dissolution that suggests that there is no corrosion. And here we are not having any corrosion and it's not forming any other species. So then this zone we call it immunity zone. The boundary would be let me fix the boundary. The boundary would be this is in this zone, in this zone, this zone, this zone always will maintain Nickel as Nickel so that is called immune zone. Immune zone or we call it immunity zone or immune zone. Now if I be at – if I am at this position if I am at this position with this potential and this pH value then we can see that Ni++ is the region. Now the situation here was we have only Nickel no ion but here we can see that there is a Nickel ion concentration, Nickel ion presence. And if Nickel ion presence is there and that Nickel ion is actually forming from Nickel that is dipped in the solution so we have the ion formation from Nickel and ion formation is nothing but the dissolution, and the dissolution means its corrosion.

So this zone we call it as corrosion zone. Now the interesting part now this zone would be this so this is my this is my corrosion zone. If I can go to this place let me go to this place with the potential of this value and with the pH of this value let's say pH is 9 now here the product is NiOH2 or the zone this place is in the NIOH whole two that is the in that region. That means the product would be NIOH whole two from Ni or Ni++. So if you go from this region so Ni++ will form NIOH whole two, I come here from here to there or if I am here if I am here if I go to this place then I form NiOH whole two.

Now NiOH whole two we have seen one problem that if at certain pH value of the solution in the [Indiscernible] [0:27:34] medium and with the solubility product of NiOH whole two at 25 degree Celsius we see that the Nickel and Nickel corrosion is not spontaneously possible. We have seen from thermodynamics. Now this NiOH whole two it forms a layer on the Ni surface which prevents Nickel dissolution. This region will come to know when we come to know, we will come to know more about this later but for the time being this zone is called passive zone because though we have NioH whole two which is a corrosion product but it forms a layer on the surface of Nickel and prevents further corrosion. So this zone is called passive zone. So that means we have immune zone, corrosion zone and passive zone. So this information what we are getting which zone would be immune, which zone would be corrosion and which zone will be passive this would be a very very essential information. We need to have and this will guide me whether thermodynamically with the Nickel is able to corrode in the solution or not. That information we would get from this. We will come to the advantage of Pourbaix diagram but let me also give you some other example. For example in case of aluminum in case of aluminum let me just put the equation. Let me just put the equation and then finally this should be a sort of exercise. If you do the calculation the way the calculations for Ni system is done you would also get a Pourbaix diagram for Al2 H2O system. Aluminum H2O system and finally would get the Pourbaix diagram for this also. The reactions would be one is Al+3+3e going to Al, this is equation number one. Equation number two would be 2Al+3+3H2O going to Al2O3+6H+3 2Al+3H2O going to Al2O3+6H++6e. Similarly four, you can also write Al+2H2O=AlO2-+4H+4+3e and the way equations are written just to maintain the overall charge balance. Another reaction that is possible which is Al2O3+H2O= 2AlO2-+2H+ and the values of Mu Mu0Al+3=-839800 joule per mole, Mu0Al2O3 would be equal to 1608900 Joule per mole. Like that you can – so similarly we can also have the Mu0 of AlO2- this data, sorry I made a mistake. This fellow would be -- this fellow would be 481200 and this is 839-800 Joule per mole and all the other values you know already because H2O you know, H+ all other values are known. So if you do the same operation then you also get a Pourbaix diagram for aluminum system and here the interesting part is this because there in Nickel system we have Ni++ ion only with the information what we had but here you have two ions, AL+3 as well as AlO2- and whenever we have a metallic ion whether it's a complex ion or a simple ion but if the metallic ion is going in the solution then always it would be a sort of dissolution. So this ion it forms from Al for example in number four if these ion forms from Al aluminum then of course the aluminum is corroding. So we have to see this relations. Again if you see these relations this is potential dependent only because we don't have any H+ ion involvement. Here we have H+ ion involvement but it's not an electrochemical reaction. So this reaction cannot be expressed in the form of Nernst equation so this will be pH dependent output potential independent.

Now if you come to this here we have H+ as well as electron involvement. So this would be potential as well as pH so this is let me write this potential dependent, this is pH dependent, this is potential, E as well as pH. Same way this would also be E as well as pH because we have H+ ion as well as electron. E and pH and this is again you see only H+ no electron. So we -- this is also only pH dependent. So if you know this two pH dependent that means it always would be a line which is vertical to the potential axis.

Okay and if you have potential pH as well as potential that would always be a line with a slope in the E versus pH diagram. Now that we have to see whether the slope is positive or negative from this Nernst equation. So you see these five reactions you can also put it in on E versus pH diagram and let me remove the Nickel part, let me put this reactions E versus pH diagram. Here I will not put any values. This would be a kind of exercise. If you do it, so it would be very clear how to plot, how to draw Pourbaix diagram for a metallic system, and if you know all those reactions which involve H2O. Now in this definitely this should be again a line which would be parallel to pH axis because this is P potential dependent, pH independent. This would be on line which is parallel to this. Now initially I will draw all the lines dotted. Let me draw it dotted because then we'll connect it. So this is dotted line which is giving the reaction number one which will be a line parallel to pH axis and at zero potential, at zero pH fellow this should be the value of the standard reduction potential. If the activity of Al+3 is 1 or the concentration of Al+3 would be 1. Now let me see the pH dependent reactions. Those would be a simply vertical line and parallel to this voltage axis or the potential axis. So this is potential. So this would be – one reaction would be this, one reaction would be this. The other reaction would be this. Now if you find out the values of K or the equilibrium constant for this reaction as well as this reaction you would see that this would be the reaction number two and the reaction number three would be reaction number five would be placed somewhere here, and you have to find out what would be the pH value from equilibrium constant. From equilibrium constant you can find out what would be the – at what pH value they should start – this vertical line would start, and if the activities of those ionic species are 1 or the concentration of the ionic species are 1. This should be equation number two and this should be equation number five. Now let me put though the region's let me demarcate all those regions. Let me put all those species on this. So definitely below this line would be aluminum. Above this line would be Al+3. Similarly left side of this for this reaction if you see the left side of this would be Al+3 and the right side would be Al2O3 and now we see this reaction the left side of this would be Al2O3 and right side would be AlO2-. So throughout this section I can have this. Throughout this section I can have Al+ so it's a mixed thing but once we draw these vertical lines we can clearly see that left side of this would always be Al+3 right side would be Al2O3 and right side of this line would be Al02-. So we can segregate, we can we can put all those species and we can specify the regions.

Now still we are not sure whether up to what extent this can remain below this line or up to what extent this can remain below this line. So that would be decided by this potential pH diagram, potential pH reaction and these two reactions 3 & 4. If you see this then find out what would be the final relation in the form of E and pH. Then you will say this would be having a negative slope and that negative slope you have to find out with the help of Nernst equation. So this should be a line which would be going like this and line, this line, and this line will merge at this point. If you take unit activity of different species and let's say if you are taking aluminum plus three activity to be one then you have to take all activities of ions as one and if you take it 10 to the minus 2 then this is one ionic species, this is one ionic species if it is 10 to the minus 2 you also take it as take this concentration of ionic current species to be 10 to the minus 2. And this would always be 1 because this is a oxide phase which is settling down and which is not dissolving in the solution. And this would also be 1 because this is a pure metal.

Now this line indicates the equilibrium between aluminum and Al2O3 if you consider the species which are formed by aluminum. Now again you can see that below that slope line would be aluminum because we already know that this region would be aluminum and beyond this line would be a Al2O3. Now if you see that this zone below – above this line would be Al+3 so that means there must be if we have this line let's say we have this line, so there must be some reaction which involve Al+3 and Al+3 and Al2O3 because above this line would be Al2O3. But since we have already Al+3 so this line will have a virtual presence but actually it will not be present because which is a demarcation line between Al+3 and Al2O3 so left to that line there will not be any Al2O3 and at the same time this line indicates the equilibrium between Al and Al2O3 so this line will have a virtual presence but actually it will not be present in the diagram. So if it is actually not present in the diagram so we will just put this dotted part here. Now we know that this line we can make it a solid line just to indicate that below this line would always be aluminum, beyond this line would be above this line would be Al+3. So now we know what is one solid line which indicates that actually that line is present. Now similarly we can also have relation which again let me take it little down this axis. Now again this is equilibrium between Al and Al2O- so that means it should start, this line should start from this point because beyond this line or right side of this line will have that existence of AlO2- so left to that line this line, this equation will not happen. So again I can see that this is again having a slope which is negative. Okay. This is basically for equation number three and this is equation number four. So this four is basically equilibrium between aluminum and AlO2-. Now we have and this line will have virtual presence but actually it will not be present in the diagram that means that this will not be a solid line because this is going into Al2O3 which is not the part of this reaction. So now we can specify another region which is this. We can write draw the solid line. This is a solid line. Now similarly this relation we can also have a solid line because this would be a boundary between aluminum and AlO2- so again equation number four would be a solid like, and you will see that this line, this line, and this line all will intersect at this point if you take the same activity. Okay.

Now we see that above this line, above this point that say this line Al2O3 above this line left side of this point would be Al-+3 so again we can have a solid line which will demarcate the region between Al+3 and Al2O3. Then this would be another straight line. Another solid line. Similarly this would also be a solid line.

So after doing that, we will remove all those dotted lines. All those dotted lines. Now this would be my Pourbaix diagram for aluminum H2O system. Now we will also have all those four reactions which involve H+, O2 and H2O and that would be again the same thing, two line which are plotted in the Pourbaix diagram in the form of dotted line and these two line that means this is basically O2 reaction. I am just writing O2 reactions in one case it would be O2+4H+4e going to 2H2O which is happening in acidic medium. Now another reaction which is O2+H2O+4e going to 4OH - that is happening in neutral or basic medium. So beyond this line it would be O2 region, O2 stability line. Below this line it would be H2O stability region. Below this is H2 stability region. So again we have the stability diagram for water.

Now here the interesting part. In case of Nickel we have seen that Nickel let me draw the Nickel Pourbaix diagram in this. It would be like this. I am not drawing that H2O regions. Now here this is Ni, Ni+2, NiOH whole two. Now that case this is my immunity zone. This is my corrosion zone, because ion is forming and this is my passive zone because we have NiOH whole two formation on the Nickel surface and it passivates the metal, but here you see similar way this is immunity zone and this is corrosion zone because we have ion formation. Now Al2O3 it forms a layer on the surface of aluminum and passivates the metal. So this would be a passive zone. Now here interestingly this region again we are forming an ion which is of course a complex ion but whenever ion is forming that means it has some dissolution ability in the solution or in the H2O so if AlO2- ion is forming it also suggests that it again suggests that it's a corrosion because from aluminum we are forming an ion and aluminum is corroding in the form of AlO2-. So this is again a corrosion zone. So here we have immunity zone, corrosion zone and passive zone. But generally if we see that if the pH is increased okay if you increase the pH we see that gradually the tendency to become passive is increasing because we have the tendency to form this layer on the metal surface is increasing. But you can experience in the same way in case of aluminum you see if you just let's say this is my potential I am maintaining, this is my potential axis. This is my potential values where I am at. I can maintain the potential of aluminum rod which is dipped in H2O at this value. Now gradually I increase the pH value of the system of the solution. Now you see as we increase the pH if I am at here at this position I have immunity. You see that pH if this is my pH 7 which is the neutral solution we have common understanding that if the acidity increases we have more corrosion but that doesn't happen in this case because even if you have a very highly acidic medium but if your potential is below certain level then you can have no corrosion. The similar way we have that common intention that if we increase the pH let's say I am going to this place which is the pH is let's say 8 when we have a basic medium we always experience which OH – metal a hydroxide formation or metal oxide formation just like this then we can say that this material is going to passivate in that medium if the pH is more than 7 or if it is basic medium. It's of course, it's true. Okya, up to this in this case. Up to this it is true. So this zone we can always have a passive zone and even if and the pH gradually increase in pH it improves the passivity level, but once we cross this passivity passive zone, this line if we go to the right side of this line and that case the pH is a very high value and this would become at around 14, if you calculate all the K values or equilibrium constant and then you will see that this is coming at around 14, pH value of 14 so you will see that even the pH level goes to a very very highly basic still we can have instead of passive layer we can have a complex ion formation. So if we have a complex ion formation that also suggests the corrosion. So it's also not true always that if you have a higher pH value you can have a lower corrosion or you can have a passive zone. You can also experience corrosion zone if at higher pH value you form a complex ion.

So depending on what are the ions that you experience in a particular system aluminum, Al, H2O system this is the case. In case of Nickel system you will always have even if you increase the pH value you will have also have this region entire zone is passive zone. You can always have passivity but in case of aluminum you can experience corrosion if you have a complex ion formation at higher pH value.

So you have to judge a Pourbaix diagram for a system carefully and see at what pH value and what potential value you can go to a passive zone. I'll come to that part why we need to go to passive zone because it's very difficult to maintain at this position rather it's very easy to go this for region. We will see later on but for the time being this is my entire – this is basically the way we draw Pourbaix diagram from thermodynamic data. And it's pretty clear that it this pH versus E versus pH diagram it considers only the thermodynamic data it gives you the possibility of a different phase at different potential and pH value but it cannot specifically say that what would be the rate of the reaction because this doesn't involve any kinetics. This is to be clear may taken in mind but because this is a thermodynamic diagram not, it doesn't give you any practical rate equations, rate grade values. Thank you.

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