Indian Institute of Technology Kanpur

NP-TEL
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On
Technology Enhanced Learning

<u>Course Title</u>

Environmental Degradation of Materials

Lecture – 06
Broad Subject: Reduction Potential Series, Pourbaix Diagram

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In the last lecture we have solved some problems, those problems we have used the triangle where you have the relation between Del G0 equilibrium constant and reduction potential, and also we have seen that if you can stack all the standard reduction potential in the form of a series with respect to hydrogen electrode, then you also get a standard reduction, standard reduction potential series, and in that if you have zero potential for the standard hydrogen electrode, then the top of that electrode would be, top of that hydrogen electrode let's say if you have zero as this H+ + E half H2, this is my 0V, and if you stack all the E0 and this E0 in the form of reduction potential then you get a series, and that series you can judge if the metals or the reduction potential above zero voltage those are active, those are noble and below zero voltage all the metal potential or the reduction potential of other reduction reactions will be considered as active. Now this standard reduction potential says one is whether metal is active or noble, that means if the metal potential is above zero voltage or below zero voltage, if this is E0 should be greater than 0V, and here it is E0 should be less than 0V.

Now the second information what we get from standard reduction potential series, here where pure metal corrosion can be understood readily, for example if you have copper and zinc and if you have Cu++ ion in contact with zinc then zinc will come out plus plus and copper will deposit, so this will be the reduction, this would be oxidation, and this is also true, because we know that for this is E0, Zn++ +Zn 2Zn that means reduction potential is - 0.761V, and in this case E0 Cu++ Cu = + 0.34V, so that means this is more than this, hence copper ion will deposit, zinc will corrode in the form of zinc ion, so this information we can get for pure metal.

Now another case is it provides quick glimpse of which material will be more prone to corrosion that means in this case zinc has the more prone as to corrosion and in this case copper has less proneness to corrosion because zinc has higher reduction potential or higher reduction ability. Now there are few disadvantages, and mostly basically it gives you or something some theoretical basis that which one is noble which one is active, because it based on thermodynamic data, because Del E, what you are getting Del E or E0 what you are measuring with respective standard, hydrogen electrode in case of pure metal, because here the activity of the ionic species, all the activities will be one, so this is basically nothing but Del G0 / nF -, because this relation, from this relation you are getting E0, that is Del G0 is purely a thermodynamic data, so it's the thermodynamics, nothing about kinetics so you will not get any information about the rate of this process you know that this is possible, but you cannot tell from these relation or from this data at what rate zinc will corrode and what rate copper will deposit, this information we cannot get, now coming to another point, let say if you are considering the corrosion of an alloy, okay let say copper zinc alloy, so in that case or brass in that case this information will not tell you what would be the situation here, whether copper will at all corrode or zinc will corrode those information we cannot get from this table.

Now another point is this is a standard value, so the temperature is 298 Kelvin, so if you consider different temperature then also you cannot get any information. Let's say I am giving one information, one example zinc and iron if you combine this iron has E0 Fe++, Fe its value is - 0.44V, now if you combine this zinc and iron in HCL solution then from this it's pretty clear that this as higher reduction potential than zinc so iron should corrode more than zinc, but actually it would be reverse if you club, if you galvanically couple iron and zinc in HCL solution, so that case zinc correction would be less, iron corrosion would be more, but still from this information from this data at least we cannot, we cannot say that the reverse is happening, so that information we cannot get, so these are, that is the practical corrosion information we cannot get out of this standard reduction potential series, but it has huge importance, that importance of, where the importance of this has been found out in the problem where we have tried to see nickel, how the nickel would corrode in a deaerated h2o medium, where if you consider the last lecture problem where we have seen that whether nickel we have to find out theoretically whether nickel can corrode as nickel hydroxide in deaerated h2o, and with few information for example we know KSP of Ni OH whole 2, we know that value, we know what are the reactions redox reactions, so nickel, if nickel has to corrode it should go this way and another cathodic reaction would happen like this, and we know the pH of the solution. These are the problem, this was the problem and we had to find out whether actually in this condition set of conditions nickel would corrode or not, and we have found out that nickel doesn't want to corrode in this condition, in this set of conditions, because we have found out that Del G for this process would be positive, okay. If it is positive that means it's non-spontaneous, that means a spontaneously this reaction would not happen so rather we can say that nickel cannot corrode in this set of conditions.

Now nickel hydroxide, now you see what are the products, what are the reactants, what are the products or rather what are those species in this condition, this is one species nickel, this is another species because nickel hydroxide is forming initially it forms Ni++ ion and then Ni++ ion will react with h2o and forms NIOH whole 2, then also we have H+, we have H2, so these are the species. So that means if we, if we put all the species one by one, one is Ni, second is Ni++, third is Ni(OH)2, fourth is h2o, fifth is H+, so these are the species in deaerated h2o.

Now let's say I have aerated medium, now if I have the aerated medium then I have to add another species which is nothing but dissolve oxygen, O2, so these are the species those are available in the medium, if it is, this is in case of aerated solution. So from this in the problem we have just studied what would be the stability of different phases as a function of pH or potential, so that means we can, because when we try to find out Del, G we had to find out what is the potential difference between the cell, in the cell or between the reaction of reduction, reduction reaction and oxidation reaction, so that is one information we are getting and with the help of stability, with the help of pH, with the help of solubility product of the precipitate or the phase that is forming on the nickel surface.

So now if we try to see different reactions that can be possible combining the six species let me note down all those reactions, one reaction is Ni++ +2e going to Ni, this reduction process can take place or in other way around you can say that nickel is also going back and forming Ni++ that oxidation process can also take place, now but I prefer to write it in terms of reduction because that would help me to find out what would be my reduction potential.

Now second reaction that is possible Ni+ H2o, Ni+ H2o going to Ni O + 2H+ + 2e, or I would prefer to write it in other way around, let me write it in this way because I have to write it in terms of reduction, so I can write it as Ni + H2o, this is another reaction. Third reaction that are possible Ni++ + H2o going to Ni O 2H2o going to Ni (OH)2 + 2H+, this is also possible I am just writing all the possibilities. Now forth is again this NiO which is the product of the reaction between Nickel and H2o, in that case I can also form NiO can react with H2o and form Ni (OH) 2, so this is also possible, so these four reactions that are possible what I can frame there are other reactions but let me put all the simple reactions, these are the simple reactions.

Now what are the other reactions, five, H+ +E, half H2, this is possible. Now sixth, now this is in case of deaerated media. Now if it is aerated now you have another species O2, O2 can reach with 4H+ + 4e, it can go to 2 H2o. Seven, another reaction that is possible H2o + 4e going to 4Oh -, now one more reaction that I can think of 2 H2o + 2e going to H2 + 2H -, these eight reaction, simple reactions that I can think of considering all those six species.

Now let me see what information, what thermodynamic information I can get from these reactions. Now one thermodynamic reaction is I can find out what would be the Mu of all those species, Mu of all those species that is I can get Mu of all species. Now let me note down all those Mu's because those are thermodynamic data. Now let me note down all those Mu's first, first is, now when we try to find out Mu, let me put it in such a manner that I am having some data for Mu0 or the standard chemical potential for all the species, all the individual species. Now this I can find, I can have some data, I can have data Mu0, I can have data, now then what else? I can have data for Mu0 H+ Mu0 H2, Mu0 O2, Mu0 H2o, Mu0 OH -, so these many Mu's I can find it.

Now convention is when you consider pure metal, this is considered to be 0, again this is 0, again this is considered to be 0 again, because it's a pure gas. Now I can have this one, this is also assumed to be 0 Joule per mole. Now I can have other data, let me have other data Ni++ S – 46,398 Joule per mole, this is NiO, H2o is – 236,964.2 Joule per mole. Then I have data for Ni(Oh)2 – 108.300 this is – 452,694 Joule per mole, then I can have a data for data for NiO, NiO would be just let me find out you just find out this is 51610 x 4.18 this is in calorie per mole, so it would be equal to minus, it would be equal to let me, I will just calculate if you calculate it let me see the litter, now this value is 51610 x 4.18 = -215,729.8 Joule per mole, so let me remove this part. So this is the value for this, okay. Now I have the value, the value that is remained is Mu0 OH -, Mu0 OH - data let me also put that data, so the 1 data is missing that is for Mu0 OH - that is – 157,147.1 Joule per mole.

Now with these data sets let me find out how many what are the data I can make out of these standard data? From this, this is you see that this is an electrochemical reaction, a reduction reaction so I can find out what is E up for this reaction, E for this reaction, E0 rather, because I have considered all those standard state and it is considered at 25 degree Celsius and unit pressure, one atmosphere pressure. Now for this, this is also an electrochemical reaction and at the same time you see the difference between this and this you have considered here H+ ion, now at the same time you have two electrons, so that mean its electron accepting reaction or reduction reaction at the same time this reaction will depend on the concentration of H+ ion in the solution or in the aqueous medium and this concentration of H+ ion in the aqueous medium or H2o can also be related to pH of the solution, that means this relation depends on potential as well as pH of the solution.

Now this reaction you see here you don't have an electron associated with it, so rather it's a reaction which is not an electrochemical reaction, so now here it's basically involving, this reaction is involving Ni++ with H2o and forming Ni(OH)2 and H+ ion, so now again this reaction is pH dependent, but of course this would be definitely potential independent. Now again coming to this, this is if you see this two difference between three and four, three is pH dependent potential independent, but this is potential independent as well as pH independent, so pH of the solution as well as potential doesn't matter to have some data out of it. Now this is also electron involved as well as H+, so this is pH as well as potential dependent, this is also you see H+ an electron, so this is also potential and pH dependent, this is another reaction where you have OH- ion, so OH- ion you can also reflect in terms of basicity or in other way you can also put it as in terms of pH, so let's say pH 7, that means neutral solution, so in that case pH, you can have pH at the same time you can have pOH, okay so pOH if it is seven, so this is 7, ph7, so in that case it would be also 7, so neutral solution pOH is also 7, pOH is 7, so if you know this you can also know this from the solubility product of H2o.

Now, water dissolution, dissociation constant for this H2o, again this one again it's coming to be a potential as well as pH independent so you have few reactions, one reaction is one set of reactions, now let me come to name all those reaction, let me put in other way, let me put in such a way that we have you 3 set of reactions. One is pH dependent only pH dependent rather let me put it only pH dependent that means, let's say this reaction, pH of the solution will decide whether Ni++ will go to form Ni(OH)2 in the presence of H2 or not, this is only pH dependent.

Now second set of reactions which are potential dependent, which are potential dependent. And third set of reactions where you have pH as well as and potential dependent, so three sets let's say let me see this one is definitely pH independent only potential dependent, so let me put the number this is, it falls under category of 2, second same thing let me put it this reaction here pH as well as potential, so it falls under category 3, now this is falls under category 1, because it's only pH dependent.

Now this one, now there is one set of reaction which is not pH or not potential dependent, so we have one set which is not a pH or potential dependent, so this is falling under category 4, now again I can also put them in different categories this is pH as well as potential so category number 3, this is pH + potential, category number 3, this is again also OH - I can put it in terms of pH so this is also potential because it involves electron, so electron pH so this is also falling under category number 3, this is also falling under category number 3, because it also involves electron as well as OH – ion and OH – ion you can put it in terms of H+ ion or pH, so now you see whatever reactions that we have thought of, those are happening in H2o solution in the presence of H+ O2 dissolve oxygen, this make a reaction for the timer we can think of, which make, which leads to Ni++ formation, NiO formation, Ni(OH)2 formation or the other way around, so if we think this eight reactions, can we put it on a diagram, okay, or you have two axis, one is potential, one is pH, because all those reactions except this reaction number 4, I can put them on this E versus pH diagram, because all the reactions either they're potential dependent or pH dependent or pH or potential dependent. So when I put them in this diagram E versus pH then I can specify that which section has Ni++, which section I have Ni, which section I have H2o, which section I have H+, which section I have NiO, all those species I can specify on this diagram.

Now when I specify in this diagram that time I construct a sort of, now when I put them these reactions on this diagram then I construct Pourbaix diagram, which is known as Pourbaix diagram, okay, so E versus pH diagram is nothing but the Pourbaix diagram where it's a graphic representation of all those reactions that are happening in H2o, in the presence of oxygen or H+ ion or both, so it's a basically a kind of stability of a metal and it's corrosion products as a function of potential and pH acidity or alkalinity of the aqueous solution.

Now stability of a metal, because we have already seen in case of nickel corrosion, that nickel forms Ni(OH)2, and if it is forms, if it forms Ni(OH)2 then we can also judge from this available data that is a solubility product pH of the media whether the further from Ni to Ni++ would be happening or not, fine, and that is based on purely thermodynamic data.

Now similar way I can plot these reactions on this diagram and also I will see that for the particular region of potential and pH some phase or some species will have higher tendency to form because I am using this tendency word because we are judging from thermodynamics, it cannot tell you whether actually that thing would happen or not, but it will definitely give you some idea or tendency that this phase would or this phase or species would form or not. Now let me plot these reactions on this diagram one by one, so first let me consider this reaction this is pH and this is E or E rather E0, since I'd be using all the standard reduction potential, standard chemical potential and if I use standard chemical potential then these axis if it is a potential dependent would come as E0. Now if you consider this reaction, this reaction can be written in terms of, if you consider what would be the potential I can write in the form of E = Ni++ Ni that is a reduction potential would be E0 + RT electron 2F Ln Ni++. Now R is 8.314 Joule per mole per Kelvin, T is 298 Kelvin because I had considered 25 degree Celsius, 298 Kelvin and F is 96500, F is, this is T, this is R, which is universal gas constant, and this is F = 96500 Coulomb per gram equivalent.

Now if I put all those values here then I would get E0 + 0.059 roughly 0.059 log concentration of Ni++, now if I take from, if I convert this we would get this, instead of Ln I am putting elegy log, okay, and this is E Ni++ Ni, now if I have the situation where Ni++ ion concentration is maintained at one, this is one concentration, if the concentration is one, then E the potential for this reaction when the concentration of Ni++ ion is one unit, so then I will get E Ni++ = E0 which is standard state, standard reduction potential for nickel. Now how would we get standard reduction potential for nickel, then again I can have Mu0 Ni, Mu0 Ni++, now I know what is the value of Mu0 Ni++ and Mu0 Ni? Now what would be my, from this I can calculate what would be my change in free energy and since I am considering Mu0 so I'm considering Del G0 so it would be Mu0, this would be Mu0, Mu0 Ni – Mu0 Ni++ because this is my product, this is my reactant. So if this is my product, this is my reactant so let me put it in product, this is reactant, so Mu0 Ni which is product, Mu0 Ni++ which is reactant. Now this would, you will get let me put the value +46398 Joule per mole.

Now if I had this, what would be my potential? Potential I can put it in this fashion Del G0 = -nF E0, N is 2 here, so E0 would be Del G0 / 2 x 96500 and there will be a minus sign, and it would be if you find out this value then it would come as 46398 /2/96500 it is coming it as coming as 0.24 – volt, so E0 Ni++ Ni the potential is coming as -0.24V whatever data we have. So now you see that you have found out E0 when the nickel ion concentration is 1. Now if you know the E0 with the thermodynamic data available here then you have a relation which is nothing but E Ni++ Ni = E0 Ni++ Ni, this one is 1, and if it is not 1 then this is my relation, this is my relation and we have also found out the value of E0 Ni++ Ni with the thermodynamic data what we have now on this board. Now this is equation which relates potential to another standard potential, and this is there is no H term that is coming into this equation and if you would like to plot this equation on this diagram this should definitely be a horizontal line with respect to pH axis, because it's a pH independent reaction.

Now let me plot this on this diagram, let me put the diagram there so you can understand better because whatever calculation I will be doing that would be done on this side and the final plot would be here, so this is my pH, this is my potential and this potential is nothing but the reduction potential here I can write E ox red. Now if I know this value - 0.24, let me this is 0.24 and this is the axis which is in port, now if I would like to plot this equation on this diagram then it should be a line which is parallel to this axis and if we would like to see the nickel ion concentration if we change this nickel ion concentration to, from 1 to 10 to the power - 2 if I put the - 2 here, so then E of this Ni++ Ni of that, for that reaction if the concentration is not unit activity would reduce, okay. If it reduces that means because if you check, if you change this let me put instead of one, let me put 10 to the power – 2, so I will put E Ni++ Ni would be equal to E0 which is nothing but 0.24- minus because since I have a - 2 here, so it would be 0.059 x 2, if the concentration of Ni++ would be equal to this unit, so this is my – 0.24 so potential will drop. If I increase it, if I again further decrease the concentration again this potential will go down, so that means you see as the concentration of nickel ion concentration, nickel ion concentration is decreasing your potential is also decreasing for the reaction compared to the standard reduction potential, so which means that nickel ion ++ concentration nickel region, if I reduce this what does it mean, means that, it means that nickel ion concentration is decreasing or if you consider the other way around this way around so nickel has the less tendency to go into the solution, because as the concentration is decreasing in the solution, let's say I have two beaker, one case concentration is 10 to the power – 6, Ni++ concentration is 10 to the power – 6 where I have a nickel block and this concentration is this, however the case I have another nickel block in the water and I have nickel and concentration is 10 to the power – 1, so it's pretty clear that here corrosion is more, here corrosion is less, or if I come from this to this so I would increase I would rather increase the region so if I come from this to this, what I am doing I am basically trying to get into some situation where my corrosion tendency of nickel is going down, because I am going towards a lower called lower concentration.

So now if I place let's say Ni++ here and Ni, now this is for one concentration activity or Ni++ = 1, now if I put 10 to the power – 2, this concentration 10 to the – 2, this line would go down because here it will go down, so it will go down that means this would be my access point for the concentration for this. If I make it 10 to the power - 6 then it would be here, this is nickel site, so what I am doing I am extending Ni++ region and I am sinking nickel. Now let me understand why the nickel is not on top Ni++ is not on the bottom. Now coming to the same example, let's say I have I can measure I can measure up to the nickel concentration up to 10 to the power - 6 unit, unit this can be molarity or this can be mole fraction. Now I can measure up to 10 to the power - 6 and if the concentration of nickel ion is less than 10 to the power – 6, if the nickel ion concentration is less than 10 to the power – 6, so that means that if the concentration of nickel ion, Ni++, nickel ion goes below 10 to the power – 6, that means that I don't have any existence of nickel ion because I cannot measure below 10 to the power - 6 unit of concentration. So if I cannot measure Ni++ then what does it mean? That there is no existence of, virtually there is no existence of Ni++, so all the nickel will remain, okay. If only nickel will remain if the concentration is less than 10 to the power of - 6 or the measurement limit with the experimental setup what I have, in that situation if the measurement limit is 10 to the power – 6, so if the concentration goes below 10 to the – 6, I would say that there is no corrosion or there is no trace of Ni++, but if I have this so then I can say that there is a corrosion or nickel can remain within the presence of nickel can be present in equilibrium with Ni++ and if it is 10 to the -5 then also I will say the corrosion tendency is increasing or I would say that, the amount of nickel ion concentration is increasing and nickel is highly getting corroded or the nickel corrosion is substance here. Now like that way it will move off, now while it is moving off let's say in one case my measurement limit is 10 to the - 6 another case my measurement limit is 10 to the power - 5 and that case measurement limit is 10 to the – 4, so as you go from this to this, so you are basically lifting your line upwards or you are since this is the measurement limit so below this 10 to the - 6 let's say this is my measurement limit 10 to the – 6, so below any line I cannot have the existence of a Ni++. This is the measurement limit 10 to the – 6, if I have the concentration 10 to the – 7, then I cannot have any stress of Ni++ in this region. So if I don't have Ni++ in this region then there must be nickel only. Now my measurement limit I lift it to 10 to the – 2, my measurement limit is 10 to the - 2 then below that concentration I will only have Ni because nickel ion concentration is not there, nickel ion is not there at all actually because I cannot measure below 10 to the – 2, so that means that the lower part of this curve should consist of Ni and upper part should consist of Ni++ because this region will tell you that because of this factor, because of measurement limit or the limit what we consider as the percentage of nickel ion in the solution, that can be measured with our experimental data. So if I consider in this fashion then it is very clear that the lower part should be nickel, the upper part should be Ni++.

Now we have two regions now, the regions are, this region is Ni++, this region is Ni and of course I have to specify that this line is for concentration Ni++ = 1, if I go down to the - 6 this will also go down, fine, so now you see for the first reaction what we have considered in the beginning that can be put on this E versus pH diagram and it's a horizontal line, so one part is over.

Let me see second reaction, second reaction was Ni+ 2H2o = Ni(OH)2 + 2H + +2e, sorry I have to write it in a reverse manner, so this is, this part would be equal to Ni +2 H2o because I need to find out the reduction potential, so I can also calculate reduction potential for this process in standard state, because I know the value of Mu0 Ni(OH)2, I know the value of Mu0 H2o, I know the value of Mu0 of Ni and Mu0 of H+, this is also a process where electron accepting, electron is getting accepted or reduction process is taking place, so I can put it in terms of E which is, now let me write it in this manner (OH)2 H+ or I can say ox/red would be equal to E0 ox/red + RT, here also I have 2 electron, so 2F x Ln, ox is this side because this side is taking electron so Ni(OH)2 the concentration of Ni(OH)2 concentration of H+ square, because 2 is involved, two number of hydrogen ions that are involved and this is Ni concentration of H2o whole square. Now this is happening in pure medium, okay. Now this is a solid which is precipitating out, what would be the concentration or activity? This would be one, this is another pure metal here also I can consider it as 1, now this is also a pure H2o which is concentration would also be 1.

Now if these are 1, so I can write E0 ox/red + now I put all those values here, R, T, and F at 25 degree Celsius, then this would become 0.059 x now instead of Ln, I would write log H+ square, now if I take this square out there would be a term 2, because 2 is there, so now I can write it as E0 ox/red, I can take a minus sign and then I can put the minus sign here 0.059, 2 and 2 would get cancelled, log of H+. Let me take this out also, 0.059 - log of H+, if you see this, what is this? This is nothing but pH of the solution, so this would become E0 ox/red – 0.059 pH. Now this is E ox/red, now this is my equation, now you see this equation has a relation between E0 that is the standard reduction potential for this reduction process and pH of the solution, so this also we can plot in E versus pH, and if you see that this is also a straight line equation because this is a constant and this is the variable and that is nothing but the pH, so I can plot this on E versus pH plot and this should be having a negative slope, which is nothing but - 0.059, so I can also plot it in green color let me plot, so I can have let me put it in, this is nothing but E ox/red = E0 ox/red - 0.059 pH, this is my equation of that line and this equation was E = E0 + 0.059/2 NI++, let me stop here, I can continue in the next lecture.

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