

**Indian Institute of Technology Kanpur**

**NP-TEL  
National Programme  
On  
Technology Enhanced Learning**

**Course Title**

**Environmental Degradation of Materials**

**Lecture – 05**

**Broad Subject: Thermodynamics of corrosion,  
Electrochemical series, concentration cell**

**By**

**Prof. Kallol Mondal**

**Dept. of Materials Science & Engineering**

So we have seen few relations, those relations are based on basic thermodynamics. Now those relations let me note down all those relations one by one just to have addressing. One is reaction isotherm, which is  $\Delta G = \Delta G^\circ + RT \ln \frac{\text{product activity}}{\text{reactant activity}}$  or product divided by in the denominator it would be activity of reactant. So this is Reaction Isotherm, this is called Reaction Isotherm.

Now second relation which is coming from this, this is  $\Delta G^\circ = -RT \ln K_a$  in the standard state which is basically one atmosphere pressure and normally we consider at 25 degree Celsius temperature so that case -  $RT \ln K_a$  if we consider these things in activity so it would be A that subscript would be A, if you consider these things are in concentration unit or molarity unit that case it would be C and, A is related to C in this way, and  $A = C$  for a very dilute solution or ideal case. So that case  $K_a = \text{activity} = \text{concentration}$ .

Now we have also come across redox reaction, and in case of redox reaction we have seen a Nernst equation which is valid  $E = E^\circ - \frac{RT}{nF} \ln \frac{\text{ox}}{\text{red}}$  that means oxidant goes to reductant or the reduction process  $E = E^\circ - \frac{RT}{nF} \ln \frac{\text{concentration of ox}}{\text{concentration of red}}$ , or you can also put it in terms of activity of ox or activity of red depending on the situation if it is a very dilute solution than activity of ox you can replace with the concentration.

Now this is the N factor that is coming because  $\text{ox} + ne = \text{red}$ , so number of electrons that are associated with this reduction process is n, so that n is coming F is 1 Faraday for 1 gram equivalent substance to deposit or to come out in the solution in the form of ion.

Now again we have seen the relation between G,  $\Delta G$  and potential reduction potential, which is  $\Delta G = -nFE$  or  $\Delta G^\circ = -nFE^\circ$ , that means if you consider standard step then you replace this E in the form of  $E^\circ$ . Now if you consider a potential difference of a cell that case this E would be replaced by  $\Delta E$ , and this E would be replaced by  $E^\circ$ , in case of cell. In

case of single electrode that case this you put it as E, in fact this, in case of single electrode I am using E single E, not  $\Delta E$ , but still this has a meaning of  $\Delta E$  because you are measuring this potential in the, with respect to one standard hydrogen electrode who had the reduction potential, standard reduction potential is considered to be zero, so this is also a kind of  $\Delta E$  for a single electron.

Now with this equation we have also come across a triangle which, for a particular reaction and if it is a redox reaction then we can have this triangle  $E_0$  cell, this is  $\Delta G_0$  and this is K which is the equilibrium constant. Now these are also related like  $\Delta G_0 = -nF E_0$  cell just like this and this is  $\Delta G_0 = -RT \ln K$  and this one is  $E_0$  cell =  $RT / nF \ln K$ . You can put it  $K_a$  or  $K_c$  depending on whether you are considering activity or concentration.

Now from this also you can also judge whether a process is spontaneous or not, if let's say you have  $\Delta G_0$ ,  $E_0$  these are the values which are considered and have, this is equilibrium constant, this is energy change in the standard state, this is potential in the standard reduction potential in the standard state and when the activity of those species, ionic species are considered to be 1, so that case E would be equal to  $E_0$  because we are considering this relation if you consider this relation when these activities of this redox oxidant and reductant are 1 then  $E$  oxidation,  $E$  reduction potential of the electrode would be equal to  $E_0$ .

Now let us see whether a process is spontaneous or not, we can judge from this definitely if it is negative then it's spontaneous we have seen if it is 0 then its equilibrium and that means reactant and products are equally favored and it's positive then this is non-spontaneous, that means the process, if this process let's say reactant goes to product, so in this case whether this reactant would go to product phase or not that would be decided according to this thermodynamics.

Now similarly you can also judge it from  $K_c$  if it is greater than 1, if it is greater than 1 then this negative, this will be negative because if it is greater than 1, because we have a relation  $\Delta G = -RT \ln K$ , if K is positive and greater than 1 then this would become negative and this is fulfilling the criteria. Similar way this, if this is 1 then, if this is one then this term would become 0, so  $\Delta G_0 = 0$ , so it would be again, this is considering equilibrium, so reactants and products both are equally possible. Now if it is less than 1, and this term would become negative, this term would become negative, and there is a negative sign so this whole term would become positive, so if it is positive, so again the reaction is non-spontaneous, and how would you relate this E?  $E_0$  again, if it is positive, if it is positive from this relation, if it is positive because  $\Delta G_0 = nF E_0$  cell, if this is positive so this becomes negative, this becomes negative, so again we have the spontaneous reaction. If this is equal to 0, so again this becomes 0 so it would be, it would be telling you the equilibrium condition that means reactants as well as products both are possible so that means, that case this is going at a some rate, this is also coming back at some rate or it considers a dynamic equilibrium condition. And if  $E_0$  negative or less than 0, that case this becomes positive if  $\Delta G_0$  becomes positive, so then the reaction is not possible or it becomes non-spontaneous.

So now let us have some numeric, some examples if we see some examples then things will be much, it would be more clear, let us find out some, let us see some examples. Let's say if I

would like to calculate let say zinc, okay, so zinc electrode, zinc electrode if it is immersed in zinc chloride solution and in the zinc chloride solution the activity of  $Zn^{++}$   $a_{Zn^{++}} = 10$  to the power  $-3$ , what would be the potential develop at this electrode, okay. Now we know that  $E_{Zn^{++}/Zn}$ , that means for the reduction potential, standard reduction potential when the temperature that the activities of those ionic species or other species are 1, that case  $E$  would be equal to  $E^0$ , this is  $0.761V$ .

Now we can have the Nernst equation,  $E = E_{Zn^{++}/Zn}$ , it would be always preferred to write this one in the subscript because this will tell you whether you are taking potential in the form of reduction potential or oxidation potential, if you write in this manner that means it always says that it is a reduction potential, if you write the reverse manner let say  $E_{Zn/Zn^{++}}$  that means  $Zn$  is going to  $Zn^{++}$  this will tell you the oxidation potential, so I would always consider reduction potential, so I would always try prefer to write this  $Zn^{++}/Zn$  or ox / red.

Now this should be equal to  $E^0_{Zn^{++}/Zn} + \frac{RT}{nF} \ln \frac{a_{Zn^{++}}}{a_{Zn}}$ , the Nernst equation and here if you consider the relation  $Zn^{++} + 2e^-$  going to  $Zn$  so that means we need two electrons for 1 mole of substance to deposit on zinc electrode from zinc ion. So now we have 2 electron, so  $2F$  into  $\ln \frac{a_{Zn^{++}}}{a_{Zn}}$ ,  $a_{Zn}$  is  $1$  + here we are having the data in the form of activity, so activity of  $Zn^{++}$  and activity of  $Zn$ . Now  $Zn$  is in atom, it is in pure condition, in metallic form so this would be  $1$ , and this value is  $10$  to the power  $-3$ . So now let me put those values  $-0.761$  + now at  $25$  degree Celsius this  $T$  becomes  $298$  Kelvin,  $R$  is  $8.314$  Joule per mole per Kelvin, and  $F$  is  $96500$  roughly  $96$ , it's basically absolute,  $F = 96500$  Coulomb per gram equivalent, okay, so let me put those values  $2 \times 96500 \times \ln 10$  to the power  $-3$ , so now if you calculate this you would get the value would become  $-0.85V$ , so this is my voltage that would be developed on electrode, if you dip on zinc electrode in the zinc chloride solution and whereas the zinc ion concentration or the activity is  $10$  to the  $-3$ , these are example. Now this way you can find out what would be the actual potential on the electrode, if you are not at standard state or if you are not maintaining the activity, in activity to be one, so if the activities are different then you can calculate from this Nernst equation. Now this is one example, now let me have another example this is little bit tricky, we will be using this concept just to find out whether a reaction is possible or not, let me put all those values,  $R = 8.314$  Joule per mole per Kelvin, and  $T$  always, let us consider in  $25$  degree Celsius or  $298$  Kelvin.

Now the problem says that in a solution we have to find out let's say a nickel, nickel is corroding in a deaerated water, deaerated water, I have a nickel, nickel plate which is trying to corrode a deaerated water and deaerated means, the dissolved oxygen is absent, okay, so now if you don't have dissolved oxygen then you have some reaction and it says that the pH of the solution is  $8$ , these are given data, pH of the solution is  $8$ , and  $K_{sp}$  which is a solubility product because when nickel corrodes it forms nickel hydroxide, nickel corrodes that when it formed nickel hydroxide. So nickel hydroxide tries to precipitate out because its solubility is very less in deaerated water so we need to find out what would be the solubility product of nickel hydroxide in the aerated solution it's given, data is given  $1.6 \times 10^{-16}$ , these are the given data.

Now another thing is we know  $E^0_{Ni^{++}/Ni} = -0.25$  this is also obtained from reduction potential series, standard reduction potential series, the last class we have already started talking

about what is the standard reduction potential series, after seeing this example I would again consider the standard reduction potential series and there we will consider what is the half cell and what the full cell reaction, all sort of things will come into picture.

Now again, now another data which is given as, now the reaction that are happening, of course nickel is going into  $\text{Ni}^{++}$  and  $\text{Ni}^{++}$  plus is reacting with  $\text{OH}^-$  and forming  $\text{Ni}(\text{OH})_2$  precipitate.

Now the another reaction that is happening, one is  $\text{Ni}^{++}$  from nickel, this reaction is happening if you have to have some corrosion of nickel so nickel has to come as nickel ion, then it is basically a corrosion, so now we have two electron that is released by nickel to form  $\text{Ni}^{++}$  ion so this two electrons should be consumed by some cathodic reaction or reduction reaction. The reduction reaction here it is some hydrogen gas is forming, so if hydrogen gas is forming so the reduction reaction should be then  $\text{H}^+ + 2\text{e}^- = \text{H}_2$ , so that means this reduction reaction is happening, this oxidation reaction is happening.

So we need to find the main question is we need to find with this set of conditions if the pH is 8, if the solubility product of  $\text{Ni}(\text{OH})_2$  which is basically  $1.6 \times 10^{-16}$  and the standard reduction potential of  $\text{Ni}^{++} / \text{Ni} = -0.25$ , where that the nickel has any tendency to corrode in the solution which is deaerated water.

Now let us try to solve this, now let me remove this, now let us assume that nickel is actually corroding, so we have to find out theoretical of nickel to corrode in this solution, fine, so now let us assume that this reaction is happening actually in the system and this reaction is also happening, so if this are the two reactions so in this case we have to find out what is the potential, just like the previous example, we have to find out the potential which will be dependent on the nickel ion concentration in the solution, so for that we need to find out what is the nickel ion concentration in the solution same way we need to also find out what would be the potential for this, because this is also a reduction process, so that case also we can find out, we can find out what is E for this, because here we are not maintaining the hydrogen ion activity to be one, because we have already specified what is the pH, when the activity is 1 that time pH would become pH is mentioned as  $-\log$  of concentration of  $\text{H}^+$  if we consider a very dilute solution then this is equivalent to activity, so when this becomes 1, so that time you can see that  $\log 1$ ,  $\log$  of 1, so pH would become, so pH is defined as  $-\log$  of concentration of  $\text{H}^+$ , now here we have considered pH to be 8, so if pH is 8, then hydrogen ion concentration is having some value, so you can put  $8 = -\log \text{H}^+$  so you can find  $\text{H}^+$  concentration in the media, so then also you will see that the concentration is not 1, so if these are not 1, so what would be, what would be the concentration of  $\text{H}^+$  ion, that we have to find out as well as we have to find out what is the potential for this reaction, if the species are not in unit concentration or activity or same way like this we have to find out for this.

Now let us find out this 2, and one case what would be  $E_0$ ,  $E$  of  $\text{Ni}^{++} / \text{Ni}$ , though we are seeing that this is going into the solution, but we can also consider in terms of reduction potential, so reduction potential for this reaction would be  $E_0$ ,  $\text{Ni}^{++} / \text{Ni} + RT$ , now for this we involve 2 electron, so  $2F \ln$  activity or concentration of  $\text{Ni}^{++} / \text{Ni}$ , and this is pure state and in the metallic condition so this would be 1, now we know this relation.

Now another case which is  $E_{H^+ / H_2}$  would be equal to  $E^0_{H^+ / H_2} + RT/F \ln a_{H^+}$ , because in this case you can consider, you can write in terms of  $H^+ / H_2$ , and if you, in that case it would be, that would be concentration of  $H^+$  and concentration of  $H_2$ . Now if I would like to write in this form and if this is happening in 1 atmosphere pressure condition, so I can write  $\ln 2$  because here also we involved 2 electron so  $2F \ln 2$ , now we have  $H^+$  to the power 2, because we involve,  $2H^+$  ion and because whenever we consider let say  $aA + bB = cC + dD$ , that case we consider that  $AC$  of  $C$  to the power  $C$ , this monomer of moles  $AD$  to the power  $D$ ,  $AA$  to the power  $A$ , this is number of moles, and  $AB$  to the power  $B$ , this is my nothing but  $K$ . We have already seen this so now here also this power 2 would become because 2 hydrogen ion are involved in this process and now this is  $H_2$  because since this is gas so it would be considered as  $p_{H_2}$ . Now this is also 1, since I am considering this is happening in at one atmosphere pressure.

Now if you consider this two reaction, this is one, this is two. Now we have assumed that nickel oxidation is taking place, so if nickel oxidation is taking place that means the potential at this electrode should be having lower value than this, because whenever we considered that means let say 2 electrode, 2 electrode we have considered that 2 electron if it is connected with a salt bridge, this is a salt bridge and this is a solution. Now if you would like to find out which direction the current will flow, this is  $M_1$ , this is  $M_2$ , if current is flowing in this direction  $I$ , so electron flow is going in this direction, so this side would be anode, this side would be cathode, we have already seen this, this side would be cathode, this side would be anode and electron here oxidation reaction is taking place, here reduction reaction is taking place, so now this would be, what would be the cell potential? Cell potential would be the  $E_{cathode} - E_{anode}$ . So now, if in this case which is anode, where the anodic reaction happens, so this is anode and this is the cathodic reaction, this is cathodic, so we have to consider this is the cathodic region, this is the anodic region, so what would be the overall cell potential? Cell potential would be  $E_{cathode} - E_{anode}$ .

So now if we would like to find out what would be my cell potential which is  $\Delta E$  equal to minus, which would be equal to  $E$  of cathode minus  $E$  of anode, and the cathode is this and anode is this, so  $\Delta E = E^0_{H^+ / H_2} + RT/2F \ln a_{H^+} - E^0_{Ni^{2+} / Ni} - RT/F \ln a_{Ni^{2+}}$ , simply  $2 - 1$ , equation number 2, minus equation number 1 +  $RT/2F \ln a_{H^+} - RT/F \ln a_{Ni^{2+}}$ , since I have considered this is to be 1, this is to be 1, so  $- \ln a_{Ni^{2+}}$  concentration, so this is my overall cell reaction. And what is my overall cell reaction?  $Ni + 2H^+ = Ni^{2+} + H_2$ , this is my overall cell reaction, and this is my overall cell potential and here also you see you have a redox reaction, the redox reaction is this to this is reduction this to this is oxidation, so this is oxidation, this is reduction. So you have redox reaction, so this is a corrosion process. Whenever you have a redox reaction that should be a corrosion process, okay, now if this is the case we know what is the value of this standard reduction potential for hydrogen, so that is zero, so this also we know that means  $0 - 0.25 - 0.25$  minus because this is basically  $- 0.25 + RT/2F$ . Now what is the hydrogen ion concentration? Now I can write  $\ln$  in the form  $2.303 \log$  of hydrogen and concentration into 2 to the power hydrogen ion concentration square -  $2.303 \log a_{Ni^{2+}}$ .

Now I have to find out what is my hydrogen and concentration? Hydrogen ion concentration can be found out from this pH it would be equal to  $8$  equal to minus log hydrogen ion, so it's nothing but  $10$  to the power, hydrogen concentration would be, so even you don't have to find out hydrogen concentration because this term you can write - - it's becoming  $+ 0.25V + RT/2F \ln a_{H^+}$

2.303, I can put a minus sign and then I can replace it with pH, so this would be 2 pH, so 2 x pH because I have taken minus sign, so if you take the minus sign out so there should be a minus sign, you can write it as minus minus the log H<sup>+</sup>, so this is equal to -2 pH because only this term, forget about this two terms, so this term is basically minus of this term is pH, so minus 2pH, so this is coming this - 2.303 have taken out, log Ni + 2, concentration of this. So this is my, let me just remove this, so I can have this formula. Now once you have this formula so then simplify again 0.25 + RT x 2.303 by 2F - 2pH - again minus would come so minus log of Ni<sup>2+</sup>, so now I have to find out what is the concentration of Ni<sup>2+</sup>? Now also we know KSP for Ni(OH)<sub>2</sub>. So KSP solubility product should be Ni<sup>2+</sup> OH<sup>-</sup> whole 2 because Ni<sup>2+</sup> + 2OH<sup>-</sup> - would be equal to K<sub>sp</sub> OH<sup>-</sup> whole 2, for this reaction you can write this, which is solubility product with this.

Now what would be my concentration of OH<sup>-</sup>, because I know pH from this also we can find out the concentration OH<sup>-</sup>, now again for water H<sub>2</sub>O ⇌ H<sup>+</sup> + OH<sup>-</sup> for this I can write 10 to the power minus 14 would be equal to H<sup>+</sup> OH<sup>-</sup>, I can write this, so if I write this then from this I can write log of H<sup>+</sup> + log of OH<sup>-</sup> would be equal to -14, now let me put a minus sign here, let me put a minus sign here so this would become plus, so this is nothing but pH so pH - log of OH<sup>-</sup> = -14, so OH<sup>-</sup> concentration would be equal to 10 to the power - 6 unit, let me put it as unit.

Now this is my OH<sup>-</sup> concentration so let me put OH<sup>-</sup> concentration here, see if I put OH<sup>-</sup> concentration here, so then my nickel ion concentration would be equal to, K<sub>sp</sub> is nothing but 1.6 x 10 to the power - 16 / OH<sup>-</sup> whole 2 = 1.6 x 10 to the power - 4 unit, so nickel ion concentration plus, plus ion concentration in the solution I can also find out from this relation, so if I see the nickel ion concentration here let me put all those values here now. In this case let me put so E cell would be equal to 0.25 + RT x 2.303 by 2F into - M because here I have taken the minus sign out into pH, so here 2, 2 would get cancelled, so finally I'll have this minus log of nickel ion concentration is this, so 1.6 10 to the power - 4, so if you simplify it so you would get the final value ΔE cell would be equal to minus 0.1106, why? Because you just put R equal to this, T equal to this, and F equal to this, so you would get this value, this is the ΔE cell of the reaction, fine, so if you have this then what would be my ΔG and E relation? ΔG = - RT - nF E<sub>0</sub>, n is equal to 2 here, so 2F into here is ΔE and here ΔE is positive, negative, so these become positive, so if this becomes positive here we should not consider ΔG<sub>0</sub> because I am not considering it in terms of, in the standard state, so here it would be ΔG, so ΔG equal to a positive value. If it is positive value then it should be non-spontaneous, okay, so if it is non-spontaneous that means what we have considered that nickel will go into nickel ion, and hydrogen will come out as a hydrogen gas, that assumption is wrong, so that reaction is non-spontaneous. So in fact nickel corrosion would not happen or, nickel dissolution would not happen in this condition.

So we find out this relation that is ΔE cell for this process, this is in gas form and the relation what we had, what we have after considering all the concentration of nickel ion in the solution and that is found out from solubility product as well as the hydrogen ion concentration that is found out from pH of the solution, so we can have this relation 0.25 - RT x 2.303 / 2F, so 2 will get cancelled, because we have 2 pH F x pH - RT x 2.303 / 2F x log of 1.6 x 10 to the power - 4, since the nickel ion concentration we have found out this value, this much unit. So from this we can find out this is ΔE, we can find out this.

Now the same time now we can find out what would be my free energy change? Free energy change  $\Delta G$  would be  $-nF$ , here  $n$  is 2, into  $\Delta E$  cell, so  $\Delta E$  cell here it is negative, so if it is negative, so there is a negative sign, so finally it would become positive. So when  $\Delta G$  becomes positive so that reaction is not feasible or not spontaneous, so this reaction will not happen in the condition what we have stated here, so this is a non-spontaneous process so we can also state in other way so if nickel ion, nickel ion is not forming from nickel so then rather we can say that corrosion will not happen, the condition what we have said, that is the pH8 deaerated water solution and if the solubility product of nickel hydroxide is  $1.6 \times 10^{-16}$ , so this is one example. So by applying the knowledge what we have gathered the  $\Delta G^0$ ,  $\Delta G$ ,  $E^0$ ,  $E$  as well as the reaction equilibrium constant we can have all those, all those values combined together we can have some idea or feasibility of a reaction or the spontaneity of a reaction.

Now let me again come back to reduction potential series, the reduction potential series when you have found out that time we have considered the values of all the reduction reaction with respect to hydrogen electrode, so if you consider all the reduction reactions, all the potential measurement with respect to hydrogen electrode then we can have a series, this is a series where you can put all those values of standard reduction potential series from positive value to a negative value, let's say last class we have seen, let's say this reaction  $Fe^{2+} + 2e^- = Fe$ , let's say  $Ag^+ + e^- = Ag$ , this is a reduction process and this can be  $E^0$ , if this is at unit activity, and so and this is also measured with respect to hydrogen electrode.

Now we have also come to know that this, this is one particular value is assigned to it, that is nothing but 0V, so now with respect to 0V, if you would like to find out the reduction potential or the standard reduction potential for this reaction they should become 0.8V. Similarly you can find out what would be for copper, that case it is basically nothing but 0.34V. Now you can also find out for let's say I have 0, let's say  $Sn^{4+} + 2e^- = Sn^{2+}$ , so this is also a reduction process and you have two ions, now you have to maintain this two ion concentration unit activity, so that case you would get  $E^0$  for this reaction and with respect to this, this would be equal to +0.15V, so like that way you can have a series, above 0V or the hydrogen, standard hydrogen reduction potential, also you can have below 0V, so that case let me find, let me put some value, let me say  $Pb^{2+} + 2e^- = Pb$ , this is also reduction reaction, that case if you measure the potential of this reduction reaction with respect to hydrogen electrode, then you will have a value which is negative 0.13V.

Now similar way you can find out for  $Zn^{2+} + 2e^- = Zn$  that case my reduction potential would be 0.761 or 0.761V, so now we have some values which positive, we have some values which are negative, compared to 0V, what are the importance of this minus sign and positive sign, let's say you have two reactions that are happening, one is this reaction, another one is this reaction, so this is also considered in this form, in this form. So now if you combine this two reaction then you can form these values, you can directly infer that this reaction, this reduction reaction would happen and this reduction reaction would not happen. And let's say I combined these two so this reaction reduction reaction would happen because this has a reduction potential which is positive and this are negative value. So if reduction potential which is positive compared to the other reduction potential and if we combine this two, then the one which has the higher

reduction potential that reduction reaction would happen and consecutively the other reduction reaction would not happen, so this information we can have.

Now from this also we can say, let's say I combine this two, in some situation I can have this reaction as well as this reaction. Now if we would like to find out or try to compare what case would be more feasible then we can say that this value has a higher reduction potential than this that means the silver ion would have higher tendency to get reduced and copper ion would have less tendency to get reduced. So this information we can get, so that means we can also say that this one is more active than this one, so if the reduction potential, now we can have one, information what we can get, we can have one which one which reduction process is more feasible, that means let's say if we have  $\text{Ag}^+ + \text{e}^- = \text{Ag}$  in that case  $E^\circ_{\text{Ag}^+/\text{Ag}} = 0.8\text{V}$  and if we have  $\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}$ , so that case  $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34$ , so this value is greater than this, so since this value is greater than this, this has higher tendency to get reduced or that means if we, from this we can easily tell that which one is more active compared to the reduction process and if this is more active compared to reduction process, so here the deposition reaction would always take place compared to this.

Now if we compare, you can also place it in this manner, so if let's say some metal M, if it has a higher tendency or the tendency to get corroded, so or metal ion formation tendency is very easy, so metal ion formation tendency is very easy, so then what we say that the oxidation process for this metal is very high or we can also say that this is very active metal, very, very active metal, so that means if the oxidation tendency is very high then we can say that this is active metal.

Now similar way if another metal N, so that has also the tendency to form  $\text{N}^+$  ion but there we can see that if we have this situation if we combine this two then all as you will find that this will go and deposit on this, if the reduction potential is greater than  $E^\circ_{\text{M}}$ , and so now if you combine this two process, if this condition is satisfied so  $\text{N}^+$  always has the tendency to get deposited on this, similarly we can see that if we have zinc and copper, zinc and copper so in that case we have seen that if we have this situation, so always the spontaneous reaction would be  $\text{Zn}^{2+}$  ion will form and copper will deposit, so this reaction would happen if we have a voltaic cell in this, in case of voltaic cell we can have this relation, this kind of reaction. So this kind of reaction also it can be predicted from this.

Now let say this and this, so this has higher reduction potential so it has the higher reduction ability and this has lower reduction potential, it has a lower reduction ability and if you combine, so in other way around this has higher oxidation tendency than this, sorry this has higher oxidation tendency than this, because it has a negative value. Now if you compare this two, so this has a negative reduction potential so it has a lower reduction ability, and if you have a lower reduction ability it also means that it has higher oxidation ability, so zinc always will try to form  $\text{Zn}^{2+}$  and copper will always try to deposit from copper ion and it will take two electron and deposit copper, so from this source we can say that which one is active and which one has a tendency to deposit, and if something has a tendency to deposit that means it doesn't want to go into solution, if it doesn't go into solution that we can also mention it as some nobility, or we can say that it has higher nobility or it has a lesser tendency to go into solution. So from this zero above zero it would always have noble metals and lower zero we consider at



this is active metal. So this are all the metallic system so this are noble system and this is a active system and because we compare with respective zero potential, beyond zero potential we consider as a noble metal, below zero potential it's considered to be active metal, what does it mean? Active means, it has the higher tendency to get oxidized and noble means it has the higher tendency to get reduced, this information we get. But we cannot get many information from this what are those information we cannot get from?

Now here we consider  $E_0$ , okay, if it is  $E_0$  that means it's a standard condition at the same time the activities of those ionic species here that the activity of those species are not 1, if these are not 1, so then we can have, we cannot say that this will, if you combine this and this then copper and zinc, if the activities are not 1, then we cannot specifically say that zinc will corrode or zinc will from  $Zn^{++}$ , and copper will deposit, copper ion will deposit in the form of copper, we cannot say that, because if we change the concentration the actual potential on the electrode will change.

Now because let's say  $E_{Cu^{++}/Cu} = E_0$ ,  $Cu^{++}/Cu + RT/2F$ , because two electrons are involved here  $\ln Cu^{++}/Cu$ , similar way this is one, second case is  $E_{Zn^{++}/Zn} = E_0$ ,  $Zn^{++}/Zn + RT/2F$ ,  $\ln Zn^{++}/Zn$ , let's say we have this relation, we have this reaction, that case what would be my cell potential?  $\Delta E = E_0_{Cu^{++}/Cu} - E_0_{Zn^{++}/Zn} + RT/2F \ln Cu^{++}/Zn^{++}$ , since these are 1, these are in metallic condition. Now if you see this if these are at unit activities so these would always be  $0.34 - 0.76$ , so it would be  $0.1$ , this is  $1.1V$ , so this is positive. So if this is positive, so it's a spontaneous reaction, we have seen the relation.

Now if these are not at unit activities, so if these activity is more than this, and if the value of this if,  $Cu^{++}/Zn^{++} + RT/2F$ , if this value is negative, if this value is negative and let's say it values becomes  $0.12 - 1.2$  this value becomes  $-1.2$ , so if it is  $-1.2$  depending on the concentration of  $Zn^{++}$  and  $Cu^{++}$ , so what will be my  $\Delta E$  cell? It would be equal to  $-0.1$ , so now we see that the cell potential is minus, if it is minus then the reaction is non-spontaneous, so this reaction would not happen rather opposite reaction would happen so that case copper will come out as copper ion and zinc ion will deposit as zinc, so that means from this we cannot predict, we cannot have any idea what will be the effect of the concentration on the cell reaction.

Our second thing is another case is this is always standard state, so if we have a non-standard condition we cannot predict what would be the reaction or standard state means it's always considered as 25 degree Celsius and unit activity, if it is different the temperature is different then we cannot predict, which way it should go. Similarly, if it is alloy, let say copper zinc alloy in the copper zinc alloy we cannot have the simple relation like  $E_0$  of Cu,  $E_0$  of Zn because in the alloy we are not maintaining a pure condition, because this is always with respect to the pure metal, so these three conditions we cannot have any idea or we cannot predict anything from this  $E_0$ , or the reduction potential series. Thank you.

#### Acknowledgement

Ministry of Human Resource and Development

Prof. Phalguni Gupta

Co-ordinator, NPTEL IIT Kanpur

Prof. Satyaki Roy  
Co Co-ordinator, NPTEL IIT Kanpur

Camera

Ram Chandra  
Dilip Tripathi  
Padam Shukla  
Manoj Shrivastava  
Sanjay Mishra

Editing

Ashish Singh  
Badal Pradhan  
Tapobrata Das  
Shubham Rawat  
Shikha Gupta  
Pradeep Kumar  
K.K Mishra  
Jai Singh  
Sweety Kanaujia  
Aradhana Singh  
Sweta  
Preeti Sachan  
Ashutosh Gairola  
Dilip Katiyar  
Ashutosh Kumar

Light & Sound

Sharwan  
Hari Ram

Production Crew

Bhadra Rao  
Puneet Kumar Bajpai  
Priyanka Singh

Office

Lalty Dutta  
Ajay Kanaujia  
Shivendra Kumar Tiwari  
Saurabh Shukla

Direction

Sanjay Pal

Production Manager  
Bharat Lal

an IIT Kanpur Production

@ copyright reserved