Indian Institute of Technology Kanpur

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On
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Course Title

Environmental Degradation of Materials

Lecture – 04
Broad Subject: Thermodynamics of corrosion

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In the last lecture we have come across a relation for a particular reaction, let's say aA + bB, if it is already equilibrium cC + dD for this reaction if it is happening at a particular temperature T, then del G we can have a relation del G, del G0 + RT Ln, activity of C to the power C, activity of D to the power D, activity of A to the power A, and activity of B to the power B, here if this reaction is going towards this direction then the activity of C and D is coming here and activity of A and B are coming in this section, so now we have this relation, this is called reaction isotherm and also we have gotten another relation action which is del G0 equal to - RT Ln Ka, now this is true when the reaction goes to equilibrium, so if it is equilibrium, so this is going to 0, so if this goes to 0 then this is my relation with respect to equilibrium constant and free energy change at standard state. Now this K, I can replace it with Kc RT - RT Ln Kc, Del G0, if I take all those activities in terms of concentration or molarity.

Now this is one important relation, now while doing that, now we have to see how would we relate an electrochemical relation, electrochemical reaction with the free energy change and equilibrium constant. Now in this lecture, we would be talking about the relation between potential that is developed due to some electrochemical reaction and the free energy as well as equilibrium constant. Now we have already seen that for any corrosion reaction there must be a redox reaction that should be going on.

Now let's say we have already, we have also seen that there are two kinds of cell, one is electrolytic cell, and another one is galvanic cell. The galvanic cell where you have chemical energy according to electrical energy, and in another case where you supply current and get chemical reaction, now that is electrolytic cell, so one case you let's say you have one zinc electrode dipped in zinc chloride, zinc sulphate solution, zinc sulphate solution and that to in one mole, concentration is one mole, now another beaker you have copper electrode, that is zinc and here it is copper and it is dipped in copper sulphate solution, now if you see it separately then you can let's say you have some reference electrode and would like to find out what should be the potential at this metal surface then you can connect it to another reference electrode, reference electrode you will see that there is a definite potential at this electrode because of something that is happening and if you see that reactions that are going on under equilibrium Zn++ +2e going to Zn and at the same time since this has reached equilibrium it also goes back, so this electron accepting as well as electron giving away reactions both the reactions are occurring at the same rate, so redox reaction is occurring at the same rate, because this is reduction, this is oxidation, so you just connect oxidation, you just take this two term, that means this is redox reaction and this redox reactions is occurring, both the reactions are occurring at the same rate.

Same thing you will also see that some potential is developed here and there the reaction is Cu++ +2e both reduction as well as oxidation both reactions are occurring at the same rate. Now let's say you have salt bridge which is K+ Cl- you have a salt bridge and at the same time you connect it to a voltammeter, now you will see that this voltammeter gives some reading, and this reading is basically when this is not connected then this reading shows that this would be some value, some value E, some definite value, for example Cu++ +2e if you see it's E0 for the time being let us understand this is a reduction potential, this reduction potential value is of the order of 0.34V, now e04, Zn++ +2e going to Zn e0 is at the order of -0.76, so this voltage would be 0.34 + 0.76 is of the order of 0 1.1, 1.1V you will see.

Now 0.34 I'm just matching the data, 0.34 for Cu+2 +2 is Cu and for zinc, let me also match the data, zinc is 0.76, this is fine, so your voltammeter reading will show 1.1V, so that means you are, and now if you connect it if you sock it then you will see that there would be a current, okay, so actually you are having some reaction here and you are getting some current so this current, some current it will flow through the circuit.

Now what is the source of this current? What is the source of this potential difference? This potential difference is becoming because of a redox reaction that is going on throughout this system and now if you see the reduction potential of Cu++ +2e going to Cu that case its value is positive and here it is negative, what does it mean? It means that the Cu++ has the higher tendency than Zn++ to get reduced and going to copper, and in case of zinc if it is having higher reduction potential so preferably the Cu++ +2e will go to copper, from copper sulphate and it would deposit on this surface. Now if you have this reaction here so that means you must supply two electron, where from this two electron will come? Two electron would come from this place because it has a lower reduction potential or in other way it has higher oxidation tendency, so zinc will oxidize, so zinc will oxidize, zinc it will release two electron and going to Zn++ so oxidation reaction will occur here. So these two electrons which is released here, these two electron will flow from this end to that end and then we have this two electron will be consumed by this reaction.

Now here you see two chemical reaction, one is oxidation, one is reduction and giving rise to some current and the source of the current is the basically a potential difference, now that means here you have chemical energy going to electrical energy. Now let us come to again, Del G part, what is Del G? Del G is the difference in free energy between state one and state two, let's say this is one state and this is second state, and now we have a change which is spontaneous, if the change is spontaneous so the free energy for this state two, and free energy of state one if you see the value than this one must be having a lower value than this. If it is having lower value end of this so what would be Del G? Del G would be negative, and this negative value because any spontaneous reaction if you consider the free energy and reaction coordinate you have this kind of nature, so this is my activation energy, this is my activation energy Ea, and this is my gradient, free energy gradient if it is negative the system would have a reaction which is spontaneous in nature, but what would be the rate of the process that would be decided by Ea, but if you have a negative nature so we can say that the system, there is a possibility that this reaction can happen spontaneously. Now if it is negative, we have already seen that the negative free energy change is nothing but the kind of work that is available, that kind of energy that is available for doing useful work, the energy available for doing useful work. Now here, now there must be some sort of free energy change for this chemical energy and that should be negative and this must give rise to some work which is nothing but here it is electrical energy or electrical work, okay. Now electrical energy how would we quantify? Electrical energy is quantified by E versus charge.

Now if you have let say one gram mole of copper that is getting deposited here for that process what would be the charge that is required? The charge is nothing but 1 Faraday, which is nothing but 96500 Coulomb, Coulomb per gram mole, so this much charge you need for converting 1 gram mole copper ion to 1 gram mole atomic copper, so that means here we have two electron that is associated with it, so how many gram mole, how many faraday you need to deposit 1 mole of copper, you need to 2f, 2f so that, if you supply 2f amount of charge so you can have 1 mole of copper that would be deposited on the copper surface.

So now if you have this Q, let us consider per mole if you would consider per mole of free energy change, let's say this is per mole of free energy change what would be Q then, in case of this system where you have supplied, you have had chemical change and that gives rise to electrical energy or the chemical energy change gives rise to electrical energy, so Q here would be Q would be 2F. This 2 is coming because you need to supply 2F amount of charge to deposit one mole of copper, since here we have 2 electrons that is associated with a discharge of, with the deposition of 1 mole of copper.

Now similar way in this surface if you consider if you supply 1 Faraday electricity, then there would be 1 gram equivalent change that would be coming out in the solution. Now if you consider 1 mole of zinc that is coming out of the solution then you should supply 2 Faraday electricity, so that means for the process just like this, let's say Mn+, let's say Mn+ ne you have this reaction, this reduction reaction, that time what would be the number of Faraday that you need for the deposition of one mole of metal and so that case it would be nf, this is the total charge that is required. So what would be the electrical energy? NF into potential develop in this case, okay. So if it is the potential difference and this is one faraday charge and this is the number of electron that is associated to reduce 1 mole of metal ion, 1 mole of metal M, so this is my electrical energy.

Now if we consider that there is energy conservation, so then del G which is the free energy change for the chemical energy, for the chemical process, for the chemical process that means oxidation and reduction combine the redox reaction so for that chemical process it would be del G, which is nothing but a minus sign because here we have a lower in your free energy because we have the spontaneous reaction, if you connect it spontaneously zinc will come out and copper will deposit.

So now if this is the relation so Del G equal to –nFE, for a process for this kind, if this is the case now let's say I would like to consider in standard state what would be the value of this. In standard state this would be nothing but Del G0 and here you change it with E0, so now we have these two important relation, this is nonstandard state and this is standard state. And standard state you have to have a standard sign which is nothing but a note sign, the superscript which is not superscript for a particular quantity, that is a standard state, indication of standard state. Now this is too important reaction, too important relations.

Now let us have this entire reaction let us write it down, now here initially you have Zn Zn++ +2e that reaction is spontaneously happening and another case Cu++ +2e this reaction is happening on the surface which is nothing but cathode here it is anode. Now combinedly you can see that this reaction is taking place. If you combine this two then this reaction is taking place. Now if this is the reaction, so how to do a free energy change, free energy change would be Del G equal to Del G0 + Rt ln. Now writing in terms of concentration not in activity, in terms of activity so this is Zn++, Cu. Now if this is going in this direction so these are my reactants because this will come on top, so now another part would be Cu++ Zn. So now this is my relation, and this is my reaction I should come for this reaction. In similar way I can have, similarly I can have let's say for this process I can express E value, now this E value I can express it as E0+ RT ln Zn++, Zn the concentration of Zn++ and the concentration of zinc, now what is this relation? This relation is termed it as Nernst equation. Nernst Equation, and if you consider the way have written this, it's written like Zn++ is coming on top and zinc, metal concentration is coming at bottom. Now if you see this, this is considered to be a reduction potential. Now, for that always we write it as when we consider reduction potential we see the tendency of a metal ion to get reduced to metal. This is my reaction and for this if I would like to find out what would be my Nernst equation, in terms of reduction potential then this is my relation, so what do we write to more precisely write this reduction potential, we write Zn++ Zn, so if you see that E and subscript Zn++/Zn that means that this is a reduction potential. If you write it reverse E Zn/ Zn++ so then it's nothing but oxidation because from Zn++ it goes to Zn it's kind of reduction, then only you can have from Zn++ to Zn, so that's why it's a reduction potential. If you write in this manner so then zinc which has a tendency to go to Zn++ which is nothing but oxidation so then this is oxidation potential.

But in my lectures I'll always consider reduction potential, so reduction potential and oxidation potential if you would like to find out relation is nothing but -E Zn++ Zn, so there is a negative sign associated with this, so this is my relation. So if you consider anyone of this you can consider any one of this but I would consider all is this reduction potential.

Now if you have this relation I can also write it in terms of Ox which is oxidant, + 2e going to nothing but a reductant. Now if you place it here so what would be my final relation? My relation would come E ox/red, this is oxidant goes to reductant equal to E0 oxidant goes to reductant + RT ln Ox, concentration of oxidant and consideration of reductant. So this is my relation.

Now if you consider what is my reduction potential for this reaction then reduction potential for this reaction is this, and what is this? This is at standard state and when these are at unit activities, okay. If these are at unit activities or unit concentration then this potential is equal to E0 and this is nothing but my standard state.

Now what is the relation between E and concentration of oxidant and reductant for this case? Same way I can write, in this case oxidant is this, this copper so E Cu++ Cu equal to E0 Cu++ Cu + RT, sorry I have missed one important point nF, Our nF here it is 2, n is the number of electron, so here I have to put 2 here so that is the number of electron associated with this reaction and F is the Faraday. Now this is my relation RT by 2F into Ln concentration of ox oxidant Cu++ and concentration of copper.

Now what would be my let say, I have developed some potential here, I have develop some potential here and let's say it is not connected, not sorted, then what would be my potential here if I have one mole of Zn++ ion so if I have one mole Zn++ ion and this is solid, so it would be 1, so now E equal to E0, so in the beginning of the process when this is not connected and if this has reached to equilibrium at some temperature T, then they appear the potential is E0 Zn++ Zn and here the potential is E0 Cu++ plus goes to copper. Now what would be my potential difference? Potential difference is nothing but simply if this is my positive terminal because here we have electron that is getting consumed so here it would be positively charged and this is negatively charged because here an electron is coming into that metal ion because, into the metal surface because of metal ion formation, so this is negative, this is positive, so what would be my potential difference? Potential difference is nothing but in this case E equal to or Del E equal to which is the potential difference E Cu++ Cu - E Zn++ Zn and since this is at standard state because it's one concentration is one or unit activity then this would be replaced by this.

Now let us see why it is 1.1, now here it is 0.34 for E0, Cu++ Cu and here Zn++ Zn so this is 0.76 and now if you do this same operation potential on the positive terminal minus potential on the negative terminal so then it goes to 1.1V, fine. So now this is my potential difference, now if this is my potential difference so potential difference Del E into nF would be equal to what? Would be equal to - Del G, now again nF Del E0, if it is standard then here it should be zero here in the superscript equal to - Del G0. Now replace this two, we have two equations in this, what you get? Del E equal to Del E0 + RT N, N is what? In this case N is 2, let me put 2, so 2F into Ln Zn++ Cu++ Zn, now I have to see the negative sign here, so if you replace those negative sign, this positive sign would become a negative here, so if it is coming negative so my final expression would be Del E which is nothing but E Cu++ Cu - E Zn++ Zn equal to E0 Cu++ Cu - E0 Cu Zn++ Zn - RT 2F, this is 2 Faraday into Ln Zn++ Cu++ Cu, Cu++ Zn.

Now similar way this is my relation which is coming from this, now similar way if we would like to see the E Cu++ Cu equal to E0 Cu++ Cu + RT 2F which is coming from Nernst equation into Ln ox divided by concentration of red which is nothing but copper, similar way E Zn++ Zn equal to E0 Zn++ Zn + RT 2F into Ln in this case ox is Zn++ and the red is zinc metal atom, okay. Now in this case also I can have from the Nernst equation I just, this is equation 1, this is equation 2, if you subtract 2 from 1 then this part I am getting, 2 from 1 that means this is 1, this is 2, in this case also this is 1, this is 2, now let me see whether I would get the same thing here, okay, so now this things are taken care of by this two things, this is basically this minus this equal to this, this minus this equal to this, now let me subtract this minus this, so if you subtract this minus this so RT 2F + Ln Cu++ Cu, now if you subtract it then this would go up so Zn Zn++, now what is the difference here? Here we have the difference, there is a negative sign here but here it is a positive sign, so now I can make it positive, how? I can make it positive by simply changing. I'll just change the sign here so accordingly this sign will get changed.

Now even if you go via Nernst equation we are also going it the same equation what you are getting from reaction isotherm. Now that means we have the final relation, final relation E which is Del E equal to Del E0 + RT 2F, here we have 2, n is 2, Ln Zn Cu++ Zn++ Cu which is nothing but if you consider this one and if you consider the standard state then this is nothing but 1 by Kc since I have considered concentration, not the activity. Since because I have to, if you consider Kc, Kc is nothing but for this reaction Zn+ Cu++ going to Zn++ +Cu if that equilibrium so Kc would be Zn++ Cu Cu++ Zn, now one by KC is nothing but it was on top, 1 by Kc equal to, see if you consider 1 by Kc so this is going out, this is coming in, this is going out, this is coming.

So now I can replace it Del E0 + RT 2F into Ln 1 by KC, so this is another relation between potential change with Kc. Now I can think of, now what are the relation I have got in, Del G0 equal to - RT Ln Kc, see where I have gotten Del G0 equal to - RT E0, now I can, sorry this is nF now I can relate this to so E0 would be equal to - RT nF into Ln Kc. So now I have three important relations, so we are saying three important relations one is Del G which is related to equilibrium constant for a reaction, now del G is also related to the potential difference or the potential developed at some electrode and this aim is basically nothing but the number of electrons that are associated to convert one mole of metal ion to one mole of metal atom and this is another relation which is the relation between the potential developed at some electrode with respect to, with the equilibrium constant.

Now you can have a triangle, we can have a triangle, now this triangle we can put some value Del G0, I can have K here which is nothing but KC which is the equilibrium constant when the species are the reacting as well as product phases are configured in terms of molarity and then we can have E0 which is cell or electrode.

Now in that case now how Del G0 related to E0 cell, it is nothing but Del G0 equal to - nF E0 cell, now for this M n+ + ne for this reduction reaction. Now similar way Del G0 is related to Kc in this form and similar way this is related to this in this form, RT nF Ln Kc, so this is my triangle, with this, with the help of this triangle I can have a complete picture of some chemical reaction.

Now let us come to, we have now seen what is E0 cell? E0 cell is nothing but the potential difference between the red oxidation reduction reaction and oxidation reaction occurring in the system and this E0 cell is nothing but Del E0 in this case. And Del E is nothing but when this is not under standard state, Del is nothing but when this is occurring under known standard condition E2 - E1 where reduction potential of E2 is greater than the reduction potential of E1.

Now once we have this let us try to see how to quantify this Del E. In order to quantify this we need to have some standard, what is the standard? The one standard is hydrogen electrode, one standard is hydrogen electrode. Now how to write hydrogen electrode? Hydrogen electrode is written in the form H2 1 atmosphere on platinum electrode H + ion the activity is 1, this is my notation for hydrogen electrode. How would we construct this? We construct this in this form this is a sematic, now you have a small glass made pipe and where you have a platinum, platinize platinum electrode and now here you have a hydrogen supply, you supply hydrogen gas to maintain the pressure at 1 atmosphere and this is dipped in HCL solution where the activity of H+ is maintained at 1. Now if this activity is 1, now what sort of reaction that is possible on this electrode? This electrode the reaction that is possible hydrogen plus electron going to H2, this reaction is possible.

Similar way if it is reaching equilibrium so that case this reverse is also happening and you are maintaining the pressure of H2 this is gas as 1 atmosphere and you are also maintaining the hydrogen ion activity in the solution to be 1. Now if these are 1 then I can, since this is a process where the electron exchange is taking place so I can express this reaction in terms of Nernst equation and Nernst equation in terms of electrode potential or the reduction potential I can write it as E H + half H2, now what is the reason for writing this? Since I am considering reduction potential so it has to be hydrogen ion should go to H2 because of some reduction reaction and here this is my oxidant and this is my reductant. Now equal to E0 H+ half H2 + RT, how many electron is riveted for this reaction? For one mole of discharge of hydrogen, this is hydrogen atom, this is 1F because if you consider, if you write it in this fashion then this is be clear, so one hydrogen atom you need one electron, and to reduce 1H + ion. Now this is Ln, and this is what oxidant, so oxidant is H + or and this is H2 this is reduction because the final product is gas.

Now this is at one atmosphere this is at one activity or you can also consider in terms of concentration, so it's a concentration is 1 and there the relation is A equal to FC and this is basically one in this case. Now if this is the relation then E equal to E0 H+ half H2, this goes to zero, when it would go to zero, because while it would go to zero because H + ion concentration is maintained at 1 and this pleasure is also maintained at 1 now this is my relation. So the potential or the reduction potential at this electrode would be equal to this which is a standard state potential for hydrogen reduction.

Now if these are maintained at 1, then whatever would be the temperature it would always be equal to this, even if you change the temperature because here the variables are faraday it will -- because this is a constant R which is also universal gas constant, this will also not change, now only thing that can change here -- but if these things you maintain at 1, so this, even if you have a change in temperature this would always be equal to the standard state electrode potential or reduction potential. Now the convention is this is considered to be 0 volt, this is the convention and 0 value is assigned to this, so if it is assigned to 0 and if you don't change the activity of hydrogen ion and the pressure of hydrogen ion, so this would be always be 0 even if you change the temperature. Now if this is 0, so then automatically you can measure potential of another electrode because this potential is not changing, so this is a standard hydrogen electrode. And which is also in short form we call it as SHE, now what is the importance of SHE, let's say I would like to measure a potential of Cu++ +2e going to Cu, for this electrode that means you have a beaker where you have a copper sulphate solution and this is at 1 mole concentration and you have a copper rod which is dipped in a solution, we will also have some potential here. Now let's say you would like to measure this potential, so we cannot, we can measure this potential if we know what is a potential difference, so now we connect it to another hydrogen electrode, we connected to hydrogen electrode, if we connected to hydrogen electrode then what you will see, you will see a potential difference if you have a voltammeter then you will see a potential difference.

So this potential difference again from our concept what we have learnt, the potential difference is nothing but the potential at higher end, potential at higher end minus potential off at lower end. Now since this is zero and you will see that these potential is coming out to be 0.34 volt and here it is plus, so if it is plus and if it is zero, so which one would be negative terminal? Negative terminal of course would be then this one, this one will be negative terminal because this is zero because it has a lower value and this would be the positive terminal. Now this is higher end, so now E Cu++ Cu – E H+ H2, this is my potential difference for this case. So it would be, now this is 0.34 I have measured that this is potential difference is 0.34 if it is one atmosphere one volt concentration in CUSO4 solution so this would be E, and if it is one mole so again it would be a standard state because if you write Nernst equation for this case Cu++ Cu equal to E0 Cu++ Cu + RT 2F Ln Cu++ Cu, what is the value here? This is 1 and this is in solid condition, this is all should be one so E equal to this. So that mean this is E0 because at this, because of this condition one mole of CUSO4 solution we have considered this is minus, this is what? If we maintain one activity and one atmosphere pressure always it would be zero, so what would be my E0 for this? E0 would be 0.34V, E0 of Cu++ Cu, so reduction potential or the standard reduction potential for copper electrode is 0.34 and this is measured by this, so you have a standard with respect to that standard you are measuring the potential of another electrode.

So what would be my circuit? You know to measure this potential, the circuit would be very simple you have this copper sulphate one mole copper electrode in that solution, now you have a salt bridge and then you have standard hydrogen electrode, for that you have a platinum rod, platinum plate and through which you are supplying hydrogen gas, same like the previous one hydrogen gas and then you have extended this part and then this part is connected, now this is a voltammeter, you have connected this, now you have sorted this, then this is copper, there is in copper sulphate, now you will get a voltage difference and by this you can measure what is the potential for the copper electrode.

Similarly you can find it for zinc electrode, like that if you have this finding and then tabulate them you have a table, so this is a table where you tabulate all standard reduction potential, why standard reduction potential? If you maintain the activity of the species reductant and oxidant as 1, then you can get potential developed at that electrode would be equal to standard reduction potential. So if you stack this E0 for all the reduction process, okay, in that case you can have a series, you can have a series and in that what would be having zero value? This would be having E0 would be 0, this is 0V. And this E0 is nothing but the reduction potential or the standard reduction potential because I have put a subscript superscript 0, similar way I can have for example I can develop up or here is where I can have let's say Co + 3 + e it can go to Cu + Co + 2 that case my potential would be 1.82V. Similar way Cu++ +2e going to Cu, so that case my potential would be 0.34V, similar way I can have let's say for this reaction AG++ E silver potential would be 0.80V, you know in case of zinc you will see that the potential would be potential difference is a negative. So in that case let me find out what would be my reduction potential for zinc, that case it would be - 0.76V, this minus means and let's say I can compare this to, if we compare copper and zinc the reduction potential for copper is higher than the reduction potential for zinc ion, so I can say that Cu++ has the higher tendency compared to Zn++ to get reduced, okay, and then that's what the reduction potential is higher than zinc.

This is the essence of this table, now I can also have other cases let's say I have lithium, Li + E so that case it is lithium, so that case it is -3.05, what does it mean? Lithium has the highest tendency to get oxidized or lithium will always form lithium ion rather going to lithium from lithium ion. Thank you.

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