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Course Title

Environmental Degradation of Materials

Lecture – 03
Broad Subject: Thermodynamics of corrosion

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The last lecture we have come across and the important parts of corrosion. First is, there must be cathodic reaction, there must be cathodic reaction, that means electron accepting reaction or reduction reaction. Now there should be anodic reaction to supply the electrons required for cathodic reaction or reduction reaction, this is oxidation reaction. Now we have already seen that if you take this part and this part then you must have redox reaction in case of corrosion.

Now third thing is there should be electrodes and cathodic reaction occurs on cathode, cathode and the sign of that electrode might change in case of a cell where you get electrical energy from chemical energy or the most common example is a galvanic cell, there the cathode is positive terminal or the cathodic reaction occurs on positive terminal, but let say in case of electrolytic cell where you supply electrical energy and get chemical reaction in that case cathode is the negative terminal, or in the negative terminal you have cathodic reaction. So you have cathode consecutively you have anode where anodic reaction occurs or oxidation reaction occurs.

Now all these things there must be one more thing that is, there should be electrolyte, there should be electrolyte which CAD is the charge in the solution, so these are the components. And now in case of aqueous corrosion, let say zinc corrosion in HCL, we have seen that these things are there in case of the corrosion cell. Now in the same way we have taken the analogy of that corrosion cell and compared in case of dry corrosion or oxidation, in the oxidation also we have seen that if you have a metal and then metal oxide and then gas environment you have interfaces, then one interface will act as anode where anodic reaction occurs or in this interface where you have metal ion formation, okay, from metal that means 2e metal, that means here anodic reaction occurs this interface is anode. And in this interface would be cathode, because oxygen will combine two electron will go to oxygen 2- this is cathodic reaction this occurs here. And this electron transfers transition takes place from this end to this end, the migration of electron takes place through this metal oxide layer, so this electron is going and this electron is taken by oxygen and then this reduction reaction is taking place.

Now depending on whether oxygen ion will come here from this surface to this surface and combine with metal oxide and then form MO which is M++ plus O- so this reaction can take place here or this reaction can take place here where metal ion will go from this end to this via this metal oxide. Here metal oxide access electrolyte. So now you have the same analogy here you have cathodic reaction, you have anodic reaction, you have electron transition, electron migration, through the metal oxide layer as well as ion transition, ion migration through the metal oxide layer either from this end to this end or this end to this end, so metal oxide reacts is acting as electrolyte, so this is also a sort of corrosion cell.

Now let us get into the basic thermodynamics of this corrosion cell. When you talk about thermodynamics in case of corrosion then, for that we should understand G, this G is known as Gibbs free energy. Gibbs free energy, see this Gibbs free energy from this we can get the idea of a spontaneous reaction or an equilibrium or non-spontaneous reaction. Now G is considered to be the energy of, energy that is, this G is, absolute G is very difficult, is not possible to determine rather we always determine del G, which is the free energy change, and this free energy change is nothing but the energy which is available for doing work, okay.

So now this free energy when it goes to zero we call it as equilibrium. We call it as equilibrium, the system has reached equilibrium. Now if this free energy is less than zero, we call it spontaneous reaction. Now if it is greater than 0, then it is non-spontaneous reaction, non-spontaneous reaction. Now here we are missing something, the missing part is a system always is to be defined with respect to some parameters, okay, until unless we define that parameter the system cannot be thought of properly, here whenever you consider this you must mention that there should be two other parameters which define the system that is pressure and temperature those are constant.

So when del G PT that means the at constant pressure and constant time it goes to zero that time it calls, it goes to equilibrium. And here also you have to mention PT which is basically nothing but at constant temperature and pressure.

Now this is the conditions, three conditions to determine whether the system has reached equilibrium or the system is spontaneous or the system is non-spontaneous reaction. In the system non-spontaneous reaction is taking place, now this let say now with this idea will go into the equilibrium constant. Now let's say we have some reaction aA+bB is having equilibrium which is the equilibrium sign, cC+dD, this a capital ABCD are the components or this case let's say this side is reactant initially I have started with A and B, capital A and B these are the two components of the system, then it, when reaction happens then it forms C and D, capital C and D these two products. Now while doing that then you have a mole of capital A and small B mole of capital B, they are reacting and forming small C mole of capital C and small D mole of capital D these are the product phase.

Now when you have this thing then you can relate this rate of this reaction by this simple expression which is a rate, let say rate of the forward reaction that means if we consider this is to be forward reaction, and this is to be reverse reaction, reverse or backward reaction, that means when you have initially you had only A and B reaction has started, now it forms C and

D, but when it forms C and D then if you have that active masses of C and D then the backward reaction also will start, but initially the rate at which the forward reaction occurs would be higher than the rate at which reverse reaction occurs because the active masses which are participating in the reactions would be different for the product phase as well as for the reactant phase.

Now that case the rate at which the forward reaction is taking place that can be related as a simple expression which is called K1 Ca the concentration of A, this C is the concentration rather since this is we are considering a C here let us put it in this term which is let us say, let us have a term like C dash, because just to have the difference between the C component and the concentration. Now this C - A now it should have because we have A mole of A, so there should be concentration of A to the power a, small a, into concentration of B to the power b, this is my forward reaction or the concentration with respect to concentration the rate at which the reaction occurs can be expressed in this way.

The same way the reverse reaction which is given by the reverse arrow can be written as k1 C – C capital C into C D capital D, and in this case it should be 2, this K1 and K2 those are rate constants and these are having, now if you consider the rate at which forward reaction occurs and the rate at which the reverse direction occurs initially the rate if you consider the rate, let's say rate and if you consider time now initially the rate at which forward reduction occurs would be at a vest faster rate because the active concentration would be much higher because initially you have started zero concentration of this and you have the maximum concentration of this. Now as it forms gradually your active masses is going down, so the rate of the forward reaction will go down like this. Now once you start forming this, because of this reaction now you have that active masses to start initiate the reverse direction reaction, so now initially you had almost let's say you had this almost zero reaction rate, now you have started a reaction for the backward direction, this is forward, this is backward.

Now after some time this rate at which forward reaction occurs and the rate at which reverse direction reaction occurs then those two react rate would become equal, so when this rate becomes equal, this two rates, it becomes equal then we call it as that the system has reached dynamic equilibrium. Now when the system has reached dynamic equilibrium that means rate forward equal to rate backward both are same. If these are same, then I can write that K1 by K2 can be written as C C – C, C – D, D by C - A A, C - B B, now this ratio K1 by K2 equal to C C C - into CD, D this is termed as Kc which is called as, which is nothing but constant if T remains constant, fine. Now if you have this thing and this is called equilibrium constant, equilibrium constant for this reaction for this equilibrium.

Now if Kc, K this K is termed as Ka then it's called as, then the species are, species is considered not in terms of mole fraction, it considered as activity, okay. Now instead of C if you replace it by A, then it is called as this thing will change from C to A, which is again equilibrium constant but the active masses are considered in terms of activity, and activity and concentration is related in according to this formula activity with, this formula it's related. And here C is molarity, molarity and F phase fugacity or the activity coefficient and this F becomes 1, when system is a very, very dilute solution or when the system is ideal solution or the solution if the system is ideal, okay. In that case A would be equal to the molarity.

Now this formation of Ka or the Kc with the active masses or the concentration that thing was found out by two famous scientists, those scientists names were, scientists name Norwegian Chemist Guldberg, and Waage and they called it as laws of mass action. This, they found it in 1867 and it says that at a constant temperature the rate of a reaction, chemical reaction is proportional to the active masses of the reacting substances, so that means in the forward side these are the reacting substances if you consider the backward reaction these are the reacting substances. So now according to that we get Ka or Kc.

Now how would we relate this one equilibrium constant with Del G, let us see that or the free energy how the free energy is related to the equilibrium constant. When a system is an open system that time the free energy of the system is a function of pressure temperature and if you have n number of components in the system then each individual species will have some effect on the free energy of the system. So it's also related to let's say n1, n2, n3, and 1, 2, 3 up to nn these are the components 1, 2 n are the components and n is the number of moles of those components in the system.

Now if you have this then, if you have a small change in the system, let's say small change is taking place of in each, each of those parameters let’s say PT, n1, n2, n3 those mole fractions they are changing and what would be the change in G that can be expressed as, plus, so now you have small, small changes in P, then what would be the change of that pressure towards that free energy of the system that is given by this. Now if you have a small change in T the temperature then what would be the change of that T towards that free energy of the system that is given by this provided the other terms are constant, now in this way you can also express, you can express the full expression, you can have the full expression for changes in individual species towards the free energy change of the system. So then again del G, n1, PTN2 because n1 we have seeing the change in the n1 and then what would be the change towards that free energy. Then other things are kept constant, like that you can have all those expression finally you can have del G, d n n of NH species PT, n1, n2 like that up to n, n-1, because we have taken nH spaces and there are n number of components, so then you have to n with n, n-1 into dnn.

Now these are the, all the contributions towards the free energy change. Now if your system temperature and pressure those are constant, then this as well as this both are becoming 0, then the overall change of the system would be decided by the change in the other components that means n1, n2, n3, n4 like that up to the nh species. Now this is basically the physical significance of this is the rate of change in G if you have one mole of addition of one component into the system if the other components are same or constant, now this is also called it as, now this is also called as partial molal quantity, and this is also called as chemical potential. And this chemical potential is termed as mu. Now if you have this then you can express by taking this part as mu1 because you are seeing the change in first component and then you are seeing the what would be the effect on free energy change of the system, so this is considered as mu1, then this is the change in one species, the first species or the change in mole in case of first component like that you can express it as dn2 + mu3, n3 like that it would move, then muN Dn and N.

So now I have the final expression like this, now let's say you have a system, you have a system, you have n number of components, pressure and temperature constant, okay, if you have n number of components pressure and temperature both are constant in that case let's say I have a small fraction of change in each component, let's say that small fraction of changes del X or del X fraction mole is changing in every component, if you have this fraction, this is fraction, and this fraction is having this change DX is going to happen in all the components. Now what would be dn1, dn1 would be if there is n1 number of moles for first component then dn1 would be the small change in the system that is the fraction into the number of total number of mole for first species, so the first component, so n1, into del X. Same way dn2 would be n2 del X like that it would move, so dnn would be equal to nn del X, and del X is a small fraction of change in each component. If you have this, so in the system initially the free energy was G, and if you have the same fraction of change, then what would be the Del G? Del G would be absolute free energy into the change, fraction change would be equal to Del G, so if you replace it then it would be equal to G del X equal to mu1, del X n1, n1 del X + mu2 into del X, because we have already seen dn1 is equal to n1 Del X like that it would move, finally it would have mu n + nn del X.

So what would be my final expression? Final expression would be G is equal to mu1, n1 because these terms are getting cancelled, so mu1 + mu2, n2 like that it would move, finally will get mu n, nn. Now this is one of the expressions for Gibbs duhem relations. There are three Gibbs Duhem relations, the first one is nothing but the first relation for Gibbs duhem, this is first Gibbs Duhem relations, this is second Gibbs duhem relation. Now you can also get the third one if you just differentiate this term, other terms and then replace this thing into this, after differentiation for example if you differentiate this then you will get mu1 dn1+ mu dn2, dn1, d mu1 like this expression you would get and replace this and finally you would get that this term and this term are same so you will get this term everywhere if you differentiate the each term there, you will get two terms one of the term will be same as this first expression, now then you replace it you will get, it will all get canceled and you will be left with these terms only. And this would be equal to 0, that is another Gibbs duhem relation, but we will stick to this part because this part will give you some idea then finally you will come to have some relation with del G and equilibrium constant, this is my relation.

Now let's come back to the same reaction, if you consider the same reaction let's say this reaction is happening in the forward reaction, and let's say I consider in terms of activity, so activity of A is a, activity of B is b, activity of C is c, and activity of D is d. Now what, let's say I go from this end to this end, the free energy change for this system would be, free energy change for the system would be G of product - G of reactant. G of product and G of reactant if you have this that means the final, whenever you consider some free energy change or the change in a state function then let's say one state to another state, this is first state, this is second state, now if you have this change then your change in the function would be, here it is del G, then change in the function would be it is G2, if it is G1, so G2 - G1.

Now if you have some free energy associated with this reactance, you have some free energy associated with this product term, now if you go from this end to this end, now you are having some change that means you are going from G1 to G2, and what would be my free energy change? Then G2 - G1 would be my free energy change, and so for this process this is my free energy change.

Now we know this relation, this relation we know and this relation is valid let's say for a particular system initially we have the reactant so let us consider only the reactant part, the reactant part if you consider so what would be my free energy for the reactant, or the G1 in this case would be equal to mu1 or muA because you have considered two components A, capital A and capital B, so muA into you have to see the number of moles there, number of moles is A+ muB, muB, what is my reactant? This is my reactant case let's say I would like to consider the free energy for this system, this system now, in that case it is basically nothing but product or in this case this is G2 is nothing but small c, which is the number of mole of C component, so muC + D muD.

Now mu is also, this chemical potential is also expressed as mu0 + RT Ln activity, let's say you are considering the activity mode, if you would like to find out what would be my chemical potential of A, then chemical potential of A would be basically nothing but, this is nothing but the standard state chemical potential for A and this is activity of A. If you find that this is the relation then you put it here you have to just replace this thing instead of muA you put this instead of B you just change this sign capital B, the A would be replaced by capital D. Similar way it would be all capital C, capital D, for muC and muD. Now if you put all those things then you would get this expression it's an A, muA0 + aRT Ln activity of A + muB0 + bRT Ln aB, similar way this can be written as C muC0 + cRT ln aC + dmuD0 + dRT ln aD, now what would be my free energy change for the system? Free energy changes is this minus this, so if you consider this is as G1, this is as G2, so del G basically nothing but G2 - G1, and if you do the simplification then you would get muC + D muD0 - A mu a0 - B muB0 + RT Ln, you just take this term to the power of this, okay, so now aC to the power of C, now aD to the power D by aA to the power aB to the power B, so you are getting this expression. Now del G equal to what is this, this part? All our standard values, so if these are standard values then it must be constant, so this is a constant Z plus RT Ln ACc, ADd, AAa, ABb, so this is one important relation.

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