Corrosion - Part I
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Lecture - 10
Thermodynamics Aspects of Corrosion-III

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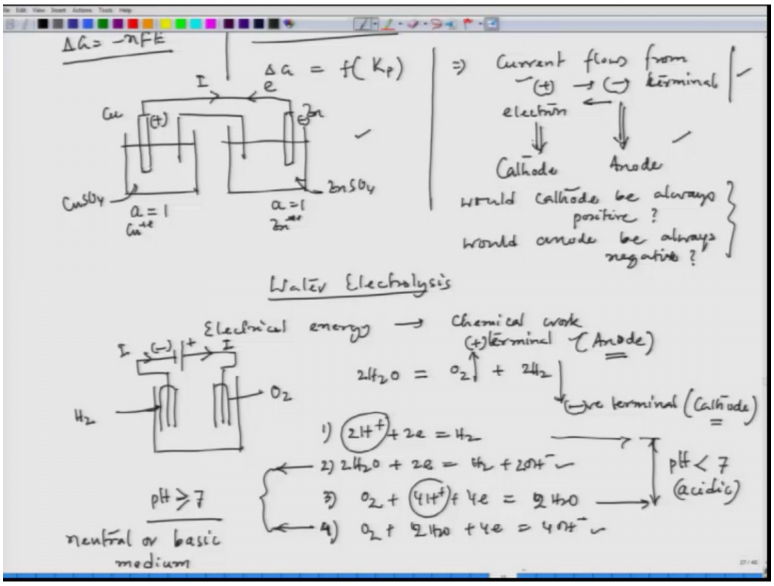

Hello everyone. We will start our 10th lecture and in this lecture, we will get into the relation between delta G and equilibrium constant. And then, over complete picture on this electrochemical behavior of corrosion would be clear. So, we already know delta G equal to minus n F E. So, before we get into this, I thought of discussing another issue, which I forgot to discuss, when we talked about sign of sign convention of cathode and anode.

If we get to the old lecture, we would see that we have started discussing on this particular cell, where we have zinc and another side is copper; and here we have copper sulphate and here we have zinc sulphate; we have a salt bridge. And now, this terminal will get to minus plus, this terminal will go to minus. And if we connect them by an external conductor, then the current will flow this way, and electron will flow this way, because we know that here oxidation happens, here reduction happens.

Now, question is we know that current flows from positive terminal to negative terminal that is what the sign becomes positive here on the copper side, and zinc side becomes negative. And remember, we are considering the concentration here or in the form of activity of irons activity of zinc, here copper plus plus, here zinc plus plus is 1. So, we will see this importance of this activity to be 1 or if it is not 1, what could be the issue.

Now, from this, it is interesting. If we try to see that current flows from positive terminal to negative terminal and of course electron would flow opposite to it. But, convention as per electrically as per the convention, we have this positive terminal to be the side, where from the current flows to the negative terminal in that external circuit or the conductor. Now, would it mean that the cathode, so this side is cathode here, and this side is anode, so would that mean, that the cathode would always be positive, and anode would always be negative.

So, the question is would cathode be always positive or would anode be always negative; we have to answer this. Now, this is a confusion that is always there in the students mind. I think it is better to clarify here that how would you take up, whether it is a cathode or anode; and whether cathode would always be positive or anode would always be negative.

Now, for that we have to bring in concept of electrolysis. So, let us say one important aspect is water electrolysis. In case of galvanic cell, the cell what we have mentioned here, here the chemical energy actually gives rise to electrical energy or electrical work. But, in case of water electrolysis, the reverse happens. The electrical energy gives rise to chemical work or chemical energy. Now, in this case, this is very popular experiment in our 10th standard, school days.

So, what we had, we had a cell, and then two platinum electrodes, and those platinum electrodes are connected to one terminal is connected to positive, one terminal is connected to negative. And then, this is negative; this is positive. And then, this here hydrogen evolves the side, which is connected to negative terminal, here we get hydrogen and the terminal, which is connected to positive terminal of that external circuit external cell, we get oxygen. So, that way so H 2 O gives rise to O 2 and H 2. So, if we balance it, this should be the balance. And this goes into positive terminal and this goes to negative terminal. So, from this concept, I should see that the cathode should be the positive terminal, but actually the cathode is here, this is cathode; and this is anode here. Why is this difference, so that means, the terminal the sign has changed for cathode and anode, so that means, it is not same. In case of cathode, we have we see that it is a negative terminal. Why, because as per this convention, current flows from positive to negative terminal. So, here current flows this way so, the current is flowing from positive to negative terminal. Now, so this current flow is this way. So, the current is flowing positive to negative terminal; with convention wise, this convention is (Refer Time: 07:42).

Now, in order to understand, why this positive terminal becomes anode and negative terminal becomes cathode, we have to understand the cell reaction. And whenever, we have water system, this water is very important, because now I am trying to say the four reactions that could be possible in water provided, there are dissolved oxygens.

So, this four reactions let me point out H plus 2 e equal to H 2, 2nd is H 2 O plus 2 e equal to H 2 plus O H minus 2 O H minus, 3rd this is not considering any oxygen dissolve oxygen, but if we have dissolve oxygen. So, oxygen plus 4 H plus plus 4 e equal to 2 H 2 O 4, oxygen plus 2 H 2 O plus 4 e equal to 4 O H minus. So, these are four major reactions that are possible in water system. And these are important, when in the with regard to the corrosion of metals; we will see later on that this reactions are extremely important.

Now, if we see that this and this (Refer Time: 09:22) two reactions, these two reactions it involves hydrogen ions. So, they are possible, when pH is less than 7, so that means, acidic. Now, if I see this two these two are possible, since they are a there are no hydrogen ions involved in this particular reactions, rather we have a generation of O H minus ion. And these two reactions are possible, when pH is equal to or greater than 7. So, neutral or basic medium, these two reactions are possible.

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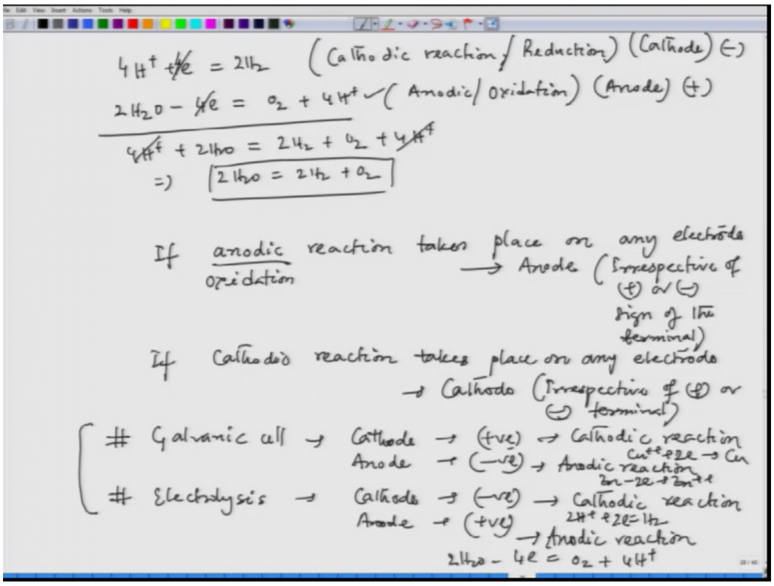

$4H^+ + \cancel{4e} = 2H_2$ (Cathodic reaction / Reduction) (Cathode) (−)

$2H_2O - \cancel{4e} = O_2 + 4H^+$ ✓ (Anodic / Oxidation) (Anode) (+)

$\cancel{4H^+} + 2H_2O = 2H_2 + O_2 + \cancel{4H^+}$

$\Rightarrow \boxed{2H_2O = 2H_2 + O_2}$

If anodic (oxidation) reaction takes place on any electrode → Anode (Irrespective of (+) or (−) sign of the terminal)

If Cathodic reaction takes place on any electrode → Cathode (Irrespective of (+) or (−) terminal)

\# Galvanic cell → Cathode → (+ve) → Cathodic reaction $Cu^{++} + 2e \rightarrow Cu$
Anode → (−ve) → Anodic reaction $Zn - 2e \rightarrow Zn^{++}$

\# Electrolysis → Cathode → (−ve) → Cathodic reaction $2H^+ + 2e = H_2$
Anode → (+ve) → Anodic reaction $2H_2O - 4e = O_2 + 4H^+$

Now, we can have two sets of reactions, those are possible in case of electrolysis of water; one set is H plus plus e equal to H 2, and then we can have another reactions. So, this is the cathodic reaction, cathodic reaction. And then, there should be an anodic reaction, which is nothing but H 2 O minus 4 e equal to O 2 plus 4 H plus plus sorry this, you see that this is (Refer Time: 11:20).

So, what I have done, this particular reaction if you see this particular reaction, I have written in the form of oxidation mode, because this is oxidation or it is anodic; we can also say that or reduction and this is oxidation. Now, if I multiply this top equation by 2, so it becomes 4; this is also 4; this is 2. So, if we add them, then it would become 4 H plus plus 2 H 2 O minus 4 e. So, 4 e 4 e, this would get cancelled equal to 2 H 2 plus O 2 plus 4 H plus, so these two gets canceled. So, finally, we get 2 H 2 O 2 H 2 plus O 2. So, this is another, this is the same one as we have mentioned here.

So, we can also have the same reaction derived from other two reaction that are possible in water system, so that means, we can consider this one; and this one, and then also we can have the same reaction products. But, interestingly now you see this is the cathodic reaction and cathodic reaction always happens on cathode. Now, since this terminal is negative so, hydrogen ion will go there and would get reduced. So, the cathodic reaction is taking place on the cathode, but interestingly this terminal is negative.

On the other hand, water would lose electron and then get to this situation, which is and this anodic reaction, this is anodic reaction, which can only happen on anode. So, the terminal is positive here. So, positive and negative terminals will be decided by which way current flows. But, whether the positive terminal is cathode or anode, it will be decided by what sort of reaction is taking place.

If so remember if anodic reaction takes place on any electrode, it would be always anode, irrespective of positive or negative sign of the terminal. Whenever, we talk about anodic reaction, definitely we can also talk about oxidation reaction. Now, if cathodic reaction takes place on any electrode, that will become (Refer Time: 15:28) cathode, irrespective of positive or negative terminal.

If we see this in case of galvanic cell, where one electrode corrodes and other electrode, there would be some cathodic reaction; either it would be deposition like in case of copper zinc system, copper deposits on the cathode. In the galvanic cell, cathode is positive and anode is negative the sign of that electrode.

And in case of electrolysis, cathode negative, anode positive. Since cathodic reactions and here also cathodic reaction so, here the cathodic reaction is copper plus plus plus 2 e equal to copper and here anodic reaction, zinc 2 e equal to zinc plus plus and here the cathodic reaction, H plus plus e H 2. And anodic reaction, H 2 O 4 e equal to O 2 plus 4 H plus. So, this should be the basic fundamental the basic behind considering, which one should be cathode, and which one should be anode.

Now, remember, corrosion is always corrosion does happen in the form of galvanic fashion, so that means, the part which is corroding, which would always be anode and the part which is not corroding, where cathodic reaction is taking place. That would be always cathode, and the negative terminal in case of corrosion, would always be anode, so that should be remembered.

But, in case of let us say kind of industrial practice, what we have is basically the coating let us say electro deposition. They are definitely the part, which is to be coated is to be made cathode, there the terminal sign should be negative, because then the deposition should happen by taking electrons by the positively charged ions. So, once we know this conventions at the now we should not have any problem with this convention, that which one should be anode, and which one should be cathode. Not the sign part is important; is the reaction part that is important.

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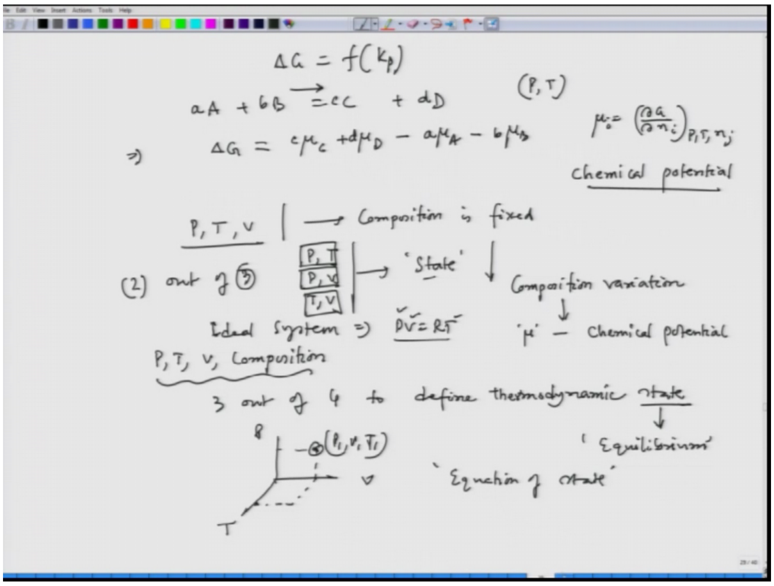

$$\Delta G = f(K_p)$$

$$aA + bB \overset{\longrightarrow}{=} cC + dD \qquad (P, T)$$

$$\Rightarrow \quad \Delta G = c\mu_C + d\mu_D - a\mu_A - b\mu_B \qquad \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j}$$

Chemical potential

P, T, V | → Composition is fixed

(2) out of ③ P, T / P, V / T, V → 'State' ↓ Composition variation ↓ 'μ' – Chemical potential

Ideal system ⇒ $PV = RT$

P, T, V, Composition

3 out of 4 to define thermodynamic state ↓ 'Equilibrium'

'Equation of state'

Now, let us get to the concept what we have been talking about is the relation between delta G K p. In order to do that, let us take a basic relation, when any chemical reaction let us say A plus B equal to C plus D. And now, let us say number of b atom, a atom, this is the number of molecules that are involved in this reaction. Now, if this system reaches equilibrium, let us say it does not reach equilibrium in the beginning, I do not know, whether it has reached equilibrium or not.

Now for this reaction, if it is happening at a particular temperature and pressure and if these are condensed system ok. So, those condense system, initially we will talk about condense system; and then we will see k what happens, if we have a kind of gaseous system. There the situation would be little different, but in case of condensed system, we start looking at free energy change for this reaction.

And if we see that the free energy change in this direction if we consider, then the free energy change would be mu of C plus mu of D minus a mu A minus b mu B. Now, question is what a mu and what is mu, mu is nothing but this is written in the form of n i let us say i P, T, n j. Now, this is a kind of definition, what we have for the mu; mu is considered as a chemical potential.

Now, as we know that if there is no composition change, then we can define any thermodynamic system, rather we can define a state of a thermodynamic system by three parameters and two independent parameters. So, if you have pressure temperature and volume, and let us say the composition is fixed. And if it is a closed system, then we can either have P or T or P or V or T or V to define the system. And define the system means, define the state. And state is nothing but the equilibrium position of that particular system of that particular thermodynamics system.

Now, once we have the composition variation, then we have to introduce one more parameter to define the state of the system. And that parameter is defined in the form of chemical potential, because the composition becomes also another factor. So, when we have, so that means, when we have a system like P, T, V and composition in order to define the state of the system, then we need to have 3 out of 4 to define thermodynamic and state.

Now, we have been talking about state, the state is nothing but the state of equilibrium until or unless the system has gone to place itself at some position, where the all the parameters are fixed, we cannot define the system. If the system is moving in that particular space P, V, T space, we will not be able to define its system its state.

Now, for example, if we have a P, V, T P, V, T system for example, if it is here, now we know, what is the what is the temperature of this particular point. So, this is basically a three-dimensional situation, where I need to find out the position of that coordinate of that particular space; this is P 1, V 1, T 1. So, this coordinate we have to fix.

Now, in this case, we see that two parameter out of three 2 out of 3. Since, we have equation of state in case of ideal system, for example, ideal system, we have equation of state as PV equal to RT. So, now if we fix P if we fix V, so T is automatically fixed, because this relation has to maintained so, now that means, my state is fixed. Now, in this case, 3 out of 4 we have to fix, then the last one is automatically fixed by equation of state. So, what is that equation of state, we have to find out ok.

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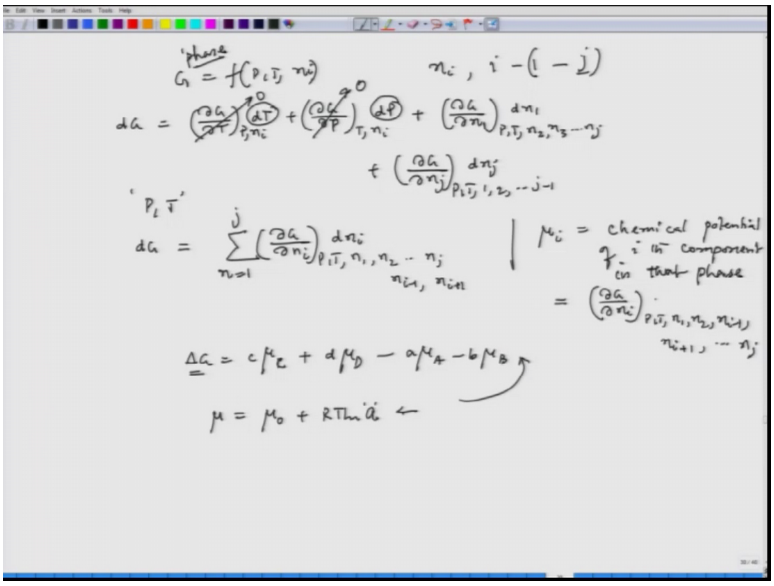

'phase'

$$G = f(P, T, n_i) \qquad n_i,\ i - (1 - j)$$

$$dG = \cancel{\left(\frac{\partial G}{\partial T}\right)_{P, n_i}} \boxed{dT}^{\,0} + \cancel{\left(\frac{\partial G}{\partial P}\right)_{T, n_i}} \boxed{dP}^{\,0} + \left(\frac{\partial G}{\partial n_1}\right)_{P, T, n_2, n_3 \cdots n_j} dn_1$$

$$+ \left(\frac{\partial G}{\partial n_j}\right)_{P, T, 1, 2, \cdots j-1} dn_j$$

'P, T'

$$dG = \sum_{n=1}^{j} \left(\frac{\partial G}{\partial n_i}\right)_{P, T, n_1, n_2 \cdots n_j,\ n_{i-1}, n_{i+1}} dn_i$$

μ_i = chemical potential of i^{th} component in that phase

$$= \left(\frac{\partial G}{\partial n_i}\right)_{P, T, n_1, n_2, n_{i-1}, n_{i+1}, \cdots n_j}$$

$$\underline{\underline{\Delta G}} = c\mu_C + d\mu_D - a\mu_A - b\mu_B$$

$$\mu = \mu_0 + RT \ln a \leftarrow$$

So, if we try to see G as a function of P, T and number of components compositions, so this n i, i varies from 1 to n let us say or n 1 to j let us say varies from 1 to j. Then I can write this partial I can write this equation n 1 P, T, n 2, n 3 like this n j and d n 1. So, similarly I can write del G d n j P, T, 1, 2 j minus 1 j plus so j minus 1, because I see that only up to j is available in the system.

So, now if we fix P and T, then we get del G equal to so, this goes to 0, if we fix P and T. So, this term goes to 0; this term goes to 0; so this is also 0. So, we are left with so ith 1 is missing, so then I can write n i minus 1 n i plus 1 d n i. So, and here n varies from 1 to j. So, chemical potential of i that means, chemical potential of that component in that particular phase. This is talking about a particular phase; this is a phase.

In that particular phase, the variation of the rate of change of free energy if we add one atom, one mole of ith component or if we take out one mole of ith component from that particular phase, that particular change is termed as mu. So, this mu is also called at chemical potential of i, ith component in that phase so, this is defined as j. And this is of course is intensive property, because it does not depend upon the size of the system.

So, now getting back to this particular relation, so any reaction we can have reaction like what we mentioned here, what we mentioned here. So, we can write the free energy change as the product chemical potential of product minus chemical potential of reactant; so, this is we can write.

Now, from that also we can convert this into the standard value, because chemical potential also can be written as RTL n activity of that component. Now, here I am putting activity, because we are seeing that this is a condense system, we have said that it is a condense system. But, if it is a gas, then the situation would be little different; we will come in our next lecture. But, for the time being, we will stop by saying this particular equation that this equation will be put up in this equation, and then subsequently we will progress and then see the relation between free energy and equilibrium constant. So, let us stop here, we will continue in our next lecture.

Thank you.