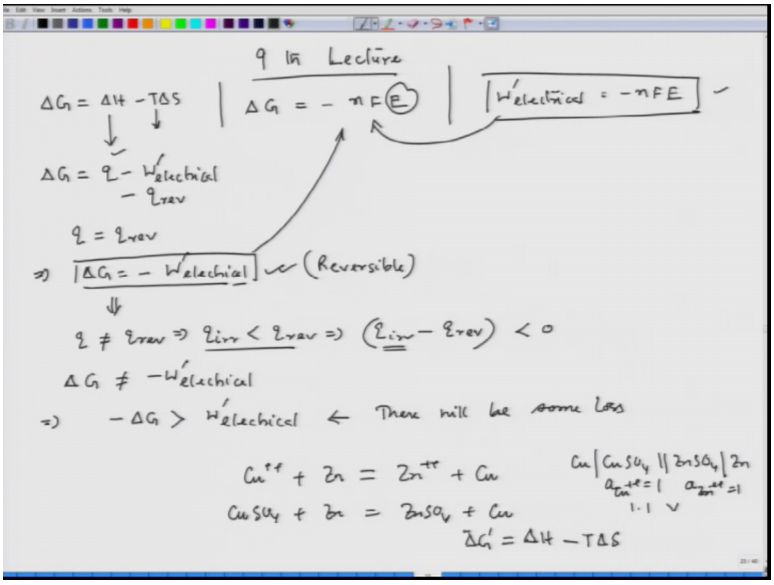
Corrosion - Part I
Prof. Kallol Mondal
Material Science Engineering
Indian Institute of Technology, Kanpur

Lecture - 09
Thermodynamics Aspects of Corrosion-II

Hello everyone, today we have our 9th lecture.

(Refer Slide Time: 00:20)



9 th Lecture

$\Delta G = \Delta H - T\Delta S$ | $\Delta G = -nF\boxed{E}$ | $\boxed{W'_{electrical} = -nFE}$

$\Delta G = q - W'_{electrical} - q_{rev}$

$q = q_{rev}$

$\Rightarrow \boxed{\Delta G = -W'_{electrical}}$ (Reversible)

$\Downarrow$

$q \neq q_{rev} \Rightarrow q_{irr} < q_{rev} \Rightarrow (q_{irr} - q_{rev}) < 0$

$\Delta G \neq -W'_{electrical}$

$\Rightarrow -\Delta G > W'_{electrical}$ ← There will be some loss

$Cu^{++} + Zn = Zn^{++} + Cu$

$CuSO_4 + Zn = ZnSO_4 + Cu$

$Cu|CuSO_4||ZnSO_4|Zn$

$a_{Cu^{++}} = 1 \quad a_{Zn^{++}} = 1$

1.1 V

$\Delta G' = \Delta H - T\Delta S$

And here we would continue our discussion on Thermodynamics Aspects of Corrosion and in our last lecture we have come across relation which is nothing, but del G equal to minus n F E, and this relation was obtained from the basic classical thermodynamics as well as electrical work. One side was classical thermodynamics which started from delta G equal to del H minus T del S and finally, we have got to the situation which is delta G equal to q minus w prime electrical plus minus q reversible.

This is the relation we obtain and then finally, we consider reversible situation in the reversible situation q equal to q reversible. So, we got delta G equal to minus w prime electrical. Whereas, on the other side we have tried to see the work done which is w prime electrical if there is some charge flow across a potential difference and that goes to n F E that one also we have seen.

And from this two conditions since this is this is one relation and this is another relation, we got to this relation. Now, this is the work which is the maximum work that is possible when we have one mole of substance either coming into the solution or getting deposited on a metal surface. Now whether this is the maximum work or not that we can also prove from this relation, let us say if it is e irreversible process. Then irreversible process q is not equal to q reversible and also we can see the q irreversible is if I put it as irreversible is less than q reversible the heat for reversible heat is more than the irreversible heat.

Now, we are considering that the system is going irreversibly; that means there is a spontaneous reaction a spontaneous process. Now once we have this relation, then delta G is not equal to minus w prime electrical work. Rather if this is true then q irreversible, minus q reversible and this q irreversible is nothing, but this in case of irreversible is process is less than 0 because q reversible is more than q irreversible. If it is less than 0 then, we can get minus delta G is greater than w prime electrical.

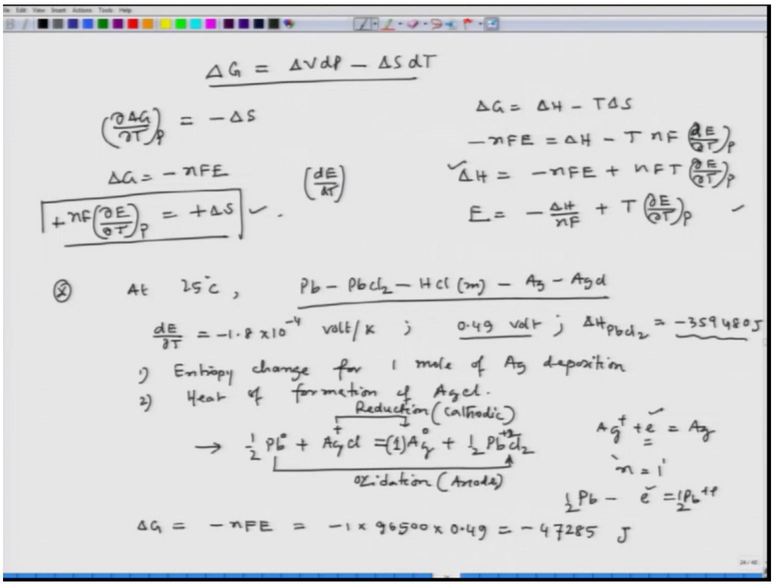
What it means? That the amount of free energy that is available for doing work, that work is that amount of free energy will not be able to produce the same amount of work what we have noticed in this case which is reversible. So, in this case there would be some loss. So, entire thing entire free energy will not be available for doing electrical work. Of course, we have seen that the mechanical work part gets cancelled when we start from this.

So, this is the maximum work that is possible if the system goes reversibly. Now once we see this, then we can also derive some useful relation in order to know some of the thermodynamics parameters. Like for any reaction like what we have in our situation which is copper plus plus plus zinc equal to zinc plus plus plus copper, which is the relation, which is the reaction that takes place in galvanic cell which of this cell, this cell and now we saw that the potential goes to potential difference goes to 1.1 volt provided the concentration of copper plus plus is 1 or activity of copper plus plus is 1, and activity of zinc plus plus is equal to 1 in the solution of copper sulphate as well as zinc sulphate respectively

This concentration has got huge importance, we will see later on that how the concentration of oxygen in atmospheric condition affects the corrosion of iron, we will later on when we talk about Nernst equation. Because the Nernst equation will tell us why that kinds of situations arises if there is change in concentration of oxygen.

Now this reaction the complete reaction of course, copper sulphate plus zinc is equal to zinc sulphates or copper. And these reactions must have some enthalpy change, it also involves some entropy change and then we know this relation this is nothing, but the free energy change for this reaction and these free energy change actually give rise to a potential difference.

(Refer Slide Time: 07:36)



$$\underline{\Delta G = \Delta V dP - \Delta S dT}$$

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S$$

$$\Delta G = -nFE$$

$$\boxed{+nF\left(\frac{\partial E}{\partial T}\right)_P = +\Delta S} ✓$$

$$\left(\frac{dE}{dT}\right)$$

$$\Delta G = \Delta H - T\Delta S$$

$$-nFE = \Delta H - T nF\left(\frac{\partial E}{\partial T}\right)_P$$

$$✓ \Delta H = -nFE + nFT\left(\frac{\partial E}{\partial T}\right)_P$$

$$E = -\frac{\Delta H}{nF} + T\left(\frac{\partial E}{\partial T}\right)_P ✓$$

Ⓧ At 25°C, $\underline{Pb - PbCl_2 - HCl\,(m) - Ag - AgCl}$

$\frac{dE}{\partial T} = -1.8 \times 10^{-4}$ volt/K ; $\underline{0.49 \text{ volt}}$; $\Delta H_{PbCl_2} = -359480\,J$

1) Entropy change for 1 mole of Ag deposition
2) Heat of formation of AgCl.

$$\rightarrow \frac{1}{2}\overset{0}{Pb} + \overset{+}{Ag}Cl = (1)\overset{0}{Ag} + \frac{1}{2}\overset{+2}{Pb}Cl_2$$

Reduction (cathodic)

Oxidation (Anode)

$Ag^{+} + e^{-} = Ag$

$n = 1$

$\frac{1}{2}Pb - e^{-} = \frac{1}{2}Pb^{++}$

$$\Delta G = -nFE = -1 \times 96500 \times 0.49 = -47285\ J$$

So, is other relations that we know those are existing in classical thermodynamics. One such classical thermodynamics relation is del G equal to del V dp minus del S d T this is a very very useful relation. Now from this we can know that del delta G, d T constant pressure is equal to minus del S.

Now, we know that delta G equal to minus n F E, then I can get n F because n and F both are constant for a particular reaction, F is faraday one faraday which is constant this becomes d T P minus equal to minus del S. So, I am replacing del G with minus nFE. So, both sides this would get cancelled. So, this is the entropy change of a process. Now, if we know the variation of potential with temperature for a particular cell we can also get the entropy change for that particular reaction.

Now in the other hand we have this relation which is delta G equal to delta H minus T del S, now we have found out a relation like this which will give me minus n F E equal to delta H minus T, which is of course, become n F d T at a concentration. So, del H we can find out as minus n F E plus n F T del T p. So, this is the relation we can get.

Or we can so, get E equal to minus delta H n F plus T del E del T p this also we can get. So, this is these are two important relations what we can obtain from our understanding on classical thermodynamics, and from there we can also find out this for that particular reaction. Now, we can have an example on this. The example what I would like to put up the problem statement if I try to see that problems statement let us say at 25 degree Celsius for a particular cell like this Agcl.

So, this is the cell if I consider, now if these many data are provided let say del E del T is equal to 1.8 into the 10 to the power minus 4 volt per Kelvin, and cell potential I can have the cell potential for the cell 0.49 volt, and then one can find out entropy change for one mole of silver deposition. In this case on the right side there will be deposition of silver, on the left side there will be formation of light electrolyte.

Now, we can also calculate the heat of formation of silver chloride, and the data another data that is provided is del H of Pbcl 2 is equal to minus 359 480 joule. So, now, first we gave to write down the cell reaction and the cell reaction is half Pb plus Ag cl equal to Ag plus half Pbcl 2 this is the relation.

So, where I could see that this is plus this is 0. So, this is my reduction or cathodic and here this is 0 this is plus 1 sorry plus 2 which goes to oxidation or anode. Now this silver will be deposited on that silver silver chloride plate that interface. Now here we have written this equation in such a fashion that I have one mole of Ag.

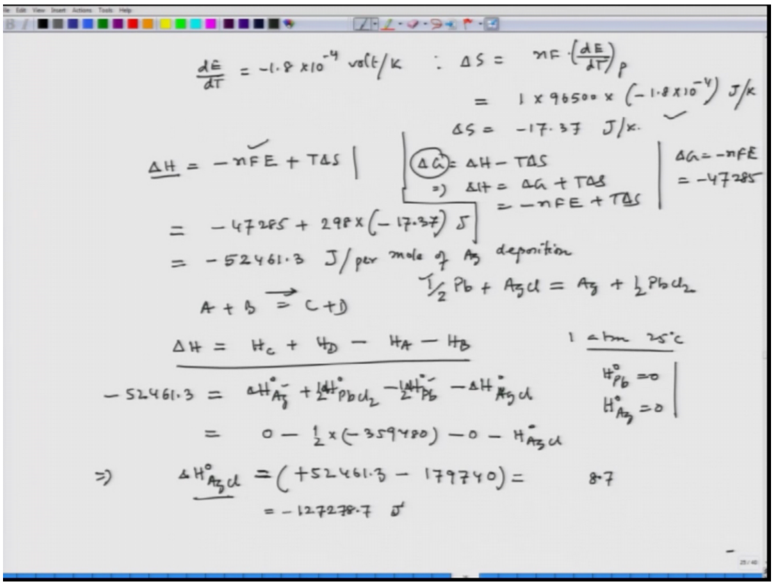
Now, when we have one mole of Ag the number of electrons that would be participating in cathodic reaction is. So, this is 1 so, n would be 1 here, and accordingly it is exhausted because once we need one electron. So, Pb minus 2 e equal to Pb plus plus. So, if put half so, this becomes 1. So, this two would get cancelled and now we see that the charge conservation is followed.

Now once we have this, now let us go and find out delta G for this particular chemical reaction, which gives me the potential difference that is 0.49 volt. So, this is equal to n F

E which is minus 1 into 96500 as we have understood from our previous class that one faraday is equal to 96483 or something like that.

So, roughly it is considered as 96500 coulomb 1 faraday and into this much volt so, which is equal to minus 472852 joule. So, this much is basically my free energy change.

(Refer Slide Time: 15:38)



$$\frac{dE}{dT} = -1.8 \times 10^{-4} \text{ volt/K} \quad \therefore \Delta S = nF\left(\frac{dE}{dT}\right)_P$$

$$= 1 \times 96500 \times (-1.8 \times 10^{-4}) \text{ J/K}$$

$$\Delta S = -17.37 \text{ J/K.}$$

$$\underline{\Delta H} = -nFE + T\Delta S$$

$$\boxed{\Delta G} = \Delta H - T\Delta S \Rightarrow \Delta H = \Delta G + T\Delta S = -nFE + T\Delta S$$

$$\Delta G = -nFE = -47285$$

$$= -47285 + 298 \times (-17.37) \text{ J}$$

$$= -52461.3 \text{ J/per mole of Ag deposition}$$

$$\frac{1}{2}Pb + AgCl = Ag + \frac{1}{2}PbCl_2$$

$$A + B \overset{\longrightarrow}{=} C + D$$

$$\underline{\Delta H = H_C + H_D - H_A - H_B}$$

1 atm 25°C

$$H^\circ_{Pb} = 0$$

$$H^\circ_{Ag} = 0$$

$$-52461.3 = \Delta H^\circ_{Ag} + \frac{1}{2}\Delta H^\circ_{PbCl_2} - \frac{1}{2}\Delta H^\circ_{Pb} - \Delta H^\circ_{AgCl}$$

$$= 0 - \frac{1}{2} \times (-359480) - 0 - H^\circ_{AgCl}$$

$$\Rightarrow \underline{\Delta H^\circ_{AgCl}} = (+52461.3 - 179740) = \quad 8.7$$

$$= -127278.7 \text{ J}$$

Now once we know that, then we can calculate we have the data d E d T equal to 1.8 into 10 to the power minus 4 volt per kelvin from there we can calculate del S.

Del S equal to n F del E del T constant pressure. So, this becomes 196500 into minus 1.8 into 10 to the power minus 4, this is also joule per kelvin. So, this value would be minus 17.37 joule per kelvin.

So, heat of reaction for this particular reaction this particular reaction would be then delta H would be, minus n F E plus T del S how come it comes? Delta G equal to delta H minus t del S. So, delta H equal to delta G plus T del S and then delta G is equal to minus F E plus T del S. So, we can put those values this is minus 47285 since this value we have calculated from this equation, delta G equal to minus n F E and we have found out that value to be minus 47285 plus and this T is 25 degree. So, which is 298 kelvin into del H we have found which is minus 17.37 joule. So, this becomes joule. So, then in total if we try to calculate then it would become 52461.3 joule.

And of course, here we are considering 1 mole of Ag deposition. So, per mole deposition now we have to calculate. So, this is our problem statement was entropy change we have found out entropy change, this is the entropy values then we have to find out second problem heat of formation of Agcl 2 Agcl. So, we have found the heat of reaction. So, heat of reaction for any reaction for example, A plus B equal to C plus D this reaction if it goes this way.

Because then our heat of reaction would be H of c plus H of D minus H of A minus H of B. So, formation enthalpy of individual species reactants as well as products. Now, if we have this particular relation so, then for this we can write as H Ag plus H half of Pbcl 2 minus H of Pb of course, half because this half sign is there minus H of Agcl.

Now if we perform because this is happening at one atmosphere and 25 degree Celsius and if we consider that these are pure substance those cases they can be written as standard values. So, this super script 0 I am putting because, these are standard values and as per convention if we have a pure metal the stable condition which is solid in case of Pb as well as Ag at 298 kelvin and one atmosphere pressure is going to be 0.

So, this is a convention. Now we know this value which is sorry there was a minus sign missing. So, minus 52461.3 this is the heat of reaction for that and then is equal to 0 this is minus we know this value, this value was this. So, this is half into minus 359480 minus 0 minus H Agcl.

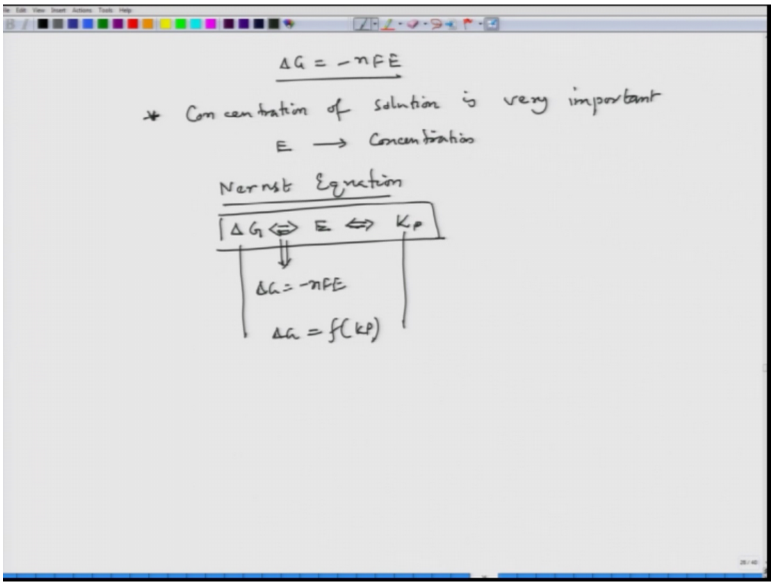
We can also put 0, now then H 0 Agcl would be equal to which is nothing, but the formation enthalpy. We can also put formation enthalpy which is equal to minus 5246.3 minus this would become plus and this would become this is 179740. So, this is the value. So, equal to around this would become 7 8 this is 8 then. So, 179740 minus 52461.3 7.87752721.

So, this becomes 127278.7. So, this is the joule this is the value of enthalpy of formation of Agcl. So, here we can see that we have not put del value here, we can also put del value because absolute enthalpy we cannot calculate we have to calculate relative enthalpy which is the difference. So, actually this is nothing, but del H 0 Agcl. So, this is the formation enthalpy of Agcl.

So, we could see that from this relations we can have lot of informations on the formation enthalpy of a species, entropy change for a particular reaction as well as we can also calculate enthalpy change for a particular reactions. Because E is experimentally determined E can be experimentally determined and as a function of temperature constant pressure I can also find out this particular relation, dE d T we can also find out say a then entire thing can be chopped out.

Now this is one example. So, we will have problems on this particular aspect in the T s will manage that and of course, I will be also interfering whenever there is a need arising.

(Refer Slide Time: 25:30)



$\Delta G = -nFE$

* Concentration of solution is very important

$E \longrightarrow$ Concentration

Nernst Equation

$\Delta G \Leftrightarrow E \Leftrightarrow K_p$

$\Downarrow$

$\Delta G = -nFE$

$\Delta G = f(Kp)$

Now, from these it is very clear that this particular relation delta G equal to minus nFE is a basically a kind of fundamental relation in electrochemistry.

Now, we have not started looking at what would be that importance of that relation on the corrosion aspects. Now before we talk about that we have also stated that the concentration of solution is very important. This is very important until unless we have some relation between E and concentration, we will not be able to quantify and that quantification would be possible if we have a relation which is popularly known as Nernst equation N e r n s t Nernst equation.

In that Nernst equation we can relate free energy with potential with k p or the reaction constant. So, this Nernst equation will enable us, we have understood this relation which is delta G equal to minus nFE we have to understand the relation between this two, this relation we have to understand. And then we will see that how this concentration comes into that. Let us stop here will continue our discussion in our next lecture.

Thank you.