Elementary Electrochemistry
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Measurement of Cell EMF

Welcome back to the course entitled elementary electrochemistry. In the previous lecture, we have discussed a few problems related to the EMF measurements. So, we will continue from there and we will try to understand how the cell EMFs are physically measured experimentally? And also how they are related to in terms of oxidation and reduction processes?

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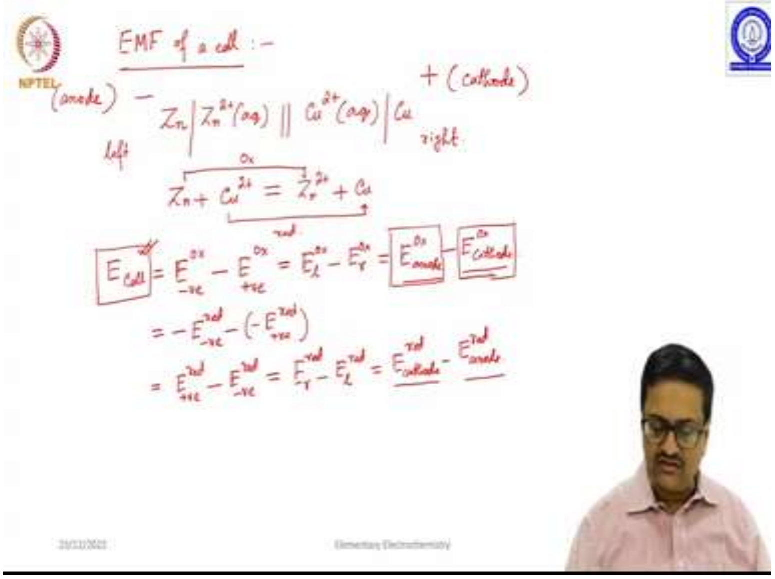

EMF of a cell :-

(anode) − left $Zn | Zn^{2+}(aq) || Cu^{2+}(aq) | Cu$ right + (cathode)

$$\overbrace{Zn + \underbrace{Cu^{2+} = Zn^{2+}}_{red}}^{ox} + Cu$$

$$\boxed{E_{cell}} = E^{ox}_{-ve} - E^{ox}_{+ve} = E^{ox}_{l} - E^{ox}_{r} = \boxed{E^{ox}_{anode}} - \boxed{E^{ox}_{cathode}}$$

$$= -E^{red}_{-ve} - (-E^{red}_{+ve})$$

$$= E^{red}_{+ve} - E^{red}_{-ve} = E^{red}_{r} - E^{red}_{l} = E^{red}_{cathode} - E^{red}_{anode}$$

So, when you try to write the EMF of a cell we first need to construct a particular cell for which we want to do the measurement of EMF. So, let us assume that we are talking about the Daniell cell which is nothing but you have already learned zinc metal dipped in a solution of Zn2 plus ions in aqueous medium and it is kept separated from a solution of Cu2 plus in aqueous medium with copper as the electrode and by convention the way we write these cells, the right hand side electrode is plus, the cathode and the left hand side electrode is the minus or the anode and in this particular cell, at anode the oxidation takes place.

So, zinc is reacting with Cu2 plus to get converted to Zn2 plus which is oxidation and copper is getting reduced to copper zero. So, this is the oxidation and this is reduction, this all of you I think you can understand.

So, we call this electrode on the left hand side is as just left and the other one as right. While considering the EMF of a cell, we should write E cell that E cell is conventionally written as if I consider in the oxidation direction, it is electrical potential of the negative electrode minus the Eox of the positive electrode which essentially means, we are talking about E oxidation of the left minus E oxidation of the right electrode or we can also write Eox anode minus Eox cathode.

Now, parallelly if we want to write both the potentials in the opposite direction that is the reduction direction, so then, immediately you will write minus of E reduction of negative electrode minus minus of reduction potential of the positive electrode. So, immediately we will write by rearranging it as E reduction positive minus E reduction of the negative electrode and then we keep writing whether positive electrode is now on the right hand side. So, when we write reduction then E right minus E left in the reduction potential direction or you can write E reduction cathode minus E reduction anode.

So, depending on whether we use the oxidation potentials or the reduction potentials, the value of E cell does not change. What changes is the corresponding values of the cathode and anode E0 values which are exactly the opposite and when you change the sign for both and then again the take a difference you will end up with the same value of E cell.

So, now, when we try to measure the EMF of a particular cell we need to know both the E anode and E cathode whether in the oxidation or reduction mode. So, to know the electrode potentials of different electrodes, one has to learn one has to know how to consider which is zero and from there we will do the calculation.

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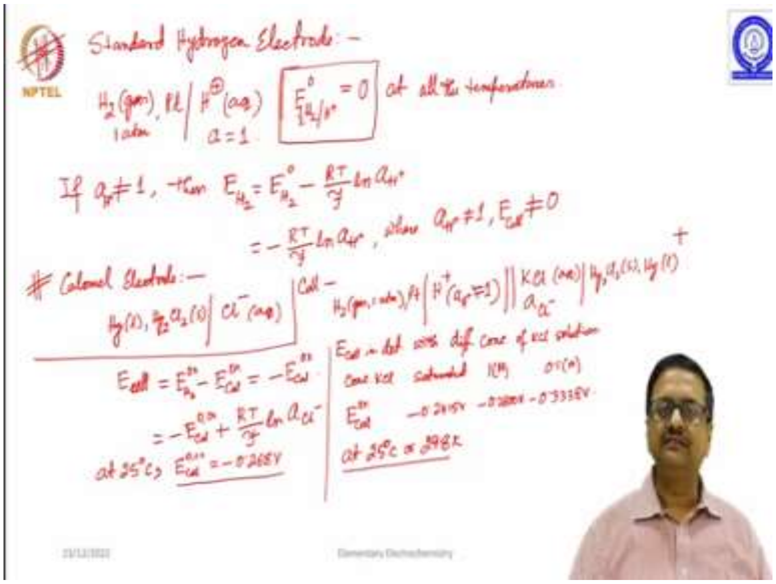

So, to consider the zero potential we need to consider a standard hydrogen electrode which is nothing but hydrogen gas bubbled at 1 atmospheric pressure along a platinum electrode and that platinum electrode is dipped in a solution of H plus ions an aqueous solution with activity equal to 1.

So, if such a condition is achieved that you have a solution of H plus ion of activity 1 and you are passing H2 gas at 1 atmospheric pressure at the platinum electrode then the reaction what happens is half H2 giving you H plus plus electron. So, the EMF of that cell or E0 of that half H2 H plus electrode is taken as 0 at all the temperatures. So, that is the potential of standard hydrogen electrode which is considered to be 0. Using this standard hydrogen electrode we have to calibrate or we have to determine the potential of any other electrodes.

Now, in case if the activity of H plus is not equal to 1 then EH2 that is the cell EMF is nothing but E0H2 which is 0 minus RT by F ln activity of H plus or you can simplify as minus RT by F ln activity of H plus where activity of H plus is not equal to 1 and in that condition E cell is not equal to 0 or EH2 is not equal to 0.

So, to determine the potential or the electrode potential of any other cell, one has to first couple it with the standard hydrogen electrode and then determine the potential of that cell. But then what happens is it is very difficult always to use hydrogen gas at one atmospheric pressure because it is a flammable gas and this electrode is a cumbersome electrode. So, to avoid such a situation, one can use another standard electrode first you couple it with standard hydrogen electrode determine its electrode potential and use that electrode to calibrate the other possible electrodes that you may be using in your lab.

So, one such electrode is calomel electrode which is used as a standard electrode and that electrode is nothing but mercury liquid is made a paste with mercurous chloride which is solid and it is kept in equilibrium with the chloride ion in aqueous medium, in general it can be the KCl solution.

So, this electrode is then coupled with the standard hydrogen electrode, so, then the cell after coupling the hydrogen electrode with calomel electrode is written as hydrogen gas at 1 atmosphere, platinum electrode, we have H plus ion with activity of H plus equal to 1 in connection with a KCl solution aqueous where the activity of Cl minus is taken as aCl minus and it is coupled with the electrode that is Hg2Cl2 solid and mercury liquid, so, it is a paste of mercury with mercurous chloride.

So, then when you try to write down the value of E cell, you will simply write, so, in this particular case this side is positive, this side is negative by convention as usual. So, when we write E cell EH2 oxidation minus E calomel oxidation and it is nothing but minus of E calomel oxidation. So, you can replace it by denounced equation, so, one can write minus E0 calomel in oxidation mode plus RT by F ln activity of Cl minus.

So, now at 25 degree centigrade in an experimental setup this value of E cell with unit activity of for KCl, one can, one has determined the E0 calomel the oxidation potential to be equal to minus 0.268 volts. So, this is experimentally determined value for E0 for calomel electrode in the oxidation mode. So, it means that this is lower than the hydrogen electrode what is also found is that this potential E cell is determined with different concentration of KCl solution and the corresponding E cell values were also determined.

So, if we write try to write down the concentration of KCl and the corresponding E oxidation of calomel it is E0 oxidation for a saturated solution this value was found to be minus 0.2415 volt, for one normal KCl solution it was found to be 0.2800 and for 0.1 normal KCl it was found to be 0.3338 minus volt all were done at 25 degree centigrade or 298 Kelvin temperature.

So, with these different values of E calomel with different concentration of KCl being determined one can couple these calomel electrodes with any other known electrode any other unknown electrode and determine their corresponding E0 value and find out whether it acts as a cathode or an anode when you couple this with your calomel electrode.

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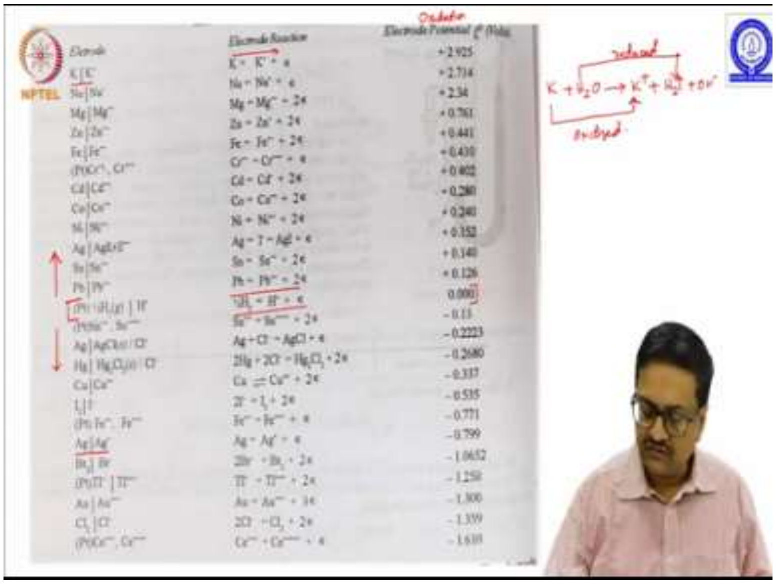

So, here what I have brought is a standard electrode reaction and the corresponding standard electrode potential table which you can find in any standard textbook, what you see here hydrogen is in the middle of it there are electrodes up and there are electrodes down below this. See this is written in the mode of oxidation, so, these are the oxidation potentials.

So now, what does it mean? It means that the potential for potassium to get oxidized to potassium plus is more compared to the oxidation of hydrogen to H plus. So, what will happen if I add potassium to water it will form K plus and release hydrogen gas. So, I am not I have not balanced it one has to balance the equation it essentially means potassium will get oxidized and hydrogen will get reduced.

On the other hand, if you use a silver silver plus electrode, so, in that case the hydrogen will be oxidized, so, hydrogen will get converted to H plus and silver will get converted silver plus will get converted to silver 0. So, the ones which are lower than hydrogen will not be able to liberate hydrogen or rather it will react with the H plus 2, it will react with H2 to generate H plus, whereas the ones which are above hydrogen in the oxidation potential table will be able to liberate hydrogen gas.

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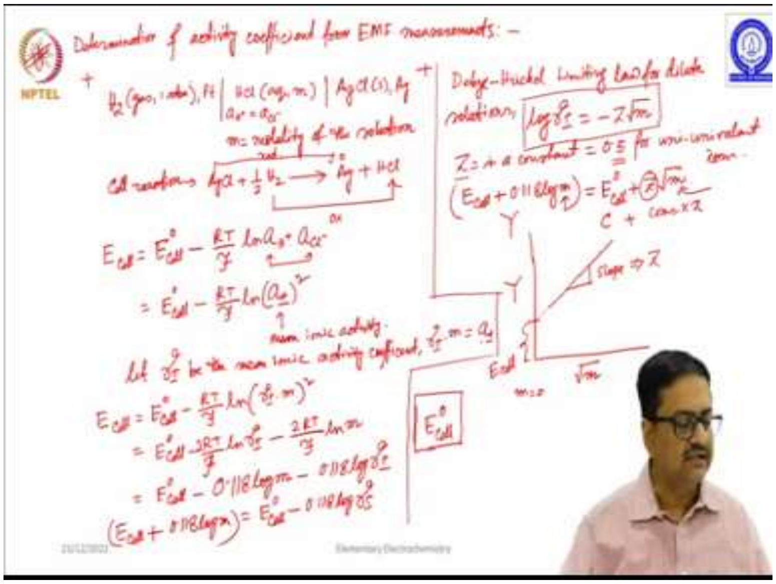

Determination of activity coefficient from EMF measurements: –

+ H_2(gas, 1 atm), Pt | HCl (aq, m) | AgCl(s), Ag +

$a_{H^+} = a_{Cl^-}$

m = molality of the solution

Cell reaction: $AgCl + \frac{1}{2}H_2 \longrightarrow Ag + HCl$

$E_{cell} = E^0_{cell} - \frac{RT}{F}\ln a_{H^+} a_{Cl^-}$

$= E^0_{cell} - \frac{RT}{F}\ln(a_\pm)^2$

mean ionic activity

Let $\gamma_\pm$ be the mean ionic activity coefficient, $\gamma_\pm m = a_\pm$

$E_{cell} = E^0_{cell} - \frac{RT}{F}\ln(\gamma_\pm m)^2$

$= E^0_{cell} - \frac{2RT}{F}\ln\gamma_\pm - \frac{2RT}{F}\ln m$

$= E^0_{cell} - 0.118\log m - 0.118\log\gamma_\pm$

$(E_{cell} + 0.118\log m) = E^0_{cell} - 0.118\log\gamma_\pm$

Debye-Hückel Limiting Law for dilute solution, $\boxed{\log\gamma_\pm = -Z\sqrt{m}}$

Z = is a constant = 0.5 for uni-univalent ions.

$(E_{cell} + 0.118\log m) = E^0_{cell} + Z\sqrt{m}$

Y

C + const × Z

So, now, we will try to use the concept of EMF measurement for determination of a few physical quantities like the activity coefficient. So, it is determination of activity coefficient from EMF measurements. Let us consider the cell as usual hydrogen gas at 1 atmosphere is in touch with platinum electrode and we have a solution of HCl in aqueous medium having concentration m molality m molal solution is again in connection with AgCl solid with silver as electrode.

As usual this side is plus and that is minus and this m is molality of the solution. Molality is a way of expressing the concentration which means a certain number of moles of a substance dissolved in one kg of this solvent. So, the cell reaction that one can easily write is AgCl plus, you see here AgCl plus half H2 getting silver converted to silver 0 plus HCl.

So, hydrogen is oxidized and silver is reduced in this particular case. So, when we write E cell is equal to E0 cell minus RT by F it is one electron transfer ln activity of H plus into activity of Cl minus. So, now, this activity of H plus is equal to activity of Cl minus because both are coming from HCl, so, the concentration of HCl is m as a result these two are same.

So, one can easily write that it is equal to E0 cell minus RT by F ln activity of the plus minus electrodes at plus minus or cation anion together as a average square. So, this is called the mean ionic activity and let gamma plus minus be the mean ionic activity coefficient such that gamma plus minus into m is equal to a plus minus. So, when you replace it in this equation E cell is equal to E0 cell minus RT by F ln gamma plus minus into m square.

Now, if we try to simplify E0 cell minus RT by F, 2RT by F ln gamma plus minus minus 2RT by F ln m and then we further simplify as E0 cell minus, I am now bringing this ln m before and converting ln to log and applying the values for R and T at 25 degrees centigrade and multiplying by 2 dividing by F that number turns out to be 118 log of m minus 0.118 log of gamma plus minus. So, now, in the next step we rearrange this E cell minus or rather plus we bring this log m to the left hand side, so 0.118 log m is equal to E0 cell minus 0.118 log gamma plus minus.

Now, I am continuing here and without changing the slide for your benefit, so, now using the Debye-Huckel limiting law for dilute solutions, this log of gamma plus minus is equal to minus Z into square root of m where Z is a constant and its value is 0.5 for uni-univalent ions, so, one can rewrite this equation as E cell plus 0.118 log m equal to E0 cell plus Z into square root of m.

So, now this equation looks like equal to Y equal to some constant into x and the constant C is another constant, Y equal to mx plus C. So, when we try to plot this Y versus x which is square root of m and with varying concentration of that HCl solution, the molality with by varying that molality one can determine the value of Y using a potentiometer that is the total potential that is coming in the potentiometer for this particular cell one can measure that and one can get a few readings like this, with increasing molality the value for the entire value of Y within the bracket will keep on increasing with increase in m this log m will increase so the value will keep on increasing and square root of m.

So, when I am increasing m square root of m is also increasing. So, one has to join those dots with a line and then when you extrapolate what you get here at m equal to 0, this value gives you the value of E cell and from the slope one can calculate the value of Z which now again is, it can be varied can be verified whether it comes out to be half or not because we as we said that Z is a constant which is true for uni-univalent pair of ions. So, when this E cell is known Y is known we know the value of Z, for a given value of m we calculate the value of E cell and one can easily calculate the value of E0 cell.

Now, E0 cell when it is found out, one can also calculate the value of gamma plus minus using this expression for different values of m from this expression because now you replace this Z square root of m by gamma plus minus log gamma plus minus and from there you can easily calculate the value of log gamma plus minus when you know the value of this Y from the potentiometer readings.

So, this is how one can determine the physical quantity, the mean activity coefficient gamma plus minus using the EMF measurement method. So, we will continue in the next lecture from here. Thank you.