Elementary Electrochemistry
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Electrochemical Cells: Liquid Junction Potential

Welcome back to the course Elementary electrochemistry. In the previous class, we have discussed about how to measure the EMF of a cell. And then from there I have shown you how one can determine the mean active ionic activity coefficient using the EMF measurement.

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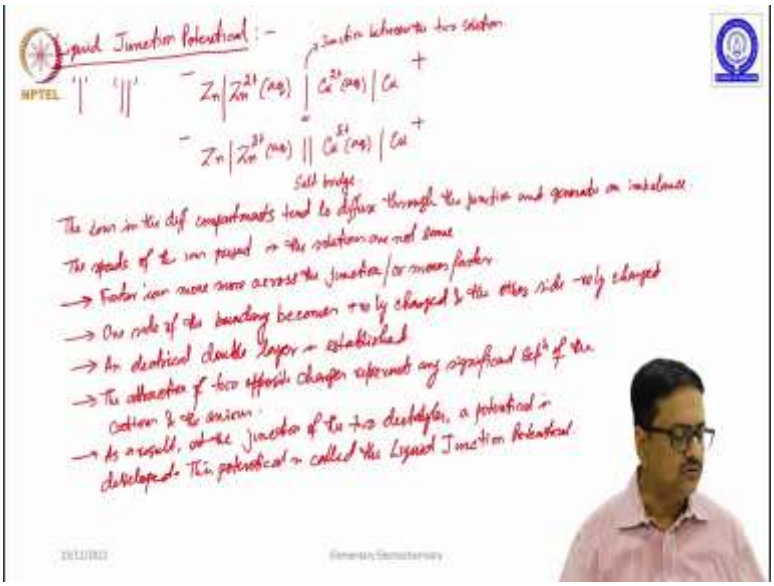

So, today we are going to continue and we will now discuss a few important aspects on how a cell is constructed and what are the meanings of some notations that I have been using over the last few classes. So, today we will first talk about something called liquid junction potential. See, when we construct a cell, we use one line like this to separate the 2 solutions and in some cases if you have noticed I have used 2 lines to separate the 2 compartments of a cell.

So, for example, if I write zinc Zn 2 plus aqueous, one separation line with Cu 2 plus aqueous with one separation line copper writing it as plus and minus and writing the same cell Zn Zn 2 plus aqueous with 2 lines here Cu 2 plus aqueous and Cu plus. So, these two have a slightly different meaning. So, when you write one, it essentially means you have a semipermeable membrane which allows for the passage of ions from one chamber to other and that creates a certain problem.

So, that is a junction between the two solutions and because of that junction being semi permeable the ions can move from one side to another, but then a problem arises because of that. So, to overcome that kind of the problem related to that passage of ions and making giving you an imbalance, one has to use something called a salt bridge which is written as a double line.

So, a semipermeable membrane is written as a single line and is salt bridge is written as a double line, why does it happen? Because the ions in the different compartments tend to diffuse through the junction, diffuse through the junction and generate an imbalance, why does that imbalance is generated?

Because the speeds of the ions present in the solutions are not same and as a result the faster ions move more across the junction or moves faster. So, as a result one side of the boundary becomes positively charged and the other side slightly negatively charged. So, as soon as a charge separation takes place immediately an electrical double layer is established. So, what happens because of that double layer that the attraction of the two opposite charges prevent any significant separation of the cations and the anions.

So, as a result at the junction of the two electrolytes a potential is developed and this opposites the potential of the cell. So, this potential is called the liquid junction potential. So, this liquid junction potential which is created inside the cell between the 2 electrolytic solution cannot be determined using a potentiometer and it prevents the passage of ions after it is developed and hence hampers the electrochemical cell and affects its actual cell EMF. So, to overcome this one has to use something called a salt bridge, this liquid junction potential is represented by this symbol.

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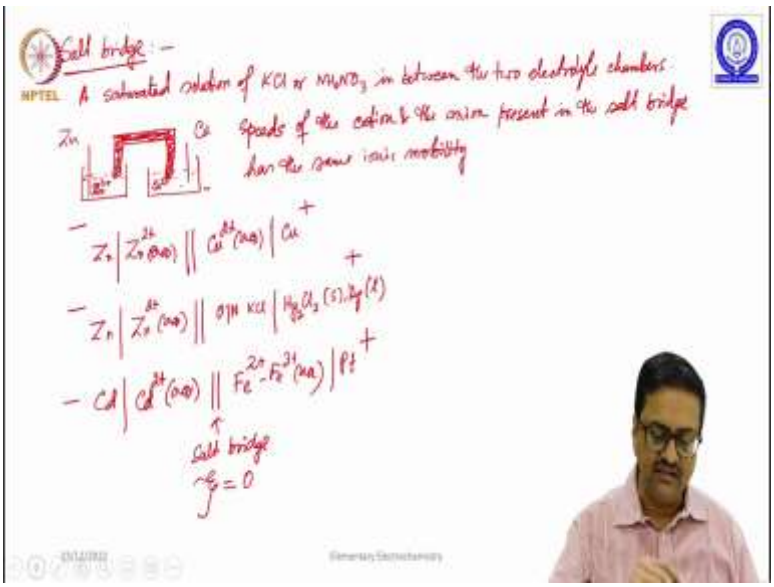

So, what we use is called a salt bridge. So, what we use is a saturated solution of KCL or NH4NO3 in between the two electrolyte chambers. So, there are different ways of making it you make an U shaped bridge filled with the saturated solution of KCL and sometimes some gel like agar-agar is used to hold that saturated solution of KCL in this.

So, this technically establishes the electrical connectivity between the two solutions which are then connected with the corresponding electrodes. Suppose, this is copper, this is zinc you have Zn 2 plus here and Co2 plus here. So, like that when you have a salt bridge connecting the two sides, then it does not allow to the generation of the charge separation because the speeds of the cation and the anion present in the salt bridge has the same ionic mobility or ionic speed. As a result the imbalance is not created across the salt bridge.

So, when as I already indicated when the salt bridge is used, then the corresponding cells are written like this as I have written for zinc zinc 2 plus aqueous is in connection with Co2 plus aqueous with Z with Cu as the electrode. Similarly, one can have Zn in equilibrium with Zn 2 plus in aqueous medium. Then, on the other side one can have 0.1 normal KCl solution which is then in equilibrium with Hg2 Cl2 solid and mercury liquid which is calomel electrode. So, then again you have a salt bright to eliminate the liquid junction potential that may develop between the two.

And similarly, one can also write another electrode just for example, I am writing cadmium in touch which Cd 2 plus in aqueous medium is now in equilibrium with Fe 2 plus Fe 3 plus system in aqueous medium with a platinum electrode. So, in every case you have a salt bridge which eliminates the possibility of liquid development of liquid junction potential. So, for a salt bridge the potential of liquid junction is 0 and it is thus eliminated. So, using salt bridge we can avoid a potential problem which gets generated because of the variation in speed of the ions present in the two different compartments.

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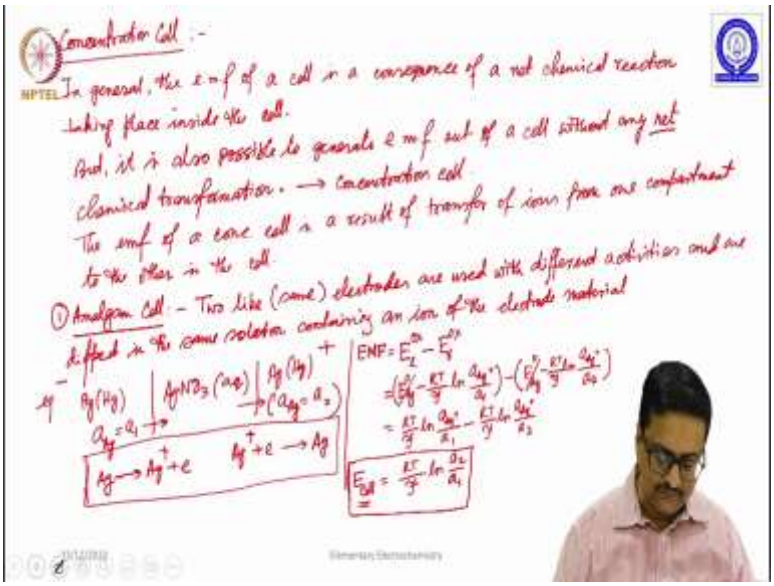

So, now, we have already discussed a little bit about different types of cells. One of them we now need to pay attention is a cell which is called a concentration cell. As you know in general the EMF of a cell is a consequence of a net chemical reaction taking place inside the cell but it is also possible to generate EMF out of a cell without any net chemical transformation. If such a cell can be constructed these are those are called the concentration cell. Why? This happens this EMF, the EMF of a concentration cell is a result of transfer of ions from one compartment to the other in the cell.

So, there are two types of such cells. Let us first talk about the Amalgam cells. Where two like or same electrodes are used with different activities and are dipped in the same solution containing an ion of the electrode material. So, what essentially means that if I just want to give an example silver amalgam with activity of silver as a1 is dipped in a solution of AgNo3 and on the other

side you have another silver amalgam electrode with activity of Ag equal to a2 this is plus and that is minus.

So, the reaction that is happening on the left-hand side is Ag getting oxidized to Ag plus and releasing one electron. What is happening on the right-hand side is Ag plus taking an electron getting reduced to Ag. So, there is no net reaction if you add this there is no change in the chemical composition of the electrode system.

So, there is no net reaction in this particular cell. But then when you write the cell EMF you will write E left oxidation minus E right oxidation as we have learned in the previous class and then we slowly write the corresponding Nernst equations then what you will get is E0 Ag minus RT by F ln activity of Ag plus divided by activity of Ag that is A1 minus E0 Ag minus RT by F ln Ag plus divided by a2.

So, now, you see that this Ag E0 Ag gets cancelled this minus and minus plus. So, we write RT by F ln Ag plus by a1 minus RT by F ln Ag plus by a2 and when you simplify you end up getting RT by F ln a2 by a1. So, here what we are getting is that the value of EMF for the cell is regulated by the values of the activities of silver on either side.

So, what is happening is there is a transfer of silver from left hand side to the solution of AgNo3 so, Ag gets converted to Ag plus here and the Ag plus gets converted to Ag on the other side. So, there is a net transfer of silver from left to right and that transfer is controlling the EMF of the cell. So, that is why this is a concentration cell where that difference in concentration to give rise in the transfer of silver ion from one side to the other and it generates the corresponding EMF of the cell.

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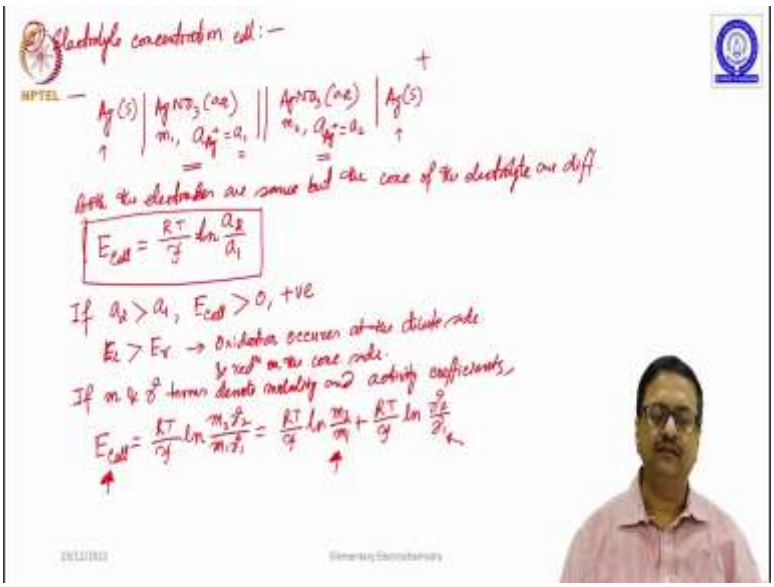

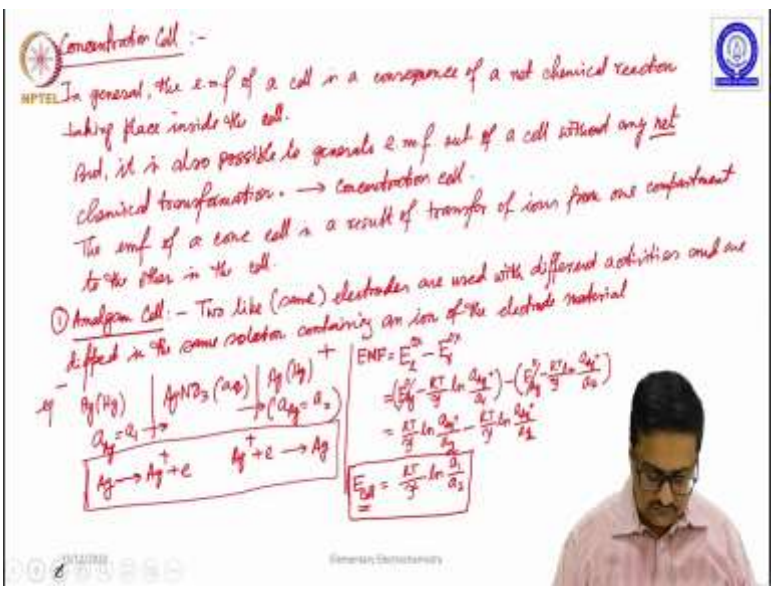

The second type of concentration cell is a electrolyte concentration cell. So, here I am straightaway writing one example so, that you can understand easily. Suppose, we have silver solid in equilibrium with AgNo3 aqueous with a molality m1 which corresponds to the activity of Ag plus as a1. It is connected to another solution of AgNo3 aqueous where the molality is m2 which means that activity of Ag plus on this side is a2 and you have again Ag solid as electrode. So, here what we have is we have on the two sides we have the same electrode, but we have solutions electrolytes of different concentration.

So, here both the electrodes are same, but the concentration of the electrolyte are different on the two sides or the two chamber of the electrodes. So, when you try to write down the E cell like before we will end up getting these explorations E cell equal to RT by F. I am again writing F because again here it is 1 electron transfer ln activity have a2 by activity of a1. Here I made a mistake you should check see this minus so, this is a2 and this is a1 as a result. This should be a1 by a2.

So, in this case, you see the difference is that it is a2 by a1. So, in the previous case the activity of the electrodes were different. So, in that case the E cell was determined by RT by F ln a1 by a2 that is a1 of the left by the right. Whereas, in this concentration cell it is a2 by a1, if you do the derivation yourself you will find it. So, now, if a2 is greater than a1 E cell is greater than 0 that is positive and that essentially means El is greater than Er which essentially means oxidation occurs at the dilute side and reduction on the concentrated side that is dilute side is this.

So, there the oxidation takes place and EMF of the cell turns out to be positive. So, if m and gamma terms denote molality and activity coefficients. So, now, if we replace the values for a1 and a2 using m and gamma you can write E cell is equal to RT by F ln m2 gamma 2 by m1 gamma 1 or simply RT by F ln m2 by m1 plus RT by F ln m gamma 2 by gamma 1.

So, now by knowing the concentrations in terms of molality and by determining the corresponding gamma using the previous expression that we have learned one can calculate the E cell for the concentration cells. So, I hope you are able to follow these topics and we will continue from here in the next class, where we will discuss about different, some more applications of measurement of EMFs in practical life. Thank you.