Elementary Electrochemistry
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Lecture 7
Estimation of EMF of a Cell Using Potentiometer

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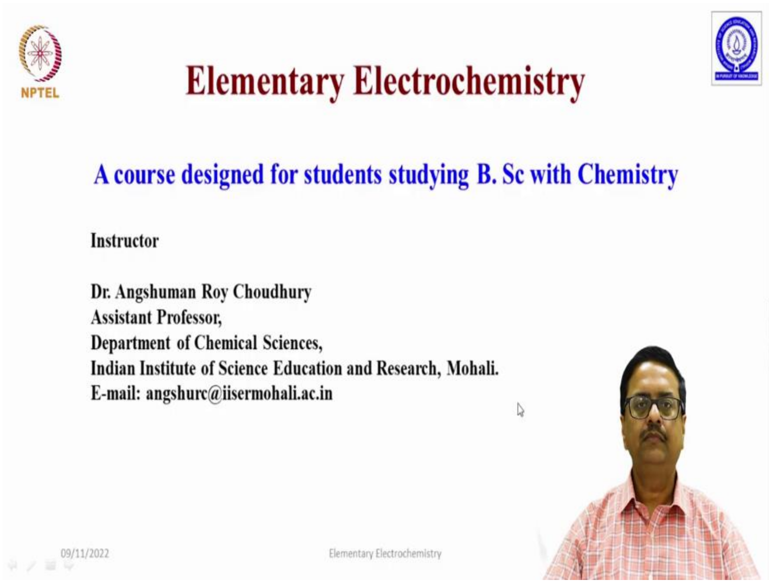

Welcome back to the course entitled Elementary Electrochemistry. In the previous week, that is the first week of the course, we have discussed some basic aspects of electrochemistry, we started discussing about the Faraday's laws of electrolysis, discussed about what are strong and weak electrolytes and then we talked about a few electrochemical cells, Daniel cell and electrolytic cell like Castner cell.

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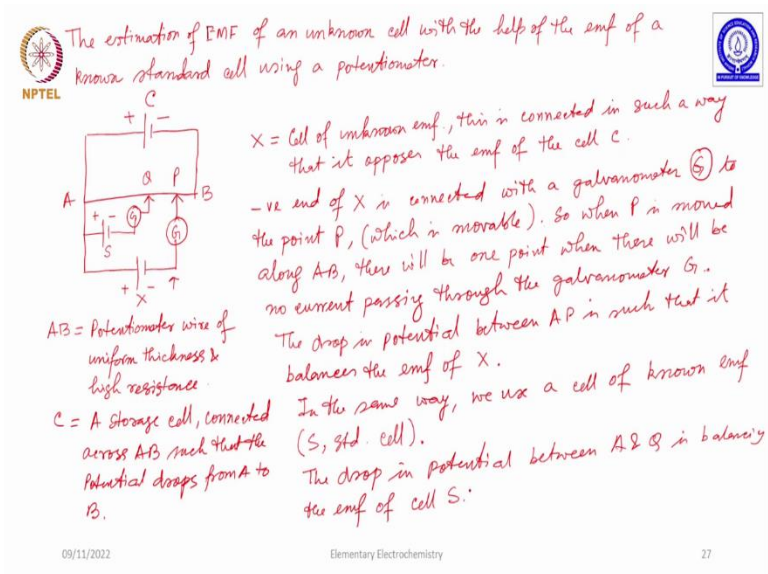

So, today we are going to start our discussion on how to determine the EMF of a cell with the help of a known cell. So, the today's discussion will be around the estimation of EMF of an unknown cell with the help of the EMF of a non-standard cell using a potentiometer. So, let us first draw the potentiometer circuit and then I will explain its function. So, we have a cell connected like this which is marked as C. And we have a wire connected from A to B of uniform cross section.

Then we need to connect our unknown cell X in such a way that it opposes the potential of the cell C, and it is connected through a galvanometer to point P which is a movable point. And then we also have one standard cell S connected in the same way through a galvanometer G and connected to point Q which is also simultaneously movable. So, what are these? What I have drawn? AB is the potentiometer wire of uniform thickness and high resistance.

And C is a storage cell connected across A and B such that the potential drops from A to B. X is the cell of unknown EMF, this is connected in such a way that it opposes the EMF of the cell C. You see we have connected the plus of this in this direction so that add the plus of C is straightaway connected which means these two cells are connected in opposition. So, the potential of X can oppose the potential of C.

So, the other end of X that is this end is connected through a galvanometer, negative end of X is connected with a galvanometer marked as G to the point P which is movable. So, when P is moved along AB there will be one point when there will be no current passing through from the galvanometer G. So, that means, the EMF of X is exactly same as the EMF of C and that is why the there is no current passing through the galvanometer G.

So, that that indicates the drop-in potential between AP is such that it balances the EMF of the cell X. In the same way, we use a cell of known EMF that is the cell S the standard cell. So, instead of using the cell X, we use a different cell S and do the experiment again. So, the cell S is connected through a galvanometer and we find a point Q on the line AB such that there is no current flowing through the galvanometer which is connected to the cell S. This means that the drop in potential between A and Q is balancing the EMF of cell S.

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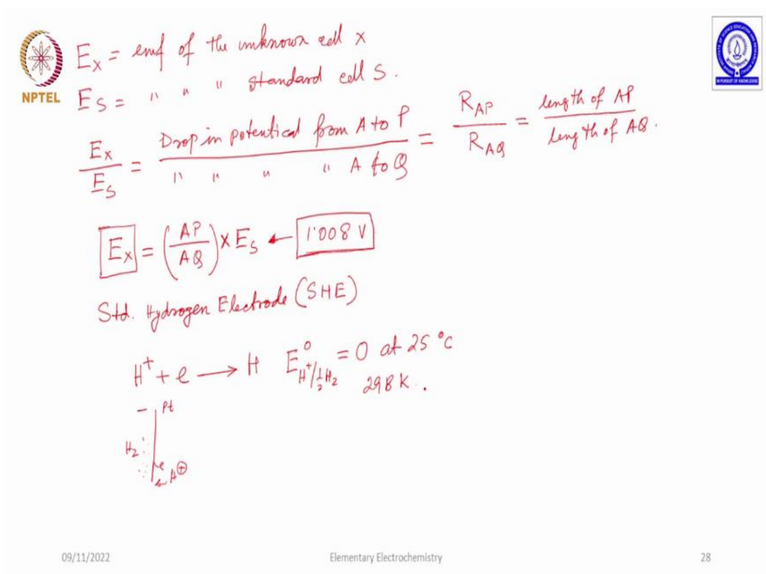

So, if we assume that Ex is the EMF of the unknown cell X and Es is EMF of the standard cell S then we can easily write Ex by Es equal to drop in potential from A to P divided by drop in potential from A to Q. Now, since AP and AQ are parts of that wire AB, which is of uniform thickness and high resistance, so one can easily write that this is nothing but the ratio of the resistance R between AP and resistance R between AQ.

And since this wire is of uniform resistance, then that resistance is nothing but proportional to the length AP, length of AP divided by length of AQ. So, one can easily write Ex is equal to the length AP divided by the length AQ, so this becomes just a number, into the Es that is the EMF of the standard cell. So, if we know the EMF of the standard cell, suppose the value is 1.008 volt or something this is used as a standard value for one particular cell. And one can use that particular cell to determine the EMF of any unknown cell that you may be forming.

So, at this point I must indicate that to have a standard cell one has to define something as 0. So, to define something as 0, what we use is called the Standard Hydrogen Electrode, in short it is written as SHE. So, what is Standard Hydrogen Electrode? It is nothing but the reaction where H plus takes off one electron and gets converted to the atomic hydrogen, the EMF of this reaction at standard state that is E0 H plus to half H2 is taken as 0 at 25 degrees centigrade that is 298 Kelvin temperature.

So, this is called the, this is taken, conventionally taken as 0 in the electrochemistry. So, one use if you use a platinum wire as electrode and this electrode is a negative electrode. So, H plus ions will come close to it, take the electron from the electrode and bubble along the electrode as hydrogen gas. So, this is the electrode that one considers as a standard hydrogen electrode. And using that standard hydrogen electrode one can actually determine the EMF of all other electrodes assuming that the potential of this particular reaction taken to be 0.

But then what you must understand here is that this particular cell is not very easy to construct. And this cell generates hydrogen gas which is highly flammable. So, for all practical purposes this hydrogen electrode cannot be used as a standard electrode in any measurements that we do in the lab, the way I have described in the previous slide, we use a potentiometer to determine the say EMF of an unknown cell, we cannot use standard hydrogen electrode.

So, what we need to do is? We need to have some other cells, where the chemical reactions are highly specific and quantitative. So, use those chemical reactions to form a new cell and that new cell can then be first coupled with a standard hydrogen electrode and the corresponding EMF is determined. And then based on the EMF of that cell, the EMF of other cells can be determined.

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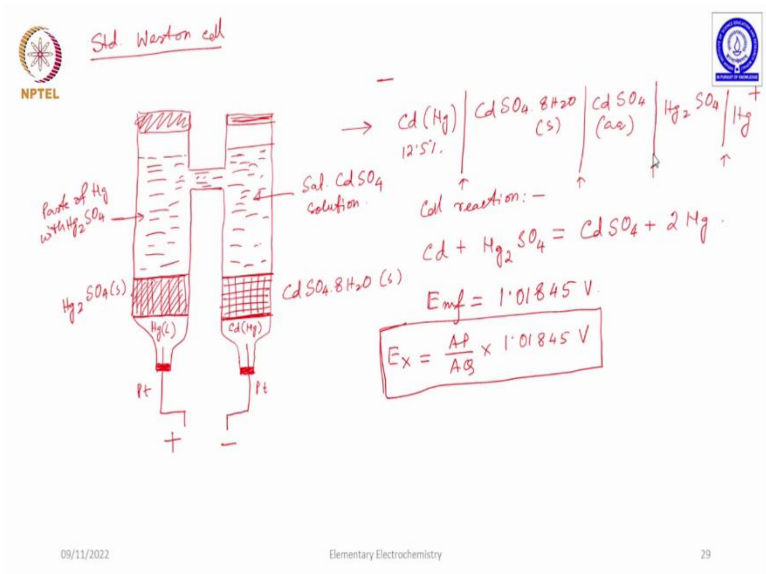

So, one such cell is the Weston cell, standard Weston cell. Let me first draw the cell how and write down it constituents and then I will discuss about the reaction. So, what I have is a tube looking like H which can contain the components or constituents of the cell and this cell will have different layers of different chemicals. I am going to discuss about that one by one. See, the bottom is sealed. So, at the bottom on either side you have platinum electrodes.

On the left-hand side at the bottom you have Hg that is markedly liquid. On the right-hand side, you have cadmium amalgam which is also a semi solid liquid substance. On top of this liquid mercury you have mercurous sulphate Hg2SO4 in solid state. On the other side you have cadmium sulphate 8H2O in solid form. Both sides the top is also closed with a lid. Then on the upper portion here this is filled with a paste off mercury with Hg2SO4 that is mercurous sulphate.

And on the other side the solution is filled with the top layer part is filled with saturated CdSO4 solution. In this cell this is the positive and that is the negative end. So, if you want to write down this cell in one line, then one should write it like this. You know cadmium amalgam is here it is the negative electrode. So, the cathode is always written on the left-hand side. Then you have the cadmium sulphate 8H2O solid. Then you have CdSO4 aqueous that is saturated solution.

Then you have Hg2SO4 and Hg as the positive electrode on the left-hand side. So, this is a 12.5 percent cadmium amalgam that is used. So, in this particular cell what is the cell reaction, cadmium plus Hg2SO4 giving you CdSO4 plus 2Hg that is mercury. So, when this cell is connected with a standard hydrogen electrode and its EMF is determined, it is observed that the EMF of Weston cell turns out to be 1.01845 volts.

So, then, when you use that formula of Ex equal to AP by AQ you use this western cell to be connected with your unknown cell. So, the potential for that Weston cell will be 1.01845 volt. So, this is how one can determine the EMF of any unknown cell. I must tell you that this cell is also not very easy to handle, because this has liquid mercury cadmium amalgam etcetera, but it is easier than handling the standard hydrogen electrode, and hence, this Weston cell is widely used to determine the EMF of an unknown cell that you may make.

So, with this, you can solve a few problems where it will be there in your textbook, you can find in standard textbook some problems related to how to determine the EMF of a cell using a potentiometer. So, there you may find some problems where the specific resistance or resistivity of the wire is given and from there you calculate the resistance or the length is given and all that. So, those problems you can try to solve yourself and practice writing and drawing the cells and then writing the cell in one line the way I have written.

You remember, all should always remember that the negative electrode is always on the left-hand side and the positive electrode is always on the right-hand side it is written. And you remember that we have written some lines, these lines mean something. And we will see at some point we will use a single line and double line. So, we will then discuss what is the difference between a single line and a double line.

For the time being the single line here indicates the phase boundaries here it is mercury liquid which is in connection with mercurous sulphate solid, so there is a boundary. Then this mercurous sulphate solid is in equilibrium with a boundary which is a paste of mercury with mercurous sulphate, so that is here. And then that mercurous sulphate and cadmium sulphate solid is again a boundary here, cadmium sulphide to cadmium sulphide solid there is a boundary here.

And then cadmium sulphide to solid to mercury amalgam that is cadmium amalgam is also a boundary here. So, these boundaries are distinctly marked as the vertical line in your cell. There is no such boundary here but this is like a flow. So, there is also a line given like that which is basically separating the marketing from the cadmium sulphate in solution. So, we will stop here in this class and we will continue from here in the next lecture. Thank you.