Elementary Electrochemistry
Professor Angshuman Roy Choudhury
Department of Chemical Sciences
Indian Institute of Science Education and Research, Mohali
Numerical Problems: Nernst Equation, EMF of Half Cell Reactions

Welcome back to the course entitled elementary electrochemistry. So, in the previous lecture, we have discussed about how one can calculate the EMF of a cell from the half cell potentials and we have discussed a few such cells and talked about how one can calculate the EMF of a cell.

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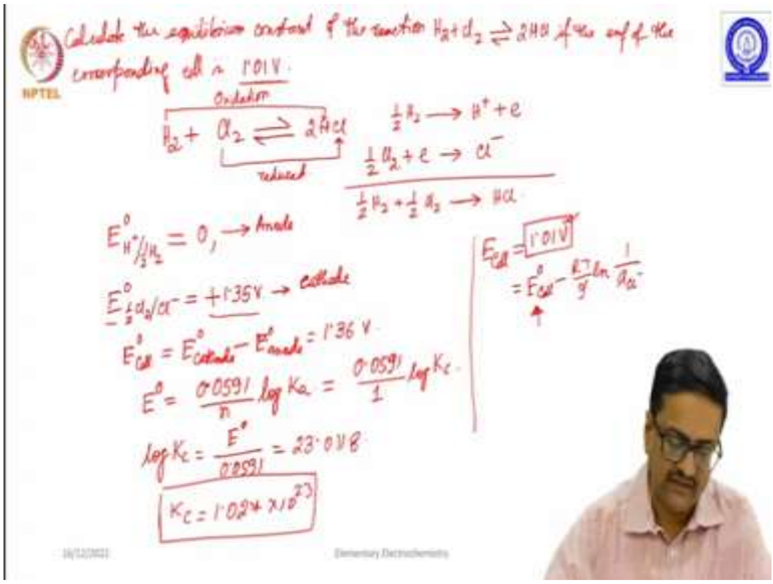

So, in today's lecture, we are going to try to solve a few problems related to those what we have learned in last few classes. So, the question number one is calculate the equilibrium constant of the reaction H2 plus Cl2 in equilibrium with 2HCl if the EMF of the corresponding cell is 1.01 volt.

So, to solve this problem what we need to do is we need to first write down the chemical reaction that is happening at this electrode at this cell H2 plus Cl2 forming 2HCl which is given. So, here this H is getting oxidized, hydrogen is getting oxidized and chloride is getting reduced. So, if we write this reaction in the two half cell reactions, one can write it as half H2 getting oxidized to H plus plus electron and half Cl2 taking up one electron is getting up reduced to Cl minus and the overall reaction is half H2 plus half Cl2 giving you just HCl.

So, now, we have two electrodes here, one is the electrode H plus and half H2 by convention we assume this potential to be equal to 0 and the other electrode which is E0 half Cl2 Cl minus is taken from the literature value from a textbook is 1.35 volt. So, here we have this electrode is used as anode and this electrode is used as a cathode. So, then when you write E0 cell is nothing but E0 cathode minus E0 anode which is equal to 1.36 volt.

So, now what we know from our previous class the Nernst equation E0 is equal to RT by NF and then when we convert it to using the T equal to 298 Kelvin, then this constant turns out to be 0.0591 by n log Ka, so, then here instead of activity one can convert it into 1 by number of electron transfer is 1, one can write log Kc and then you can calculate that log Kc is equal to E0 divided by 0.0591 which turns out to be equal to 23.0118. So, one can easily calculate the value of Kc as 1.027 into 10 to the power 23, so, that is the equilibrium constant for that particular reaction.

You see this value is given it is the E cell which is equal to 1.01 volt and you can recall E cell is nothing but E0 cell minus RT by F ln, in this case the activity of Cl minus will be here. So, in this condition this is the EMF, that is the EMF of the cell and not the E0 cell. So, here we do not need to use this value at all, one has to use the E0 of the chlorine chloride electrode to calculate the equilibrium constant of this reaction.

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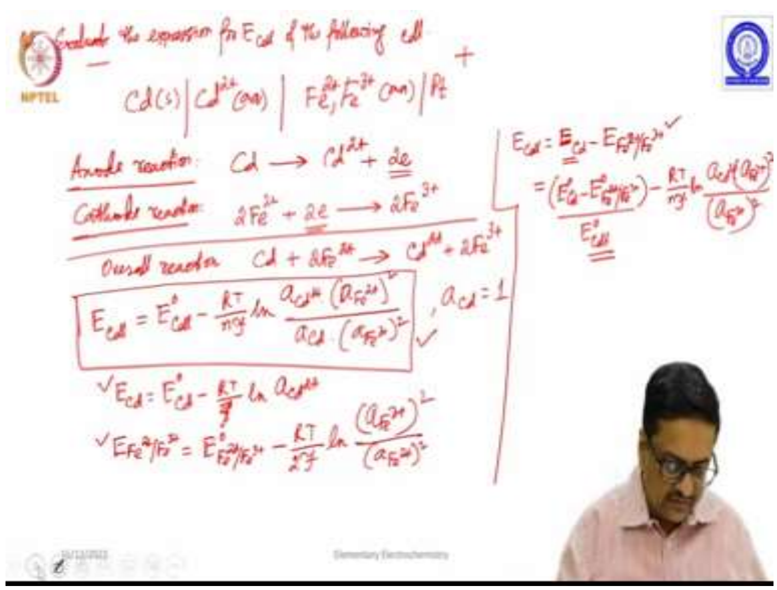

So, now, the question number two; evaluate the expression for E cell of the following cell. Cadmium solid is in equilibrium with cadmium 2 plus in aqueous medium is in connection with Fe2 plus Fe3 plus in aqueous medium with platinum as electrode and here this side is the positive electrode, this side is the negative electrode, the positive and left is negative. So, the anode reaction is Cd getting oxidized to Cd2 plus plus 2 electrons and the cathode reaction is 2Fe2 plus plus 2 electrons giving you 2Fe3 plus, so, we had to make two electron to balance that two electron.

So, when you write the overall reaction then you can write it as Cd plus 2Fe2 plus is getting converted to Cd2 plus plus 2Fe 3 plus. So, we can write E cell as E0 cell minus RT by nF ln activity of Cd2 plus into activity of Fe2 plus square divided by activity of Cd into activity of Fe3 plus square and now, one can set activity of Cd equal to 1 because it is pure metal. So, one can write the E cell without the ECd sorry, activity of Cd.

See on the other hand one can write ECd is equal to E0Cd minus RT by 2f ln activity of Cd2 plus. Similarly, EFe2 plus Fe3 plus as E0 Fe2 plus Fe3 plus minus RT by F rather 2F ln activity of Fe3 plus square divided by activity of Fe2 plus whole square.

So, one can easily write that E cell is equal to ECd minus EFe2 plus Fe3 plus which is again nothing but what we have obtained. Here if you replace ECd by this equation and E ferrosoferric by this equation and then you simplify you will end up getting the difference of E0 cd minus E0 Fe2 plus Fe3 plus which will be replaced by E0 cell minus RT by nF ln activity of Cd2 plus into activity of Fe2 plus square divided by activity of Fe3 plus whole square and this is replaced by E0 cell. So, this is how one can derive the equations for the corresponding cells for a cell from the corresponding half cell potentials.

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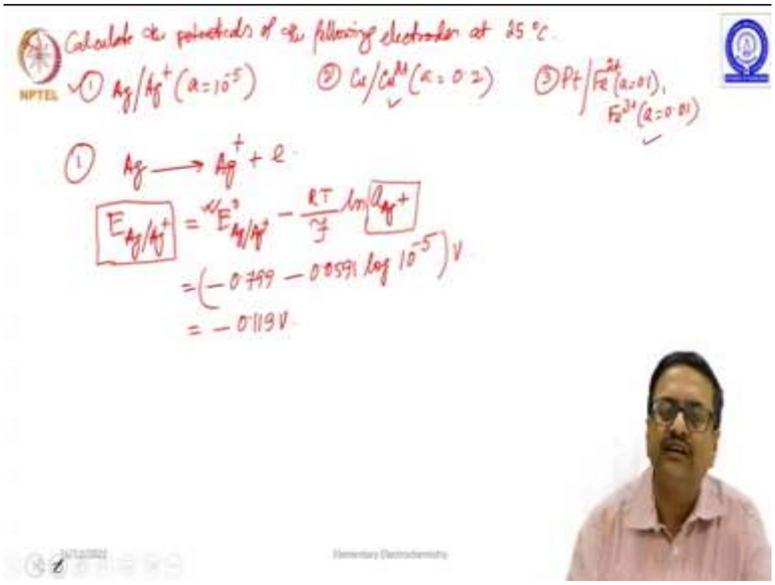

Let us see the question number 3, calculate the potentials of the following electrodes at 25 degree centigrade. So, 1 is Ag Ag plus with activity equal to 10 to the power minus 5. Number 2; Cu Cu2 plus with activity equal to 0.2. And number 3 is platinum electrode in equilibrium with Fe2 plus of activity equal to 0.1 and Fe3 plus of activity equal to 0.01. So, I will explain or I will show you how to do it with the first one and you should try to solve the other two. So, the reaction is Ag get going to Ag plus plus electron. So, EAg Ag plus is nothing but E0Ag Ag plus minus RT by F because it is one electron transfer ln activity of aAg plus.

So, now, you take the value of this E0Ag Ag plus from the literature we found it to be 0.799 volts minus 0.0591 ln, I think should be log 10 to the power minus 5 and the unit is the volt. So, once you do this you should get it as 0.119 volt. So, this is the EMF of the half electrode with a given value of activity of silver. So, similarly, if you try to do this and that using the standard values available in any standard electrochemistry textbook which are prescribed for this course.

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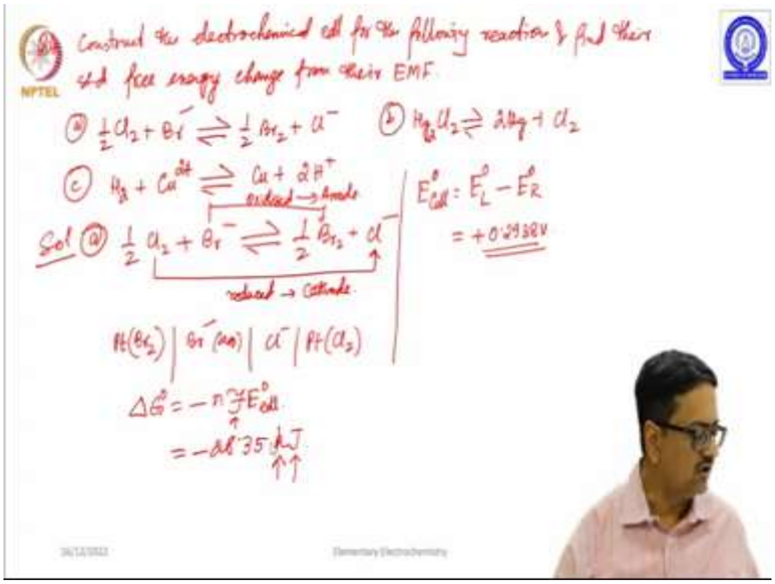

Now, question number four is, construct the electrochemical cells for the following reactions and find their standard free energy change from their EMF. Once again you need to find out these EMFs from (a) any standard textbook and I am giving you three of them, we will solve one of them. Half Cl2 plus Br minus is in equilibrium with half Br2 plus Cl minus, b is Hg2 Cl2 is in equilibrium with 2Hg plus Cl2 and c is H2 plus Cu2 plus in equilibrium with Cu plus 2H plus aqueous.

So, let us try to solve a, so, it is nothing but half Cl2 plus Br minus giving you half Br2 plus Cl minus. So, here what we see bromine is getting oxidized, so, that means this is happening at anode and chlorine is getting reduced, so, this is happening at cathode. So, as soon as we identify the corresponding cathode and anode, we quickly write down the possible cell with suitable electrode. So, what we write is platinum is in equilibrium with bromine gas and the solution and the solution contains Br minus in aqueous medium. It is in equilibrium with or it is in contact with Cl minus with platinum with chlorine.

So, now, what one can easily calculate here is E0 cell is nothing but E0 left minus E0R. And when you try to find out those values from the textbook and do the math, you will get this to be plus 0.2938 volt. So, what we know is delta G0 is equal to minus nFE 0 and this E0 is the E0 cell which is this one.

So, when you do that you place the value of f as 96500 and n is a one electron transfer, one can easily calculate this number or the delta G to be minus 28.35 kilo Joules, you see, one has to note that when we are writing kilo that k is small, and when we write the joule, it is the unit of energy, but then the unit comes from the name of a person as a result that J is capital. So, always whenever you are writing the unit one has to remember how to write the unit correctly with proper capital or small letters.

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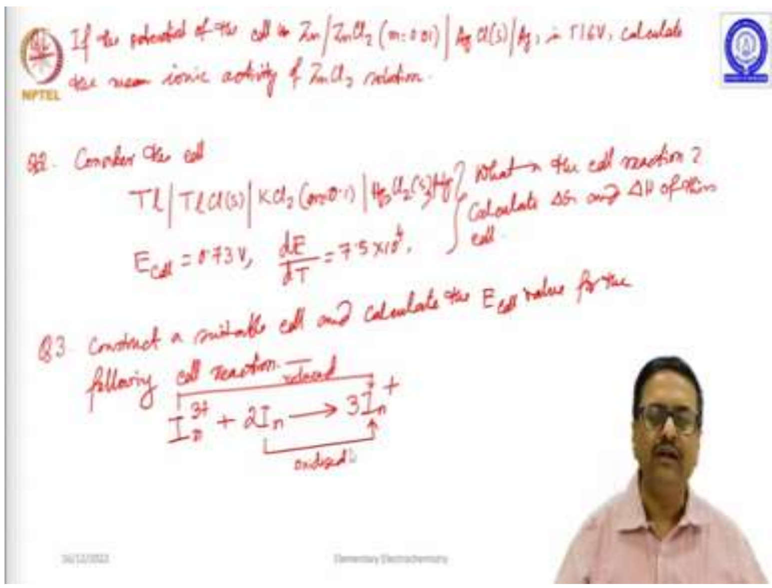

So, now, I want to give you a couple more problems for you to solve at home. So, to problems to be solved at home are this the following; If the potential of the cell is cell sorry, Zn ZnCl2 with molality 0.01 in connection with AgCl solid with Ag as electrode is 1.16 volts then calculate the mean ionic activity of ZnCl2 solution.

Question number two is consider the cell given below Tl in connection with TlCl in solid form, it is in connection with KCl solution of molality 0.1 and the other end the electrode is Hg2 Cl2 solid with mercury as your electrode. I think one should not write this slash because slash indicates phase boundary, one should write just comma. The value given is the E cell as 0.73 volt and de dt equal to 7.5 into 10 to the power 4. So, the question is what is the cell reaction? Calculate delta G and delta H of this cell.

And question number three is, construct a suitable cell and calculate the E cell value for the following cell reaction; the reaction is I indium 3 plus plus 2 indium getting converted to 3 indium plus. See here what is happening is the same element indium is getting reduced and here it is getting oxidized. So, you can understand that both the electrodes will have system of indiums. So, one has to find out the electrode potential of different indium cations with indium 0 and indium cations and another indium cations and so on to do this problem.

So, you need to find out the standard electrode potentials for various indium related systems from a textbook. So, here I leave these three problems for you to solve before the next class. Thank you.