Elementary Electrochemistry
Professor Angshuman Roy Choudhury
Department of Chemical Sciences
Indian Institute of Science Education and Research, Mohali
Lecture 11
Electrode Potential and Applications of Nernst Equation

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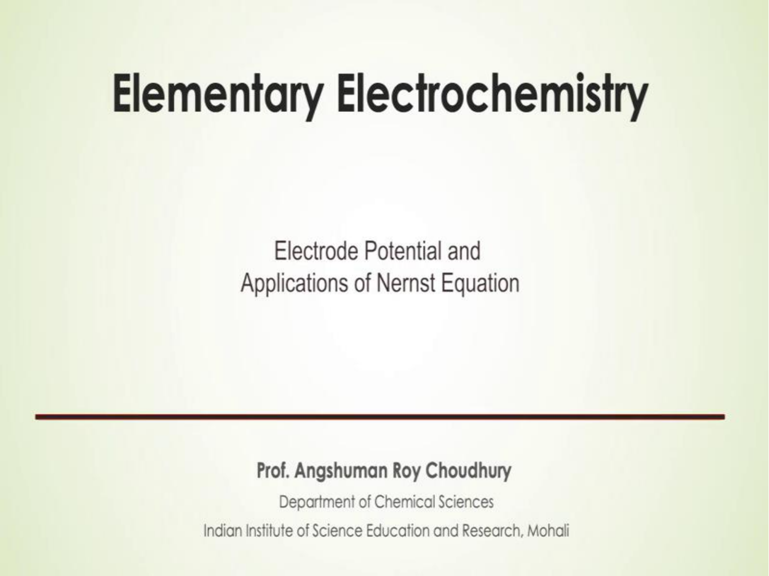

Elementary Electrochemistry

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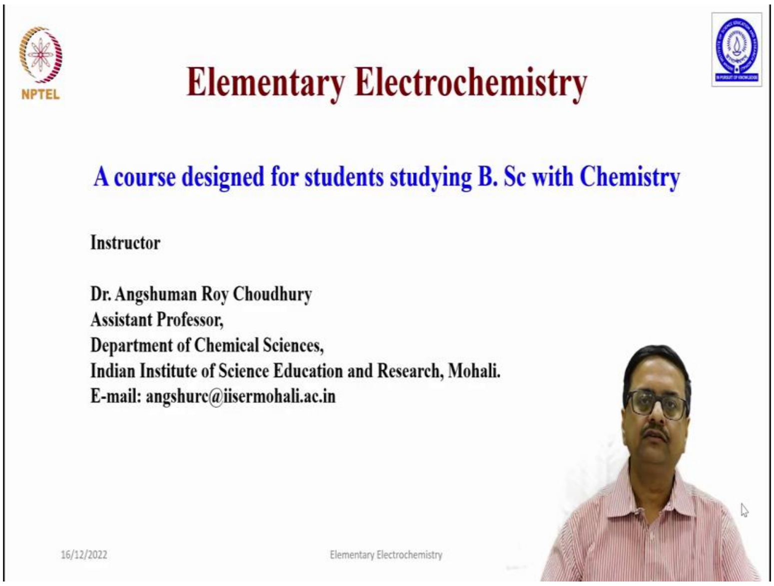

Elementary Electrochemistry

A course designed for students studying B. Sc with Chemistry

Instructor

Dr. Angshuman Roy Choudhury
Assistant Professor,
Department of Chemical Sciences,
Indian Institute of Science Education and Research, Mohali.
E-mail: angshurc@iisermohali.ac.in

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Welcome back to the course entitled Elementary Electrochemistry, we have now reached the third week of this course. So, in today's class we are going to discuss about the electrode potentials and how one can express electrode potentials of different electrodes using the Nernst equation.

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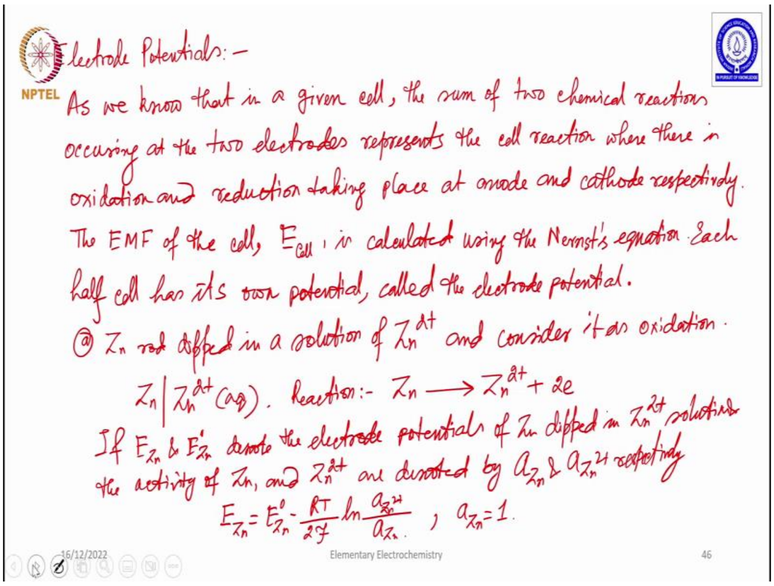

Electrode Potentials:-

As we know that in a given cell, the sum of two chemical reactions occuring at the two electrodes represents the cell reaction where there is oxidation and reduction taking place at anode and cathode respectively. The EMF of the cell, E_{cell}, is calculated using the Nernst's equation. Each half cell has its own potential, called the electrode potential.

ⓐ Zn rod dipped in a solution of Zn^{2+} and consider it as oxidation.

$Zn | Zn^{2+}(aq)$. Reaction:- $Zn \longrightarrow Zn^{2+} + 2e$

If E_{Zn} & E'_{Zn} denote the electrode potentials of Zn dipped in Zn^{2+} solutions the activity of Zn, and Zn^{2+} are denoted by a_{Zn} & $a_{Zn^{2+}}$ respectively

$$E_{Zn} = E^0_{Zn} - \frac{RT}{2F} \ln \frac{a_{Zn^{2+}}}{a_{Zn}} \quad , \quad a_{Zn} = 1.$$

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So, we are going to discuss about the electrode potentials today. So, as we know that in a given cell the sum of two chemical reactions occurring at the two electrodes represents the cell reaction where there is oxidation and reduction taking place at anode and cathode respectively. So, the EMF the electromotive force of the cell which is written as E cell is calculated using the Nernst’s equation. So, each half cell has its own potential, called the electrode potential. So, when you have a cell you have two half cells and using Nernst equation one can calculate from the half cell potentials the EMF of the cell.

So, let us take a few examples, let us take the first example a, when we have a zinc rod dipped in a solution of Z n 2 plus and consider it as oxidation. So, the electrode is written as Z n, Z n 2 plus aqueous, this is how you write the electrode and the corresponding reaction that we are talking about is Z n getting oxidized to Z n 2 plus, plus 2 electrons which are released at the electrode.

So, if E Z n and E0 Z n denote the electrode potentials of Z n dipped in Z n 2 plus solution and the activity of Z n and Z n 2 plus are denoted by a Z n and a Z n 2 plus respectively then you can use Nernst equation and write the relationship between E Z n as E 0 Z n minus RT by 2F because there is two electron transfer ln activity of Z n 2 plus divided by activity of Z n. So, now when we are talking about a pure metal zinc, one can assume activity of Z n to be equal to 1.

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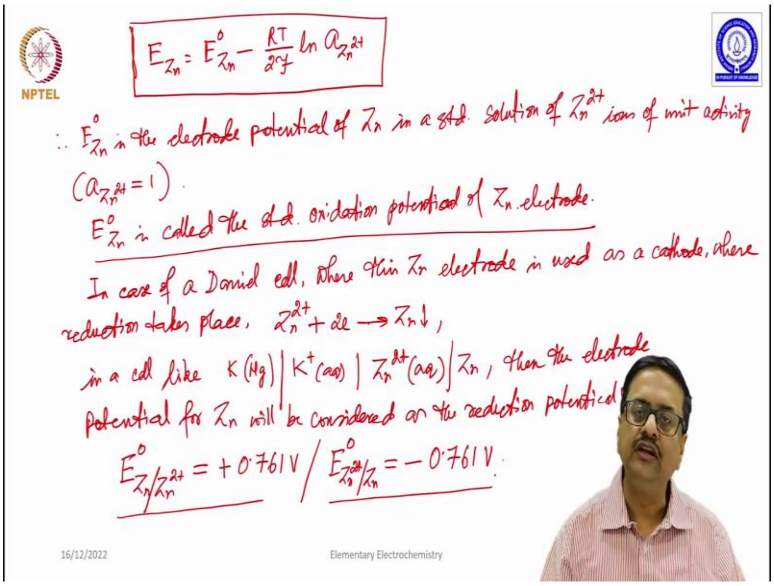

$$\boxed{E_{Zn} = E^0_{Zn} - \frac{RT}{2F} \ln a_{Zn^{2+}}}$$

$\therefore$ E^0_{Zn} is the electrode potential of Zn in a std. solution of Zn^{2+} ions of unit activity $(a_{Zn^{2+}} = 1)$.

E^0_{Zn} is called the std. oxidation potential of Zn electrode.

In case of a Daniel cell, where this Zn electrode is used as a cathode, where reduction takes place, $Zn^{2+} + 2e \rightarrow Zn\downarrow$,

in a cell like $K(Hg) \,|\, K^+(aq) \,|\, Zn^{2+}(aq) \,|\, Zn$, then the electrode potential for Zn will be considered as the reduction potential.

$E^0_{Zn/Zn^{2+}} = +0.761\,V \,/\, E^0_{Zn^{2+}/Zn} = -0.761\,V$.

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So, then this equation can be modified as E Z n is equal to E0 Z n minus RT by 2F ln activity of Z n 2 plus. So, E0 Z n is the electrode potential of zinc in a standard solution of Z n 2 plus ions of unit activity that is activity of Z n 2 plus is also equal to 1. So, this E0 Z n is called the standard oxidation potential of zinc electrode. So, when you write it as oxidation potential and if the value turns out to be positive, then when you write it in terms of reduction potential of Zinc the value will be nothing but negative because the opposite reaction is considered.

So, in case of a Daniel cell, where this Z n electrode is used as a cathode, where reduction takes place that is Z n 2 plus by taking two electrons gets converted to zinc and gets deposited at the electrode then in a cell like potassium amalgam K plus in the aqueous medium is in connection with Z n 2 plus aqueous with metallic zinc as electrode, then the electrode potential for Z n will be considered as the reduction potential of zinc.

So, this is just positive and negative when you consider the forward or the backward reaction. So, when you try to write E 0 Z n slash Z n 2 plus. So, that I am showing the reaction is in the oxidation direction the potential is reported to be 0.761 volt whereas, when you write the E 0 Z n 2 plus getting reduced to Z n in the reduction direction, then we could write this value as 761 Volt. So, one has to remember whether you are writing the electrode potential in the oxidation direction or in the reduction direction and accordingly this sign will be used.

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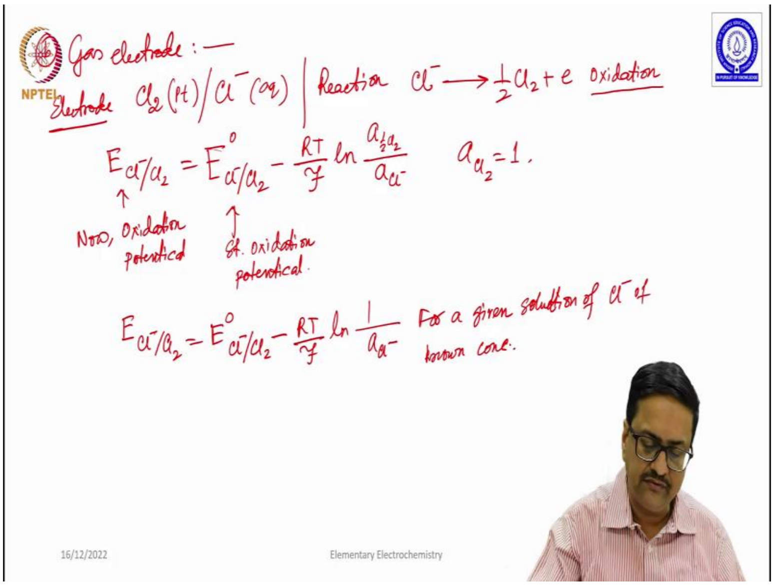
Gas electrode :—

Electrode $Cl_2(Pt)/Cl^-(aq)$ | Reaction $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e$ oxidation

$$E_{Cl^-/Cl_2} = E^0_{Cl^-/Cl_2} - \frac{RT}{F}\ln\frac{a_{\frac{1}{2}Cl_2}}{a_{Cl^-}} \qquad a_{Cl_2} = 1.$$

Now, oxidation potential

St. oxidation potential.

$$E_{Cl^-/Cl_2} = E^0_{Cl^-/Cl_2} - \frac{RT}{F}\ln\frac{1}{a_{Cl^-}}$$ For a given solution of Cl^- of known conc.

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So, let us see the second electrode which is a gas electrode. So, one of the important gas electrodes that we encountered is the Chlorine gas bubbled around a platinum electrode is in equilibrium with a chloride solution, this is the electrode and the corresponding reaction is Cl minus getting converted to chlorine gas releasing 1 electron and it is written in the oxidation direction. So, when we write E0 Cl minus, Cl 2 one should write as sorry, this is not zero this is not the standard state is the electron potential of chlorine chloride system with a given concentration of chloride in solution and this is the standard value which is Cl minus 2, Cl 2 minus RT by F ln activity of half Cl 2 by activity of Cl minus.

So, now this is the oxidation potential and this is the standard oxidation potential. So, if we assume the activity of pure chlorine gas is to be equal to 1, one can write this rewrite this equation as E Cl minus Cl 2 is equal to E0 Cl minus Cl 2 minus RT by F ln 1 by activity of Cl minus. So, this is for a given solution of Cl minus of non-concentration from which one can calculate the activity of Cl minus.

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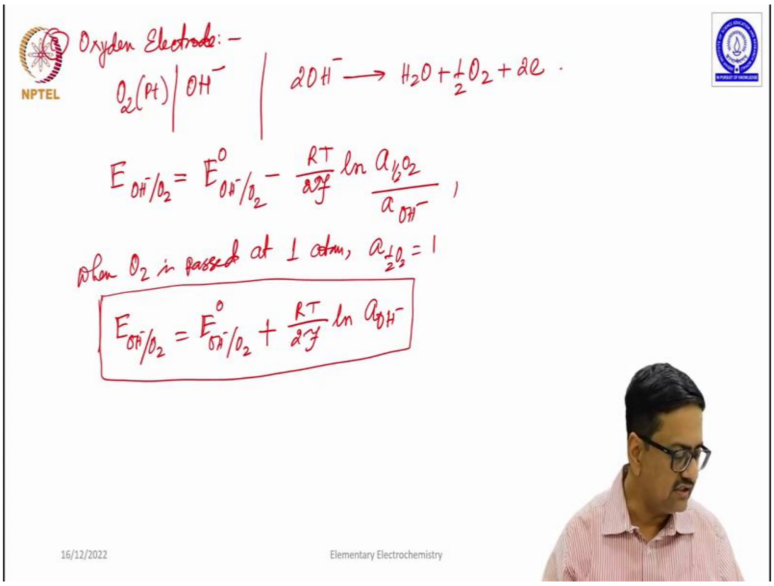

Oxyden Electrode:-

$O_2(Pt)|OH^-$ | $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e$.

$$E_{OH^-/O_2} = E^0_{OH^-/O_2} - \frac{RT}{2F}\ln\frac{a_{1/2 O_2}}{a_{OH^-}},$$

when O_2 is passed at 1 atm, $a_{\frac{1}{2}O_2} = 1$

$$\boxed{E_{OH^-/O_2} = E^0_{OH^-/O_2} + \frac{RT}{2F}\ln a_{OH^-}}$$

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So, similarly, one can consider the oxygen electrode. So, this oxygen electrode is again oxygen gas is bubbled around the platinum electrode and it is in equilibrium with OH minus and the corresponding reaction is 2OH minus giving to H 2 O plus half O 2 plus 2 electrons. So, the electrode potential that one can write is OH minus going to O 2 is equal to E0 OH minus going to O 2, sorry minus RT by 2F ln activity of half of O 2 divided by activity of OH minus and then when O 2 is passed at 1 atm one can assume that activity of half O 2 is nothing but equal to 1 and then you can write this E OH minus 2, O 2 is equal to E0, OH minus O 2 minus RT by 2F ln.

So, one can make it plus and write a OH minus because see here a OH was in the denominator and then when you take it to the numerator then it becomes the plus sign. So, this is how one can very easily write the half cell reactions and the corresponding electrode potentials.

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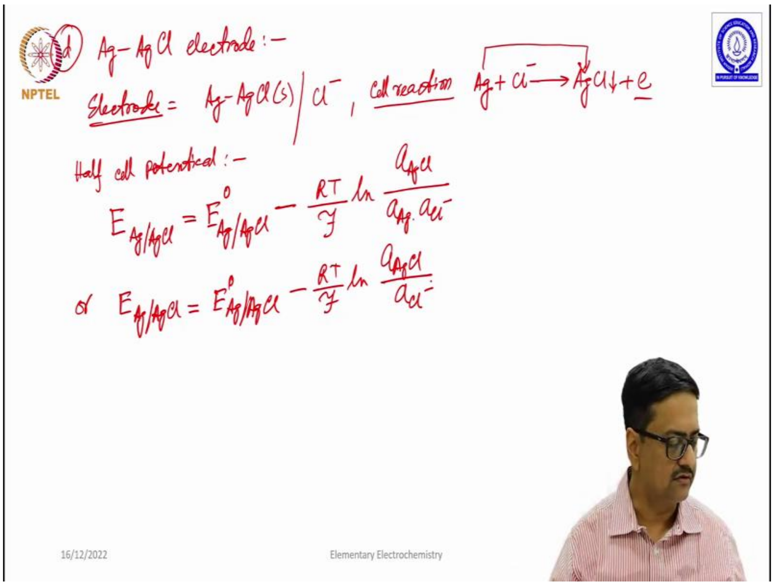

(d) Ag – AgCl electrode :–

Electrode = Ag – AgCl(s) | Cl$^-$, cell reaction $Ag + Cl^- \longrightarrow AgCl\downarrow + e$

Half cell potential :–

$$E_{Ag/AgCl} = E^0_{Ag/AgCl} - \frac{RT}{F} \ln \frac{a_{AgCl}}{a_{Ag} \cdot a_{Cl^-}}$$

or $$E_{Ag/AgCl} = E^0_{Ag/AgCl} - \frac{RT}{F} \ln \frac{a_{AgCl}}{a_{Cl^-}}$$

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So, we also learned about the silver silver chloride electrode in the previous lectures. So, we should also try to write down the same equation for Ag, AgCl electrode. So, what is the electrode here, the electrode is Ag in connection with AgCl in solid and in equilibrium chloride ions in solution.

So, the cell reaction will be Ag plus Cl minus getting converted to AgCl as a precipitate releasing one electron. So, here again it is the oxidation of Silver. So, that is we are writing in the oxidation direction. So, then what one can write is half cell potential in the oxidation manner, one can write E Ag, AgCl equal to E0 Ag, AgCl minus RT by F because one electron transfer ln activity of AgCl divided by activity of Ag into activity of Cl minus or one can write the silver activity of pure silver take taken to be one, one can write this equation as E Ag AgCl equal to is E0 Ag AgCl minus RT by F ln activity of AgCl divided by activity of Cl minus. So, this is how one can write the cell reaction for silver silver chloride electrode.

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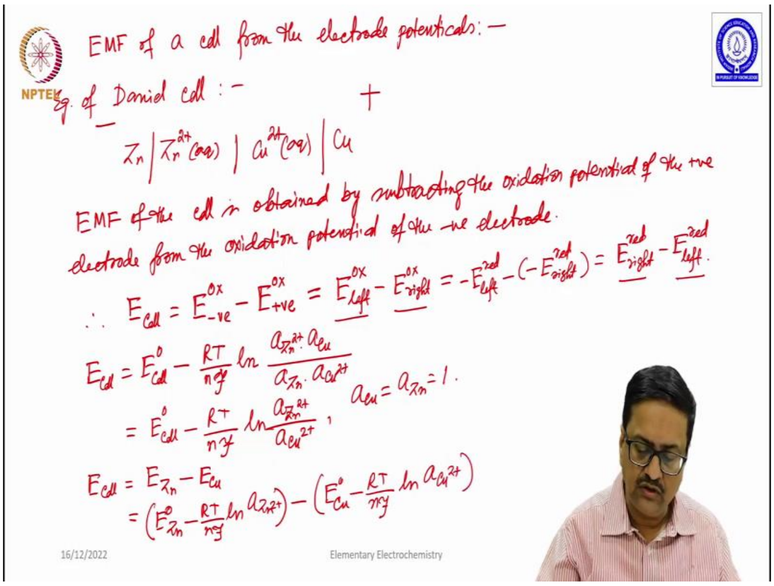

EMF of a cell from the electrode potentials:–

Eg. of Daniel cell :–

$-$ $+$

$Zn \mid Zn^{2+}(aq) \mid Cu^{2+}(aq) \mid Cu$

EMF of the cell is obtained by subtracting the oxidation potential of the +ve electrode from the oxidation potential of the -ve electrode.

$$\therefore\ E_{cell} = E^{ox}_{-ve} - E^{ox}_{+ve} = \underline{E^{ox}_{left}} - \underline{E^{ox}_{right}} = -E^{red}_{left} - (-E^{red}_{right}) = \underline{E^{red}_{right}} - \underline{E^{red}_{left}}.$$

$$E_{cell} = E^0_{cell} - \frac{RT}{nF} \ln \frac{a_{Zn^{2+}} \cdot a_{Cu}}{a_{Zn} \cdot a_{Cu^{2+}}}$$

$$= E^0_{cell} - \frac{RT}{nF} \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}, \quad a_{Cu} = a_{Zn} = 1.$$

$$E_{cell} = E_{Zn} - E_{Cu}$$

$$= \left(E^0_{Zn} - \frac{RT}{nF} \ln a_{Zn^{2+}}\right) - \left(E^0_{Cu} - \frac{RT}{nF} \ln a_{Cu^{2+}}\right)$$

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Now, if we try to write the emf of a cell, of a cell from the electrode potentials. So, let us take the example of our Daniel cell. So, where we write the electrodes as zinc in equilibrium with Z n 2 plus in aqueous medium, then you have copper 2 plus in aqueous medium and Cu as the electrode. So, here the right-hand side this copper copper 2 plus electrode is the positive electrode and the left-hand side is the negative electrode. So, the emf of the cell is obtained by subtracting the oxidation potential of the positive electrode from the oxidation potential of the negative electrode.

So, therefore, one can write E cell is equal to E ox of the negative electrode minus E ox of the positive electrode or in other words E ox left, minus E ox right. So, left minus right in the oxidation direction. So, then in the reduction direction what will happen one can replace E ox by Ered. So, one can write Ered with a minus sign and left minus of minus Ered of right.

So, overall it will become E reduction of right, minus E reduction of left. So, it depends on how you consider if you are considering the oxidation potential then it is E left minus E right. If you are talking about reduction potential then it is E right minus E left. So, one has to keep this in mind while doing the calculation for E cell.

So, now for this Daniel Cell, one can write E cell is equal to E 0 cell minus RT by nF ln activity of Z n 2 plus into activity of Cu divided by activity of Z n into activity of Cu 2 plus which then can be written as E 0 self minus RT by nF ln activity of Z n 2 plus by activity of Cu 2 plus as for pure metals activity of copper is equal to activity of zinc is equal to one. So, now, one can rewrite this equation in this way E cell is nothing but E Z minus E cu, now E Z n is nothing but E 0 Z n minus RT by nF ln activity of Zn 2 plus minus E Cu is nothing but E 0 Cu minus RT by nF ln activity of CO2 plus.

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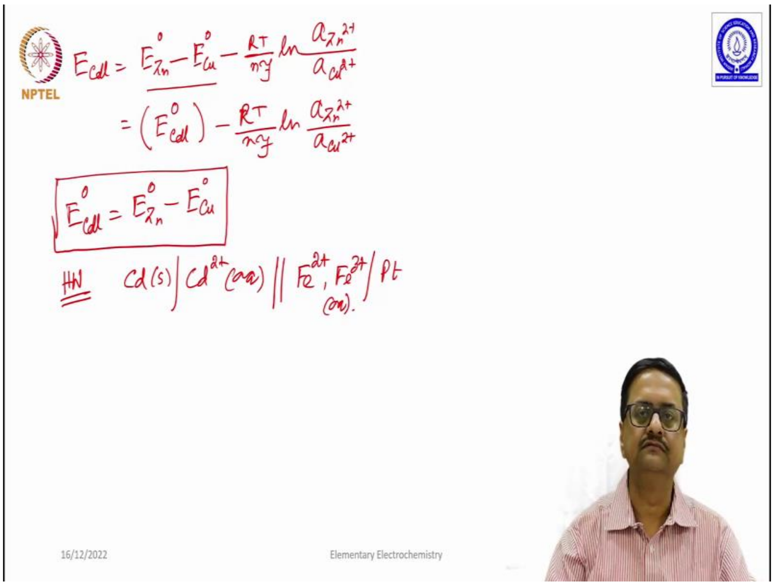

$$E_{cell} = \underline{E^0_{Zn} - E^0_{Cu}} - \frac{RT}{nF} \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$$

$$= \left(E^0_{cell}\right) - \frac{RT}{nF} \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$$

$$\boxed{E^0_{cell} = E^0_{Zn} - E^0_{Cu}}$$

HW $Cd(s) \,|\, Cd^{2+}(aq) \,||\, \underset{(aq).}{Fe^{2+}, Fe^{3+}} \,|\, Pt$

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So, what one can simplify from here is that E cell equal to E0 Z n minus E zero copper minus RT by nF ln activity of Zn 2 plus divided by activity of co2 plus. Therefore, these two can be replaced by E0 cell minus R T by nF ln activity of Z n 2 plus divided by activity of Cu 2 plus. So, what does it mean, we can easily write E0 cell is equal to E0 Z n minus E0 of copper. So, with this one can very easily calculate the standard emf of a given cell.

So, I am giving you one homework to work out what will be the E0 cell for this particular cell. Cadmium solid is in equilibrium with cadmium 2 plus in aqueous medium and then it is coupled with Fe 2 plus, Fe 3 plus system with platinum as electrode. So, from here we will continue in the next class. Thank you.