ELECTROCHEMISTRY

by Apni Kaksha :)

Class XII BOARD EXAMS (Target 100)

These notes have been verified by CBSE Science Toppers.

↳ No part of syllabus removed from these notes.

Previous 15 year Questions have been integrated in the notes.

Aman Dhattarwal

Target 100

HOW TO STUDY THE NOTES?

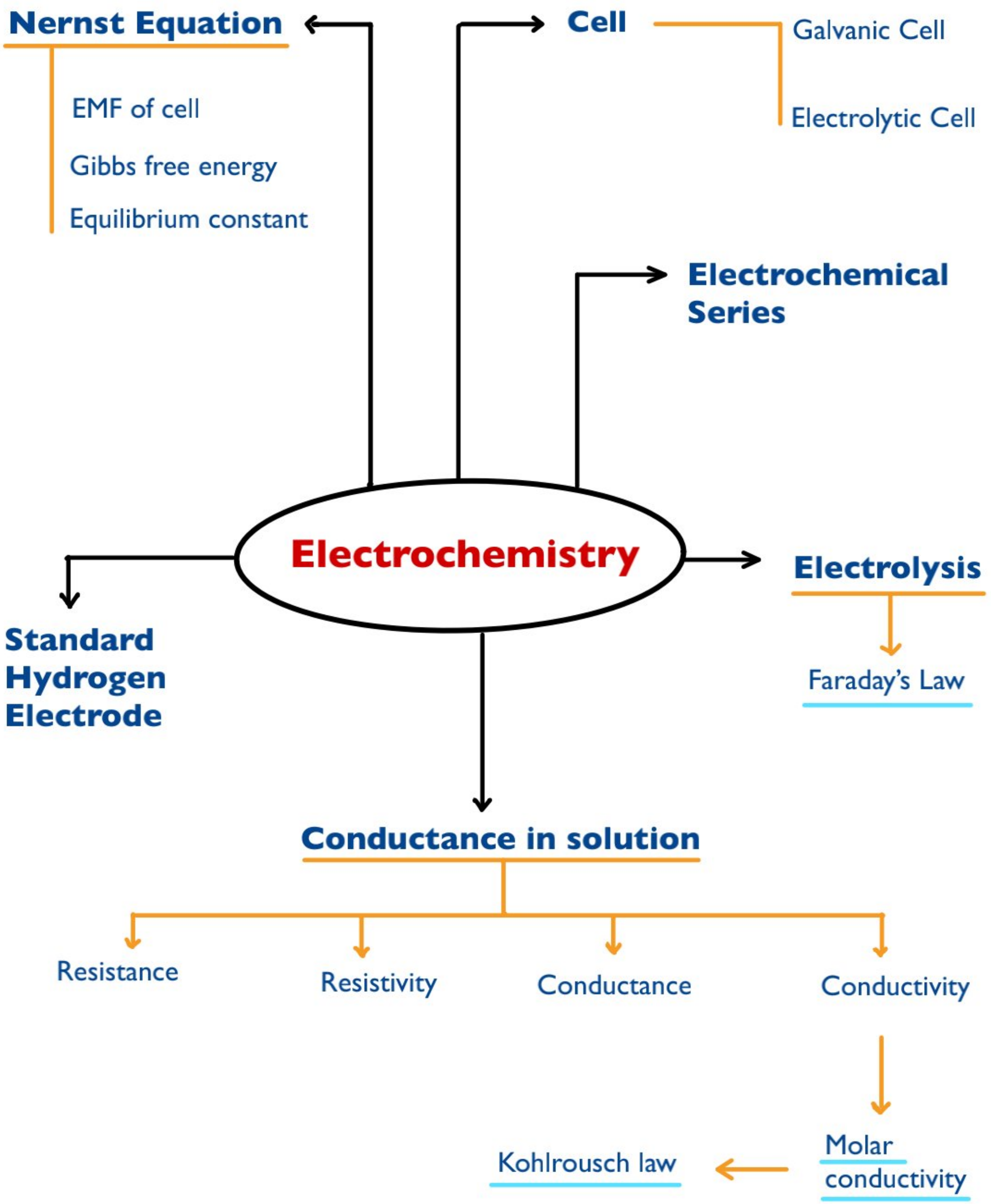
Apni Kaksha

- -Coloured and double sided print
- Revise the notes at least 3-4 time
- Write to revise | 10% rule
- Keep track of previous year qs
- See the marking scheme

Jao Ab Phodo!

Aman Dhattarwal

Flow Chart


Nernst Equation
EMF of cell
Gibbs free energy
Equilibrium constant
Cell
Galvanic Cell
Electrolytic Cell
Electrochemical Series
Electrochemistry
Standard Hydrogen Electrode
Electrolysis
Faraday’s Law
Conductance in solution
Resistance
Resistivity
Conductance
Conductivity
Molar conductivity
Kohlrousch law

Electrochemistry

→ It is study of production of electricity from energy which is released during Spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformation.

Some Basic Definitions -:

Oxidation -: Loss of electron $Zn \longrightarrow Zn^{+2} + 2e^-$

Reduction -: Gain of electron $Cu^{+2} + 2e^- \longrightarrow Cu$

Electrotyte -: A solution that contains ions is called electrolyte. Electrolyte is an ionic conductor.

Electrode -: Surface at which oxidation or reduction takes place.

Redox Reaction -: An oxidation - reduction (redox) reaction.

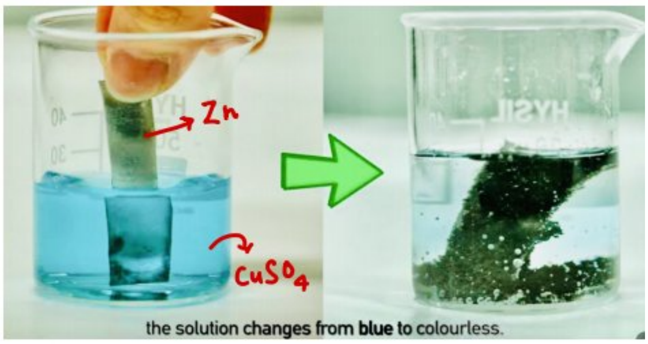
$$Zn + Cu^{+2} \longrightarrow Zn^{+2} + Cu$$

Placing a Zn rod in $CuSO_4$ solution -:

→ $CuSO_4$ solution is blue in colour. But if we place a Zn rod in $CuSO_4$ solution, colour fades out. This is because of reduction of $Cu^{+2} \rightarrow Cu$.

→ $Zn + Cu^{+2} \longrightarrow Zn^{+2} + Cu$

→ Above is a spontaneous reaction. It does not require any external work.

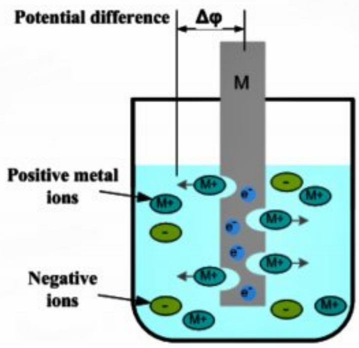


the solution changes from blue to colourless.

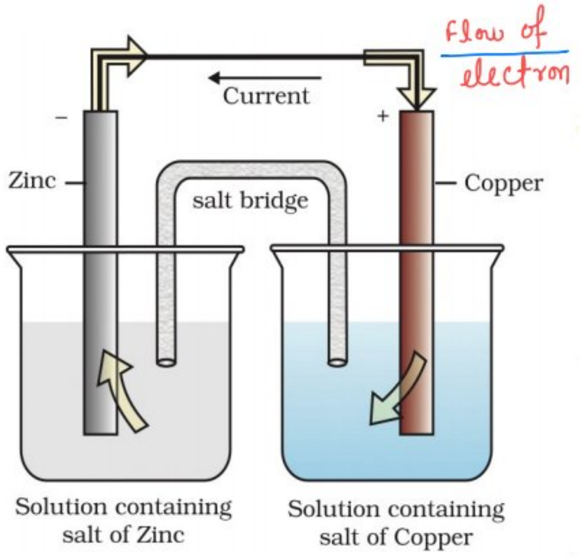
Electrode Potential -: Potential difference between metal and metal ion in which electrode is dipped is called electrode potential.

→ Electrode potential of Zn → $Zn | ZnSO_4$

Electrode potential of Cu → $Cu | CuSO_4$



Galvanic or Voltic Cell :– A galvanic cell is a an electrochemical cell that converts the chemical energy of a spontaneous redox reaction into electrical energy.



→ Spontaneous then $\Delta G = \ominus ve$.

→ In this device ΔG of spontaneous redox reaction is converted into electrical work (which may be used for running a motor, fan, heater etc.)

Construction :– It consist of two mettalic electrodes dipping in electrolytic solutions. The solution in two compartment is connected through an inverted U shaped tube containing a mixture of agar – agar jelly and an electrolyte like KCl, KNO_3 etc. This tube is called salt bridge.

→ Salt bridge is necessary because [Delhi 2011C] (1M)

(i) It connects the solution of two half cells, thus completes the cell circuit.

(ii) It prevents diffusion of solutions from one compartment to other.

→ In representation of cell, salt bridge is represented by ||.

→ In galvanic cell : oxidation at anode [negative plate]

Reduction at cathode [positive plate]

Daniell Cell :- Among the galvanic cells when cell is designed in such a manner to make the use of spontaneous reaction between Zn and Cu ion to produce an electric current, that cell is called Daniell cell.

Reaction : $Zn(s) + Cu^{2+}(aq.) \longrightarrow Cu(s) + Zn^{+2}(aq.)$

Cell Representation : $\underbrace{Zn \,|\, Zn^{+2}(aq.)}_{\text{Anode half cell}} \;||\; \underbrace{Cu^{+2}(aq.) \,|\, Cu}_{\text{Cathode half cell}}$ → phase boundary.

[Delhi 2013C] (1M)

: Anode half cell || Cathode half cell

salt bridge

→ Zn : Anode (oxidation) and Cu : Cathode (reduction)

→ The two half cell reactions are

(i) $Cu^{+2} + 2e^- \longrightarrow Cu_{(s)}$ [Reduction half reaction : Occurs at cathode]

(ii) $Zn_{(s)} \longrightarrow Zn^{2+} + 2e^-$ [Oxidation half reaction : occurs at anode]

Electrochemical Cell

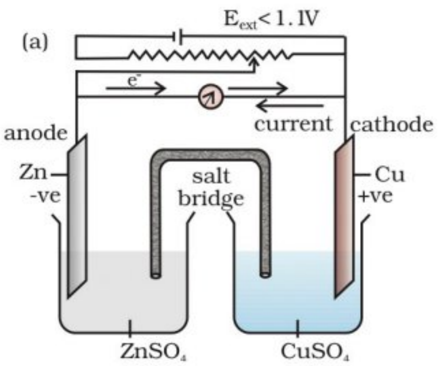
(i) Galvanic Cell

→ Chemical Energy → Electrical Energy

→ $\Delta G = -ve$ Spontaneous Reaction

→ Power is produced.

→ a

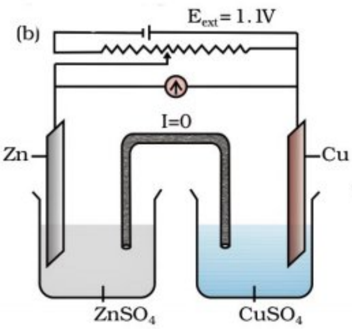


When $E_{ext} < 1.1$ V
(i) Electrons flow from Zn rod to Cu rod hence current flows from Cu to Zn.
(ii) Zn dissolves at anode and copper deposits at cathode.

(ii) Reversible

→ No Net reaction

b



When $E_{ext} = 1.1$ V
(i) No flow of electrons or current.
(ii) No chemical reaction.

$\boxed{E_{cell} = 1.1\ V}$

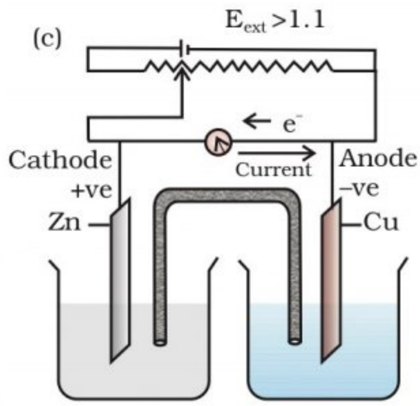
(iii) Electrolytic Cell

→ Electrical energy → Chemical energy

→ Non spontaneous Reaction [$\Delta G = +ve$]

→ Power is consumed.

c



When $E_{ext} > 1.1$ V
(i) Electrons flow from Cu to Zn and current flows from Zn to Cu.
(ii) Zinc is deposited at the zinc electrode and copper dissolves at copper electrode.

→ Functioning of daniell cell when external voltage (E_{ext}) opposing the cell potential is applied.

NOTE-: (i) When the concentration of all the species involved in a half cell is unity then the electrode potential is known as Standard Electrode Potential.

(ii) → IUPAC Convention : Standard Reduction Potential (SRP) is SEP.

(iii) → Cell Potential :- The potential difference between the two electrodes of a galvanic cell is called the cell potential and is measured in volts.

→ $E_{cell} = E_{cathode} - E_{anode} = E_{right} - E_{left}$ [Cell : Anode half cell || Cathode half cell.

a.) For a reaction $Zn(s) + Cu^{+2}_{(aq.)} \longrightarrow Cu(s) + Zn^{+2}(aq.)$

Cell : $Zn \mid Zn^{+2}(aq.) \parallel Cu^{+2}_{(aq.)} \mid Cu(s)$

$$E_{cell} = E_{Cu^{+2}/Cu} - E_{Zn^{+2}/Zn}$$

b.) For a reaction $Cu(s) + 2Ag^+(aq.) \longrightarrow Cu^{+2}(aq.) + 2Ag(s)$

→ Half Cell reactions : Cathode (reduction) : $2Ag^+_{(aq.)} + 2e^- \longrightarrow 2Ag(s)$

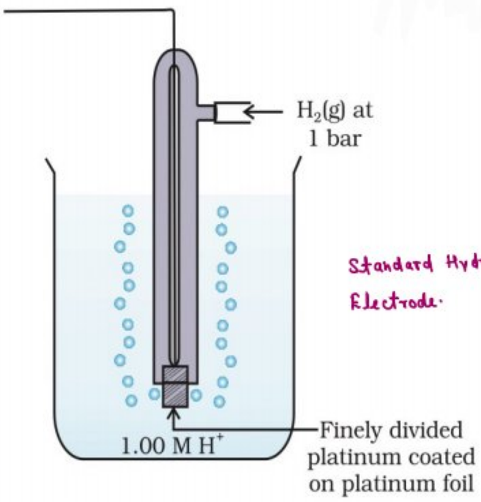
Anode (oxidation) : $Cu(s) \longrightarrow Cu^{+2}(aq.) + 2e^-$

→ Cell representation : $Cu(s) \mid Cu^{+2}(aq.) \parallel Ag^+(aq.) \mid Ag(s)$

$$E_{cell} = E_{right} - E_{left}$$

$$= E_{Ag^+/Ag} - E_{Cu^{+2}/Cu}$$

Standard Hydrogen Electrode :-



Standard Hydrogen Electrode.

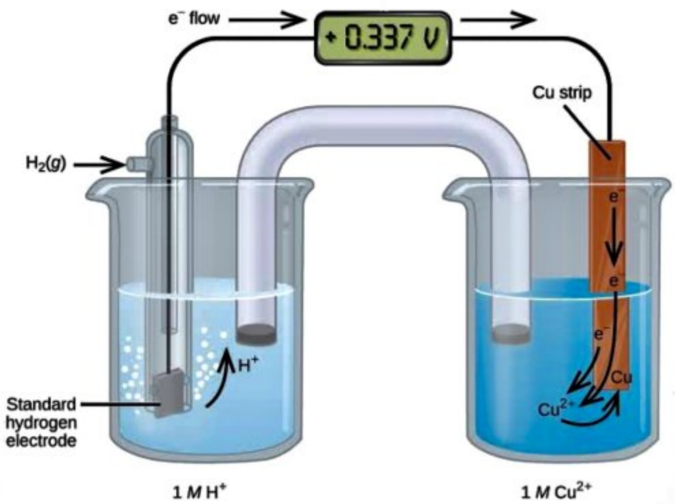
→ Representation of half cell for standard hydrogen electrode : $Pt(s) \mid H_{2(g)}(1\ bar) \mid H^+_{(aq.)}$

→ According to convention, a half cell called standard hydrogen electrode is assigned a zero potential at all temperatures corresponding to the reaction

$$H^+(aq.) + e^- \longrightarrow \frac{1}{2} H_2(g)$$

→ Measurement of electrode potential :-

→ Construct a cell by taking standard hydrogen electrode as anode (reference half cell) and other half cell as cathode, gives the reduction potential of other half cell.



Standard Hydrogen Electrode $[Pt(s) \mid H_2(g)(1\ bar) \mid H^+_{(aq.)}(1M)] \parallel$ other half cell.

→ If the concentrations of the oxidised and the reduced forms of species in the right hand half cell are unity. Then the cell potential is equal to standard electrode potential (E°_R) of the given half cell. $E^\circ = E^\circ_R - E_L = E^\circ_R - 0 = E^\circ_R$

→ (i) To calculate $E^\circ_{Cu^{+2}/Cu}$, make a cell $Pt(s) \mid H_2(g)\ (1\ bar) \mid H^+(aq.)\ 1M \parallel Cu^{+2}(aq.)\ 1M \mid Cu$

→ EMF of this cell = 0.34V

$$E^\circ_{cell} = E^\circ_{Cu^{+2}/Cu} - E^\circ_{HSE}$$

$$0.34V = E^\circ_{Cu^{+2}/Cu} - 0 \quad \text{then} \quad \boxed{E^\circ_{Cu^{+2}/Cu} = 0.34V}$$

Similarly; (ii) $E^\circ_{Zn^{+2}/Zn}$ can be calculated by following cell.

$$Pt(s) \mid H_2(g)\ (1\ bar) \mid H^+(aq.)\ 1M \parallel Zn^{+2}_{(aq.)}(1M) \mid Zn$$

→ $E^\circ_{cell} = -0.76V$ $\quad E^\circ_{cell} = E^\circ_{Zn^{+2}/Zn} - E^\circ_{SHE} = E^\circ_{Zn^{+2}/Zn} - 0$

$$\text{then} \quad \boxed{E^\circ_{Zn^{+2}/Zn} = -0.76\ V}$$

→ In first case, ⊕ve value of SEP indicates that Cu^{+2} get reduced more easily than H^+, means we can say that H_2 gas can reduce Cu^{+2} ion.

→ In second case, ⊖ve value of SEP indicates that Zn get oxidised by H^+ ion.

EMF of Daniell Cell :- cell : $Zn(s) \mid Zn^{+2}(aq)(1M) \parallel Cu^{+2}_{(aq.)}(1M) \mid Cu(s)$

$$E^\circ_{cell} = E^\circ_{Cu^{+2}/Cu} - E^\circ_{Zn^{+2}/Zn} = 0.34\ V - (-0.76V) = 1.10\ V$$

Inert Electrode -: Metals like platinum or gold are used as inert electrode. They do not participate in the reaction but provide their surface for oxidation or reduction reactions and for conduction of electrons.

For example -: Hydrogen Electrode : $Pt(s) \mid H_{2(g)} \mid H^+(aq.)$

Bromine Electrode : $Pt(s) \mid Br_2(aq.) \mid Br^-_{(aq.)}$

Nernst Equation :- It gives relation between electrode potential, temperature and concentration of metal ions.

For reaction $\quad M^{n+}_{(aq.)} + ne^- \longrightarrow M_{(s)} \quad$ $n \rightarrow$ No. of electrons

$$\rightarrow E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

$$\rightarrow \boxed{E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{0.059}{n} \log \frac{1}{[M^{n+}]}}$$

R = Gas constant = $8.314\ J\ K^{-1}\ mol^{-1}$
F = Faraday's constant = $96\,487\ C\ mol^{-1}$
T = 298 K and [M] = 1 = [Solid]

→ In Daniell Cell : Electrode Potential for any given concentration of Cu^{+2}/Zn^{+2}:

For Cathode : $E_{Cu^{+2}|Cu} = E^{\circ}_{Cu^{+2}|Cu} - \frac{0.059}{2} \log \frac{1}{[Cu^{+2}_{(aq.)}]}$

For Anode : $E_{Zn^{+2}|Zn} = E^{\circ}_{Zn^{+2}/Zn} - \frac{0.059}{2} \log \frac{1}{[Zn^{+2}_{(aq.)}]}$

Cell Potential $E_{cell} = E_{Cu^{+2}|Cu} - E_{Zn^{+2}/Zn}$

$$= \left[E^{\circ}_{Cu^{+2}/Cu} - E^{\circ}_{Zn^{+2}/Zn}\right] - \frac{0.059}{2} \log \frac{[Zn^{+2}_{(aq.)}]}{[Cu^{+2}_{(aq.)}]}$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.059}{2} \log \frac{[Zn^{+2}_{(aq.)}]}{[Cu^{+2}_{(aq.)}]} \quad — [\#]$$

Question :- For the cell $Zn(s) \mid Zn^{+2}(2M) \parallel Cu^{+2}(0.5M) \mid Cu(s)$ (3M) [Delhi 2011C]

(i) Write the equation for each half cell.

(ii) Calculate cell potential at 25°C.

Given: $E^{\circ}_{Zn^{+2}/Zn} = -0.76V$

$E^{\circ}_{Cu^{+2}/Cu} = +0.34V$

Answer -: (i) Anode ! $Zn(s) \longrightarrow \underset{[2M]}{Zn^{+2}_{(aq.)}} + 2e^-$

Cathode ! $\underset{(0.5M)}{Cu^{+2}_{(aq.)}} \xrightarrow{+2e^-} Cu(s)$

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(ii) $E^{\circ}_{cell} = E^{\circ}_{Cu^{+2}|Cu} - E^{\circ}_{Zn^{+2}/Zn} = 0.34V - (-0.76V) = 1.10V$

$E_{cell} = E^{\circ}_{cell} - \frac{0.059}{2} \log \frac{[Zn^{+2}]}{[Cu^{+2}]} \Rightarrow 1.10V - \frac{0.059}{2} \log \frac{2}{0.5}$

$E_{cell} = 1.10V - \frac{0.059}{2} \times 0.602V = 1.10V - 0.0178V = 1.0822V$

Question :- A Zn rod is dipped in 0.1M solution of $ZnSO_4$. The salt is 95% dissociated at its dilution at 298K. Calculate the electrode potential. [Delhi 2012C] (2M)

$E^{\circ}_{Zn^{+2}/Zn} = -0.76V$

Answer :- Reaction $Zn^{+2} + 2e^- \longrightarrow Zn$ $\quad n=2$

By using nernst equation, we get $E_{Zn^{+2}|Zn} = E^{\circ}_{Zn^{+2}|Zn} - \frac{0.059}{2} \log \frac{1}{[Zn^{+2}]}$

→ $[Zn^{+2}] = \frac{95}{100} \times 0.1 = 0.095M$; $E_{Zn^{+2}/Zn} = -0.76V - \frac{0.059}{2} \log \frac{1}{0.095} = -0.7901V$

Question :- Calculate the emf of the following cell at 298 K.

$$2Cr(s) + 3Fe^{+2}(0.1M) \longrightarrow 2Cr^{+3}(0.01M) + 3Fe(s)$$

(3M)

[Delhi 2016]

Given : $E^\circ_{Cr^{+3}/Cr} = -0.74V$ $E^\circ_{Fe^{+2}/Fe} = -0.44V$

Answer :- Half cell reactions ÷ At anode : $[Cr \longrightarrow Cr^{3+} + 3e^-] \times 2$

At cathode : $[Fe^{+2} + 2e^- \longrightarrow Fe] \times 3$

$\rightarrow E^\circ_{cell} = E^\circ_{Fe^{+2}/Fe} - E^\circ_{Cr^{+3}/Cr}$ then $\boxed{n=6}$

$= -0.44V - (-0.74V)$

$= 0.3V$

$$\rightarrow E = E^\circ - \frac{0.059}{n} \log \frac{[Cr^{+3}]^2}{[Fe^{+2}]^3}$$

$$E_{cell} = 0.3V - \frac{0.059}{6} \log \frac{(0.01)^2}{(0.1)^3}$$

$$\boxed{E_{cell} = 0.31V}$$

Question :- Calculate the emf of the following cell at 25°C

(3M)

$$Ag(s) \mid Ag^+(10^{-3}M) \parallel Cu^{2+}(10^{-1}M) \mid Cu(s)$$

[CBSE 2013]

Given → $E^\circ_{cell} = +0.46V$ and $\log 10^n = n$

(i) $[Ag(s) \longrightarrow Ag^+_{(aq.)} + e^-] \times 2$

(ii) $Cu^{+2}_{(aq.)} + 2e^- \longrightarrow Cu(s)$

$2Ag_{(s)} + Cu^{+2} \longrightarrow Cu + 2Ag^+$

$\boxed{n=2}$

Answer -: $$E_{cell} = E^\circ_{cell} - \frac{0.059}{2} \log \frac{[Ag^+]^2}{[Cu^{+2}]}$$

$$E_{cell} = 0.46V - \frac{0.059}{2} \log \frac{(10^{-3})^2}{(10^{-1})}$$

$$E_{cell} = 0.608V$$

Question -: Calculate the emf of the following cell at 298K (25°C)

(3M)

$$Fe(s) \mid Fe^{2+}(0.001M) \parallel H^+(0.01M) \mid H_2(g)(1bar) \mid Pt(s)$$

[Delhi 2013|2015]

Given → $E^\circ_{cell} = 0.44V$ (or $E^\circ_{Fe^{+2}/Fe} = -0.44V$ and $E^\circ_{H^+/H_2} = 0V$)

① $Fe(s) \longrightarrow Fe^{+2}_{(aq.)} + 2e^-$

② $[H^+_{(aq.)} + e^- \longrightarrow \frac{1}{2}H_2(g)] \times 2$

$Fe(s) + 2H^+_{(aq.)} \longrightarrow Fe^{+2}_{(aq.)} + H_2$

$\boxed{n=2}$

Answer :- $E^\circ_{cell} = E^\circ_{H^+/H_2} - E^\circ_{Fe^{+2}/Fe} = 0.44V$

$$E_{cell} = E^\circ - \frac{0.059}{2} \log \frac{[Fe^{+2}]}{[H^+]^2} = 0.44V - \frac{0.059}{2} \log \frac{(10^{-3})}{(10^{-2})^2}$$

$$E_{cell} = 0.44 - \frac{0.059}{2} = 0.4104V.$$