Electrolysis-

- *The substances whose aqueous solution undergo decomposition into ions when electric current is passed through them are known as **electrolytes** and the whole process is known as **electrolysis** or **electrolytic decomposition**."*

- Solutions of acids, bases, salts in water and fused salts etc. are the examples of electrolytes. Electrolytes may be **weak** or **strong**. Solutions of cane sugar, glycerine, alcohol etc., are examples of ***non-electrolytes***

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- Voltameter convert ***electrical energy into chemical energy***.
- **Electrolytic cell or Voltameter :** The device in which the process of electrolysis or electrolytic decomposition is carried out is known as ***electrolytic cell*** or ***voltameter.***

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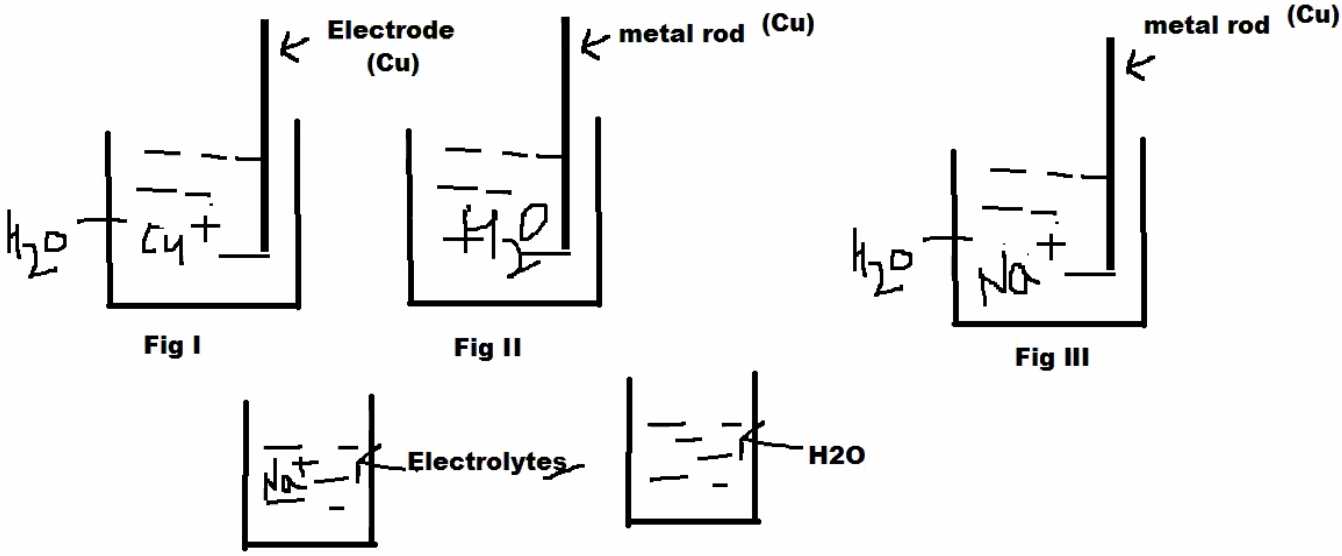

Fig I Fig II Fig III

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- ***Electrode-***
- The electrode on which oxidation takes place is called ***anode*** (or +ve pole) and the electrode on which reduction takes place is called ***cathode*** (or –ve pole).

- During electrolysis in voltameter ***cations are discharged on cathode*** *and* ***anions on anode***.
- In voltameter, outside the ***electrolyte*** electrons flow from ***anode to cathode*** and ***current*** flow from ***cathode to anode***.

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Points about anode and cathode

positive charge + negative charge -

This particular electrode is known as anode :

- On anode oxidation will take place. (release of electron).
- To act as source of electrons.
- It is of negative polarity.

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This will be known as cathode.

- At cathode reduction will take place.(gain of e^- will take place)
- To act as sink of electron.
- Positive polarity will be developed.

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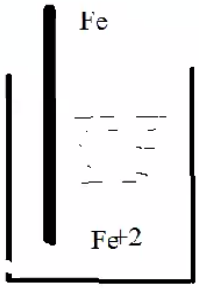

$Fe \Rightarrow Fe^{+2} + 2e$

$Fe^{+2} + 2e \Rightarrow Fe$

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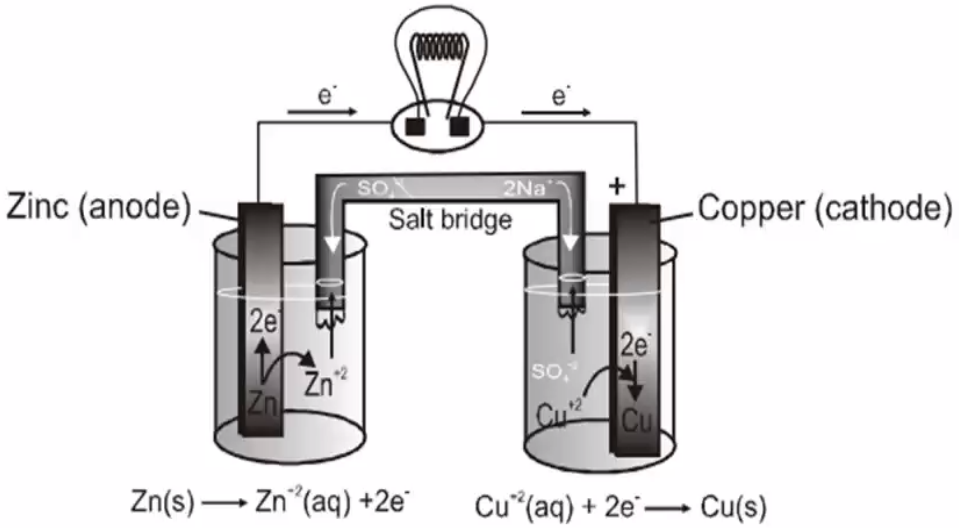
Construction of cell



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- It has two **half–cells**,each having a beaker containing a metal strip that dips in its aqueous solution.
- The metal strips are called **electrodes** and are connected by an conducting wire.
- Two solutions are connected by a **salt bridge.**
- The oxidation and reduction half reactions occur at a separate electrodes and electric current flows through the wire.

Selection of salt bridge

The electrolyte in salt bridge should be such that speed of it's cation equals speed of it's anion in electrical field.

For that charge and sign of the ions should be almost equal.

Transport number of cation = Transport number of anion

or

Mobility of cation = Mobility of anion

KCl is generally preffered but KNO_3 or NH_4NO_3 can also be used.

Function of salt bridge

A **salt bridge** is a U–shaped inverted tube that contains a gel permeated with an inert electrolyte.

It connects the solution of two half cell to complete the circuit.

It minimise the liquid junction potential. The potential difference between the junction of two liquids.

It maintains the electhical neutrality of the solution in order to give continious flow or generation of current.

" The simultaneous electrical neutrality of the anodic oxidation chamber and cathodic reduction chamber is due to same mobility or velocity of K^+ and NO_3^- ions taken into salt bridge.

If the salt bridge is removed then voltage drops to zero.

The ions of the inert electrolyte do not react with other ion in the solution and the ions are not oxidised or reduced at the electrodes.

Generally tube is filled with a paste of agar-agar powder with a natural electrolyte/generally not common to anodic/cathodic compartment with porous plugs at each mouth of tube.

It prevents mechanical mixing of two electrolytic solution.

Electrode potential

The potential difference devepoled between metal electrode and its ions in solution in known as electrode potential.

Electrode potential depends upon :

- Concentration of the solution.
- Nature of the metal.
- Nature of the electrolyte.
- Pressure temperature coditions.

The potential difference developed between metal electrodes and the solution of its ions at 1 M concentration at 1 bar pressure and 298 K is known as standard electrode potential.

Standard electrode potential

- **Standard Electrode Potential**

Oxidation Potential (O.P.) :

- The electrode potential for oxidation half reaction
- Tendency to get oxidised.
- **Greater the O.P. than greater will be tendency to get oxidised.**

Reduction Potential (R.P.)

- The electrode potential for reduction half reaction
- Tendency to get reduced.
- **Greater the R.P. greater will be tendency to get reduced.**

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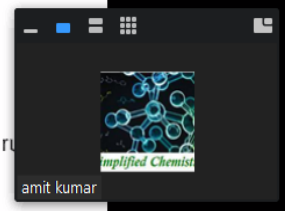
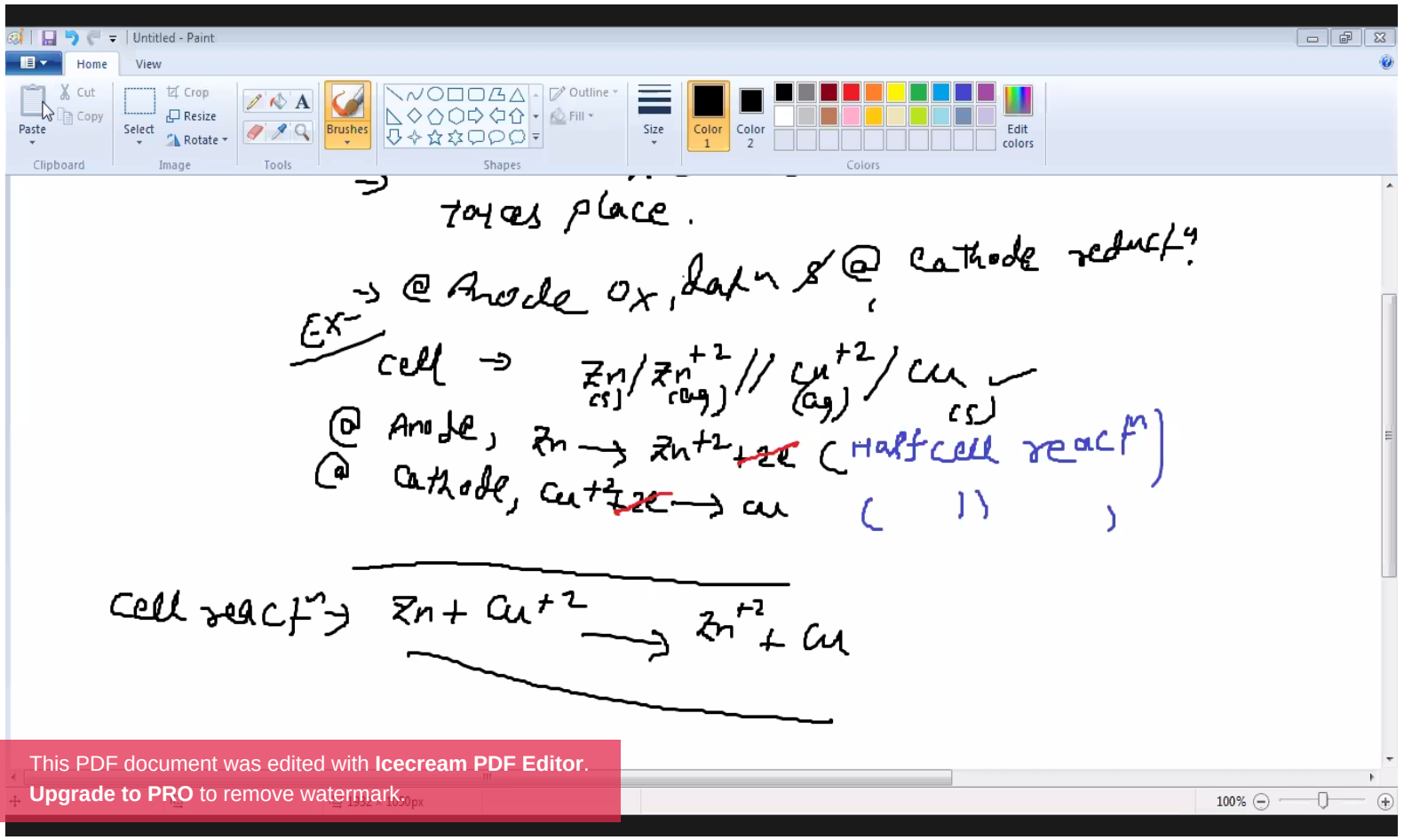


Shorthand Notation for Galvanic Cells

- We require two half cells to produce an electrochemical cell, which can be represented by follwing few r
  - The anode half-cell is always written on the left followed on the right by cathode half cell.
  - The separation of two phases (state of matter) is shown by a vertical line.
  - The various materials present in the same phase are shown together using commas.
  - The salt bridge is represented by a double slash (||).
  - The significant features of the substance viz. pressure of a gas, concentration of ions etc. are indicated in brackets immediately after writing the substance.
  - For a gas electrode, the gas is indicated after the electrode for anode and before the electrode in case of cathode. (i.e Pt H_2 / H^+ or H^+ /H_2 Pt)



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In the galvanic cell Cu | Cu^{2+} || Ag^{+} | Ag, the electrons flow from Cu-electrode to Ag-electrode. Answer the following questions regarding this cell :

(a) Which is the anode ?
(b) Which is the cathode ?
(c) What happens at anode-reduction or oxidation ?
(d) What happens at cathode-oxidation or reduction ?
(e) Which electrode loses mass ?
(f) Which electrode gains mass ?
(g) Write the electrode reactions.
(h) Write the cell reaction
(i) Which metal has greater tendency to loss electron-Cu or Ag ?
(j) Which is the more reactive metal-Cu or Ag ?
(k) What is the function of salt bridge represented by the symbol || ?

Question

Write short hand notation for the following reaction, $Sn^{2+}(aq) + 2Ag^{+}(aq) \rightarrow Sn^{4+}(aq) + 2Ag(s)$. The cell consists of a platinum wire anode dipping into an Sn^{+2} solution and a silver cathode dipping into an Ag^{+} solution therefore Pt(s) | $Sn^{2+}(aq)$, $Sn^{4+}(aq)$ || $Ag^{+}(aq)$ | Ag(s).

Write the electrode reaction and the net cell reaction for the following cells. Which electrode would be the positive terminal in each cell ?

(a) Zn | Zn^{2+} || Br^{-}, Br_2 | Pt
(b) Cr| Cr^{3+} || I^{-} , I_2 | Pt
(c) Pt | H_2, H^{+} || Cu^{2+} | Cu
(d) Cd | Cd^{2+} || Cl^{-} , AgCl | Ag

(a) Oxidation half cell reaction, $Zn \longrightarrow Zn^{2+} + 2e^{-}$

reduction half cell reaction, $Br_2 + 2e^{-} \longrightarrow 2Br^{-}$

Net cell reaction $Zn + Br_2 \longrightarrow Zn^{2+} + 2Br^{-}$ (Positive terminal : cathode Pt)

(b) Oxidation half reaction, $[Cr \longrightarrow Cr^{3+} + 3e^{-}] \times 2$

reduction half reaction, $[I_2 + 2e^{-} \longrightarrow 2I^{-}] \times 3$

Net cell reaction $2Cr + 3I_2 \longrightarrow 2Cr^{3+} + 6I^{-}$ (Positive terminal : cathode Pt)

(c) Oxidation half reaction, $H_2 \longrightarrow 2H^{+} + 2e^{-}$

reduction half reaction, $Cu^{2+} + 2e^{-} \longrightarrow Cu$

Net cell reaction $H_2 + Cu^{2+} \longrightarrow Cu + 2H^{+}$ (Positive terminal : cathode Cu)

(d) Oxidation half reaction, $Cd \longrightarrow Cd^{2+} + 2e^{-}$

[illegible] $AgCl + e^{-} \longrightarrow Ag + Cl^{-}] \times 2$

[illegible] $Cd + 2AgCl \longrightarrow Cd^{2+} + 2Ag + 2Cl^{-}$ (Positive terminal : cathode Ag)