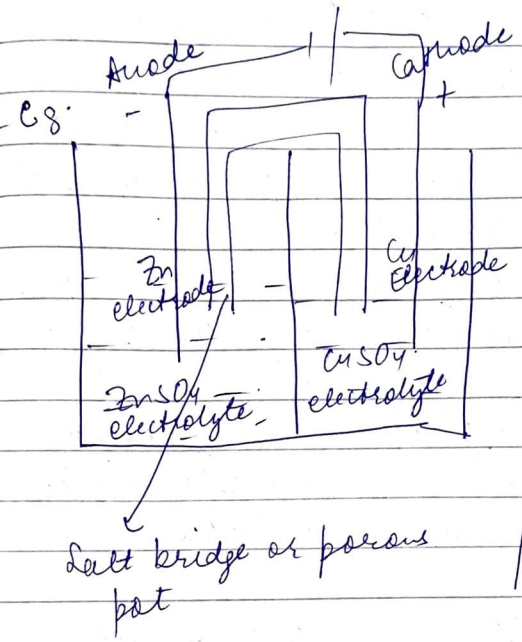
ELECTROCHEMISTRY

Two types of cell:

Electrochemical Cell
(Galvanic or Voltaic cell)

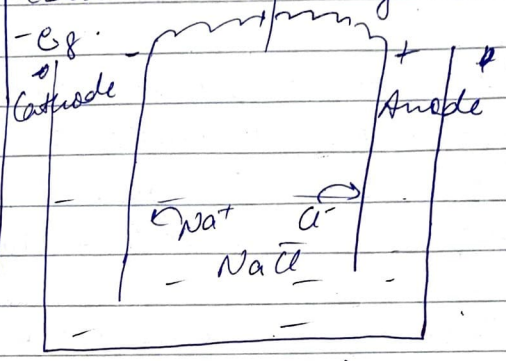
Converts chemical to electrical Energy.

- Based upon spontaneous redox reaction.



Electrolytic Cell

- Converts electrical to chemical energy.
- Based on non-spontaneous redox reactions which can be made spontaneous by electricity.
(Based on Electrolysis)



2 electrodes are in same electrolyte.

Two electrodes can be in same or different electrolytes in Electrochemical Cell

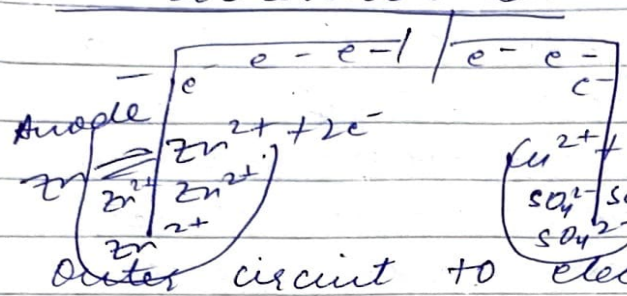
Electrode: either take part in redox reactions (when made of active metal) or provide surface for redox reaction (when made of inactive or inert metal).

Cathode & Anode terms were given from electrolytic cell.

Cathode → Electrode which attracts cation

Or on which reduction takes place. It is electron sink.
Anode – Electrode which attracts anion & on which oxidation takes place.

Electrochemical Cell:

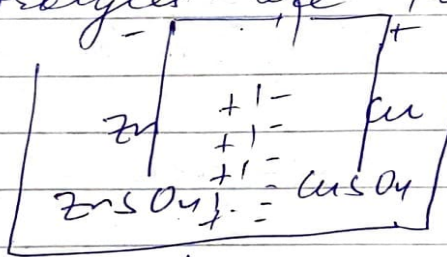


Oxidation of Zn takes place on anode. The electrons released goes through outer circuit to electron sink or cathode, where electrons are accepted by Cu^{2+} (to undergo reduction) & Cu is deposited on Cu electrode.

(1) This leads to positive charge ion solution & negative charge on electrode on Zn side.
(2) On Cu side, Cu^{2+} goes to Cu electrode, so positive charge on electrode & negative charge in solution

Oxidation & reduction reactions are called half cell reactions. A set of electrode & electrolyte undergoing oxidation or reduction is called half cell.

Because of (1) & (2), charge difference is created at both Cu & Zn side which stops further reaction. To avoid this creation of ~~to complete the cell~~ charge separation, if both electrolytes are taken together, this would

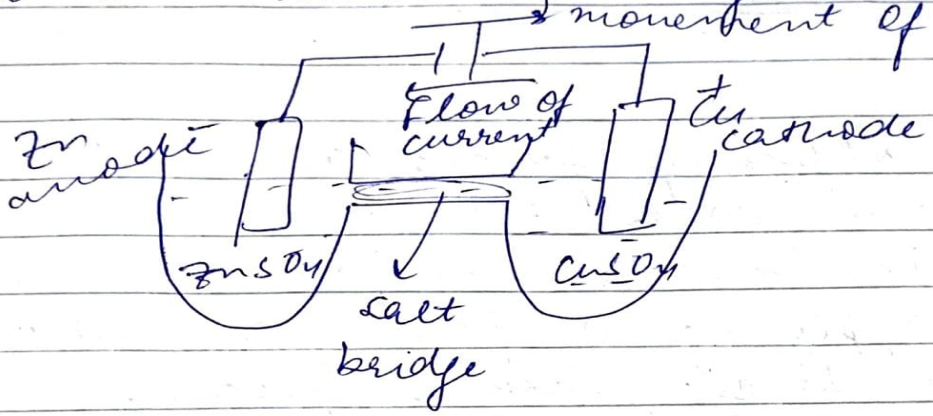


lead to charge separation in the solution called liquid Junction Potential. This would again hinder further reaction.

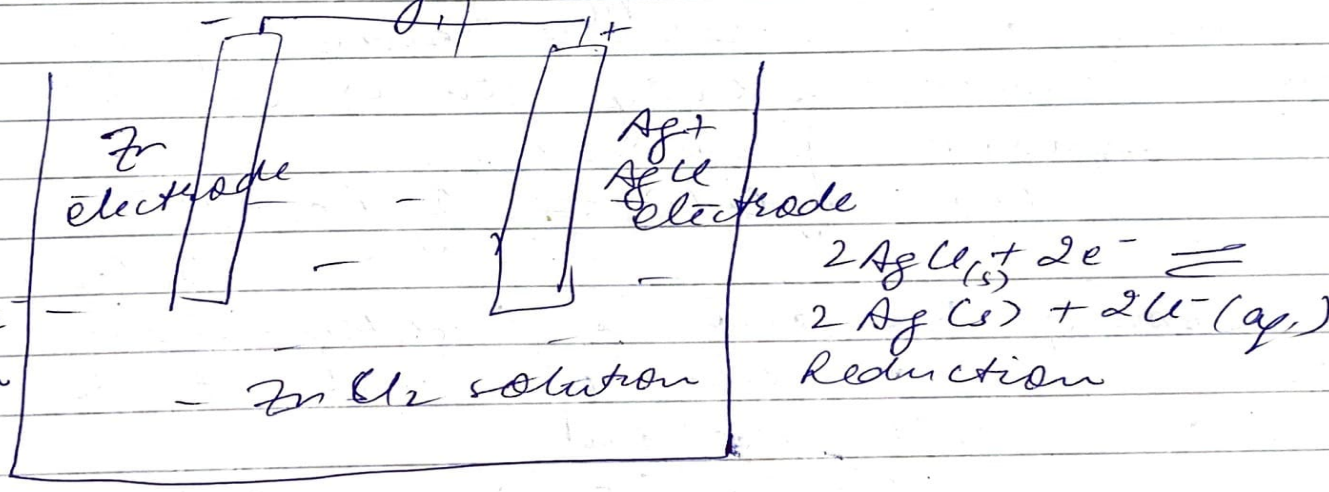
To avoid formation of liquid junction potential & creation of charge difference at respective sides, also to maintain electroneutrality & complete the cell, salt bridge is used.

e.g. of salt bridge : KCl / K_2SO_4 / NH_4NO_3 in agar-agar gel (semi-solid).

Ions of salt bridge have similar speed or transference number as that of ions of cell so as to avoid liquid junction potential..



An example of electrochemical cell with common electrolyte :



This cell does not require a salt bridge as intimate contact between 2 electrodes is difficult to made. Reaction takes place slowly.

Electrolytic cell:

Cathode: $Na^+_{(aq.)} + e^- \rightleftharpoons Na(s)$ (Reduction)

Here cathode is still an electron sink as charge is fed from external circuit

Anode: $2Cl^-_{(aq.)} \rightleftharpoons \frac{1}{2}Cl_2(g) + 2e^-$ (Oxidation)

The focus in this unit shall be electrochemical cell only.

Reversible & Irreversible Cells:

Reversible Cells:

1.) The driving & opposing forces are infinitesimally different from each other.

2.) It should be possible to reverse any change taking place by applying a force infinitesimally greater than acting force (driving force).

Reversible cells satisfy above two conditions thermodynamic relations only apply when cell is reversible & only then we can calculate thermodynamic properties.

e.g: $\frac{1}{2}Zn(s) + AgCl(s) \rightleftharpoons Ag(s) + \frac{1}{2}Zn^{2+}(aq.) + Cl^-(aq.)$

If opposing potential is slightly larger than that of cell, direction of current flow is reversed & so is cell reaction:

$Ag(s) + \frac{1}{2}Zn^{2+}(aq.) + Cl^-(aq.) \rightleftharpoons \frac{1}{2}Zn(s) + AgCl(s)$

Irreversible Cells:

e.g. Zn & Ag electrodes immersed in H_2SO_4. They do not satisfy the above two conditions.