

**Galvanic cells (Voltaic or electrochemical cells)** : It is a device which makes use of spontaneous redox reaction for the generation of electrical energy.

- Opposite to electrolytic cells.
- In these cells electricity is generated due to spontaneous redox reaction.

**Salt bridge** : A 'U' shaped glass jar with Agar agar gelly which contains KCl or  $\text{KNO}_3$  or  $\text{NH}_4\text{NO}_3$  is called salt bridge.

- The purpose of using the above substance in salt bridge is due to free mobility of ions.
- Electrolyte is taken in salt bridge in higher concentration.
- Electrolyte supplies cations and anions.

**If salt bridge is not used :**

- i) Accumulation of charges will occur, +ve charge at anode and -ve charge at cathode .
- ii) If two solutions come in contact some potential develops at junction of two liquids called "Liquid Junction Potential".
- iii) Electrochemical change stops and every thing comes to stand still.
- iv) Voltage drops to zero.

**If salt bridge is used :**

- i) It prevents accumulation of charges.
- ii) It avoids formation of liquid junction potential.
- iii) It prevents mixing of two solutions but permits the flow of ions.
- iv) It supplies the ions.
- Generally Galvanic cell contains Zn rod in  $\text{ZnSO}_4$  solution which acts as anode and Cu rod in  $\text{CuSO}_4$  solution which acts as cathode.
- To produce more current concentration of  $\text{CuSO}_4$  should be more.
- As zinc dissolves and Cu deposits thick zinc electrode and thin Cu electrode are to be taken.
- The commercial form of Galvanic cell is Daniel cell.

**Reversible cells:** When Galvanic cells are connected to external source of EMF.

- i) If cell emf is  $>$  ext. emf then  $E_{\text{cell}}^0 \rightarrow +\text{ve}$  and cell produces current and spontaneous reaction occurs.  

$$\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$$
- ii) If cell emf is  $<$  ext. emf then  $E_{\text{cell}}^0 \rightarrow -\text{ve}$  and non spontaneous reaction occurs.  

$$\text{Cu} + \text{Zn}^{2+} \rightarrow \text{Cu}^{2+} + \text{Zn}$$
- iii) If cell emf = ext. emf then no current flows in any direction.
- Galvanic cells satisfying the above conditions are called as reversible cells. Daniel cell is a reversible cell.

| Electrolytic cell                             | Electrochemical / Galvanic cell                 |
|---|---|
| 1) It requires EMF.                           | 1) It produces EMF.                             |
| 2) Electric energy is converted into chemical | 2) Chemical energy is converted into electrical |

| energy   | energy.  |
|--|--|
| 3) Anode is +ve and cathode '-ve                                     | 3) Anode is -ve cathode is '+ve  |
| 4) Oxidation takes place at anode and reduction at cathode           | 4) Oxidation takes place at anode and reduction at cathode.  |
| 5) Electrodes are just metal rods graphite electrode can be used     | 5) Atoms in contact with ion (graphite electrodes can be used) (Pt, O <sub>2</sub> , OH <sup>-</sup> ) |
| 6) Discharge of ion occur at both electrodes.                        | 6) Discharge of ions occur only at cathode.  |
| 7) Non – spontaneous reaction occurs.                                | 7) Spontaneous reaction occurs.  |
| 8) These are irreversible.   | 8) These may be reversible.  |
| 9) Flow of electrons is from anode to cathode.                       | 9) Flow of electrons is from anode to cathode.   |
| 10) Electrons leave the cell at anode and enter the cell at cathode. | 10) Electrons leave the cell at anode and enter the cell at cathode.                                   |

### Cell Notation :

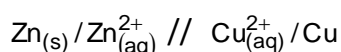
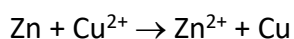
- The symbolic and short hand form of representation of Galvanic cells is called cell notation.

*Anode* *cathode*

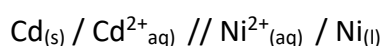
Solid phase / aq.phase // aq.phase / solid phase  
(or)

Solid ; aq.phas / aq. phase; solid

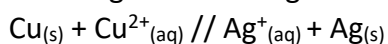
1) Daniel cell :



2)  $\text{Ni}^{2+} + \text{Cd} \rightarrow \text{Ni} + \text{Cd}^{2+}$



3)  $\text{Cu} + 2\text{Ag}^+ \rightarrow \text{Cu}^{2+} + 2\text{Ag}$



4)  $\text{Fe} + \text{Cu}^{2+} \rightarrow \text{Fe}^{2+} + \text{Cu}$



5)  $2\text{Al} + 3\text{Sn}^{2+} \rightarrow 2\text{Al}^{3+} + 3\text{Sn}$

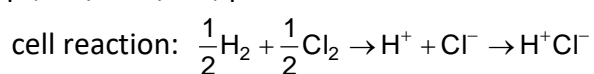


6)  $\text{Mg} + \text{Cl}_2 \rightarrow \text{Mg}^{2+} + 2\text{Cl}^-$



If same electrolyte is used in both the half cells that is kept in between (2) two single vertical lines.

i) pt, H<sub>2</sub> / HCl / Cl<sub>2</sub>, pt



### Nernst equation :

- The electrode potentials or the cell emf depends on
  - 1) concentration of electrolyte.
  - 2) Temperature
  - 3) Number of electrons involved in electrodes reaction.
  - 4) Pressure (only for gaseous electrodes)
  - 5) Nature of electrodes.

Nernst equation will explain how the potential of single electrodes and cell will change with  
1) conc. of electrolyte 2) number of electrons.

- The temperature and pressure (25°C, 1atm) are taken as constant for all the calculations.

### For single electrodes.

$$E = E^0 - \frac{2.303 RT}{nF} \log \frac{[\text{products}]}{[\text{reactants}]}$$

$E \rightarrow$  reduction potential of single electrode;  $E^0 \rightarrow$  standard reduction potential

$R \rightarrow 8.314 \text{ J}$  ;  $T \rightarrow 25^\circ\text{C}$

$n \rightarrow$  number of electrons involved ;  $F \rightarrow 96500 \text{ C}$

$$2.303RT / F = 0.059.$$

$$E = E^0 - 0.059 \log \left[ \frac{\text{productst}}{\text{reac tan ts}} \right]$$

$$E = E^0 - 0.059 \log \left[ \frac{\text{reduced formed}}{\text{oxidised formed}} \right]$$

$$E = E^0 - 0.059 \log \left[ \frac{M^{n-}}{1} \right]$$

for all metal electrodes and hydrogen electrodes

$$E = E^0 - 0.059 \log \left[ \frac{1}{M^{n+}} \right]$$

for all non metal electrodes

to calculate cell emf at given concentration of electrolyte.

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{2.303 RT}{nF} \log \left[ \frac{\text{products}}{\text{reac tan ts}} \right]$$

$E \rightarrow$  Emf of cell ;  $E^0 \rightarrow$  Standard emf of the cell

$R \rightarrow 8.314 \text{ J}$  ;  $T \rightarrow 25^\circ\text{C}$

$n \rightarrow$  number of electrons ;  $F \rightarrow 96500 \text{ C}$

### Nernst equation application to various electrodes and various Galvanic cells.

1) Zinc electrode :  $E = E^0 - \frac{0.059}{2} \log \left[ \frac{1}{\text{Zn}^{2+}} \right]$

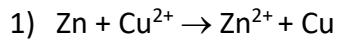
2) Copper electrode:  $E = E^0 - \frac{0.059}{2} \log \left[ \frac{1}{\text{Cu}^{2+}} \right]$

3) Hydrogen electrode :  $E = E^0 - \frac{0.059}{1} \log \left[ \frac{1}{\text{H}^+} \right]$

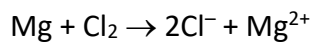
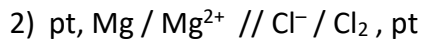
$$E = E^0 - \frac{0.059}{1} \text{pH} \Rightarrow E^0 - E = \frac{0.059}{1} \text{pH}$$

$$\text{pH} = \frac{E^0 - E}{0.059} \Rightarrow E^0 \rightarrow \text{'O' V for H}_2.$$

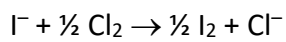
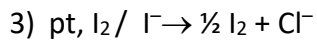
**Daniel cell:**



$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.059}{2} \log \left[ \frac{\text{Zn}^{2+}}{\text{Cu}^{2+}} \right]$$



$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.059}{2} \log \frac{[\text{Mg}^{2+}] [\text{Cl}^-]^2}{1}$$



$$E_{\text{cell}} = E^0 - \frac{0.059}{1} \log \left[ \frac{\text{Cl}^-}{\text{I}^-} \right]$$

