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 KNO_3 or NH_4NO_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 this 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 $ZnSO_4$ solution which acts as anode and Cu rod in $CuSO_4$ solution which acts as cathode.
- To produce more current concentration of $CuSO_4$ 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 $E^0_{cell} \rightarrow +ve$ and cell produces current and spontaneous reaction occurs.

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

ii) If cell emf is < ext. emf then $E^0_{cell} \rightarrow -ve$ and non spontaneous reaction occurs.

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

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_2, OH^-)
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 :

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

$Zn_{(s)} / Zn^{2+}_{(aq)} \; // \; Cu^{2+}_{(aq)} / Cu$

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

$Cd_{(s)} / Cd^{2+}{}_{aq)} \; // \; Ni^{2+}{}_{(aq)} / Ni_{(l)}$

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

$Cu_{(s)} + Cu^{2+}{}_{(aq)} \; // \; Ag^{+}{}_{(aq)} + Ag_{(s)}$

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

$Fe / Fe^{2+} \; // \; Cu^{2+} / Cu$

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

$Al / Al^{3+} \; // \; Sn^{2+} / Sn$

6) $Mg + Cl_2 \rightarrow 2Cl^{-} + Mg^{2+}$

$Mg_{(s)} / Mg^{2+}{}_{(aq)} \; // \; Cl^{-}{}_{(aq)} / Cl_{2(g)}$, pt

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

i) pt, H_2 / HCl / Cl_2, pt

cell reaction: $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightarrow H^{+} + Cl^{-} \rightarrow H^{+}Cl^{-}$

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.

$$E = E^0 - \frac{2.303\ RT}{nF}\log\frac{[products]}{[reac\tan ts]}$$

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

$R \rightarrow$ 8.314 J ; $T \rightarrow$ 25°C

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

2.303RT / F = 0.059.

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

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

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

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.

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

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

$R \rightarrow$ 8.314 J ; $T \rightarrow$ 25°C

$n \rightarrow$ number of electrons ; $F \rightarrow$ 96500 C

Nernst equation application to various electrodes and various Galvanic cells.

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

$$E = E^0 - \frac{0.059}{1} P^H \Rightarrow \quad E^0 - E = \frac{0.059}{1} P^H$$

$$P^H = \frac{E^0 - E}{0.059} \quad \Rightarrow \quad E^0 \rightarrow \text{'O' V for } H_2.$$

Daniel cell:

1) $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

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

2) pt, Mg / Mg^{2+} // Cl^- / Cl_2 , pt

$Mg + Cl_2 \rightarrow 2Cl^- + Mg^{2+}$

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

3) pt, $I_2 /\ I^- \rightarrow \frac{1}{2} I_2 + Cl^-$

$I^- + \frac{1}{2} Cl_2 \rightarrow \frac{1}{2} I_2 + Cl^-$

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