

Electrochemistry

- Electrochemistry is the branch of chemistry which deals with the relationship between electrical energy and chemical energy and interconversion of one form into another.
 - Conversion of electrical energy into chemical change involves electrolytic reaction (i.e. electrolysis). Redox reaction occurs non spontaneously.
 - Conversion of chemical energy into electrical energy involves Galvanic reaction. Redox reaction occurs spontaneously .

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Origin of electrode potential (Single electrode potential)

When a metal rod (M) is dipped into solution containing its own ions (M^{n+}) then following three possibilities can occur.

1. Metal ion may collide with metal rod and deflected back without any change

2. Metal ions , on collision with metal rod may gain electrons and changed into metal atoms i.e. M^{n+} ions are reduced.

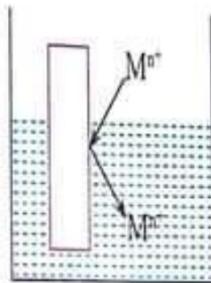
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$$M^{n+} + ne^- \rightarrow M \dots\dots (i)$$

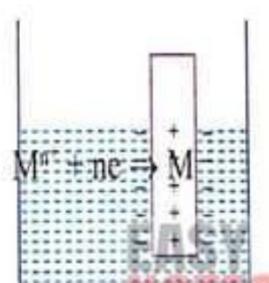
3. Metal atoms of metal rod may lose electrons and changed into M^{n+} ions i.e. metal atoms get oxidized.

$$M \rightarrow M^{n+} + ne^- \quad (ii)$$

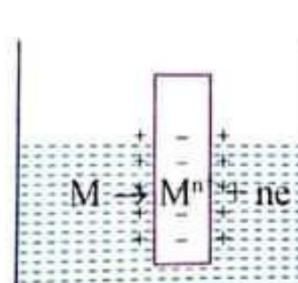
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Metal ions collide without any change



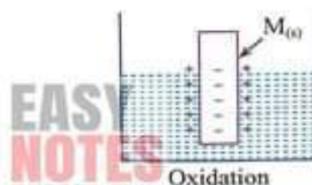
Metal ions gain electron
and converted into metal
(Reduction)



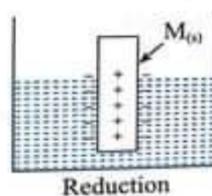
Metal atom lose electron and forms metal ions (Oxidation)

What actually happens depends upon the relative tendency of metal or its ions.

If metal has relatively greater tendency to get oxidized reaction (ii) will occur, the electrons will accumulate on metal rod, which will therefore develops a negative charge with respect to the solution. This in turn may attract some metal ions from solution which may change into metal atoms. After some time, equilibrium will establish as:



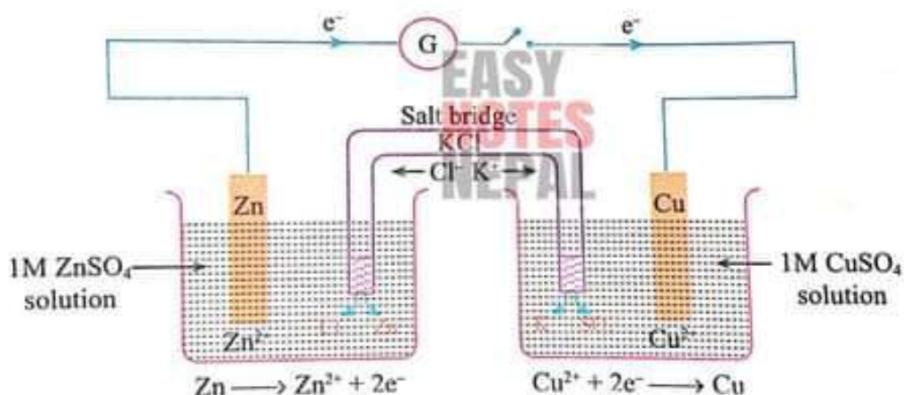
Similarly, if metal ions have greater tendency to get reduced, reaction (i) will occur. Metal ions will gain electrons from metal rod. As a result metal rod will develop positive charge with respect to solution and ultimately the equilibrium will establish as:



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Daniel cell (Zn- Cu cell)

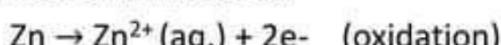
- The Daniel cell is an electrochemical cell named after John Frederic Daniel, the British chemist who invented it in 1836.



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- In the Daniel cell, copper electrode is immersed in 1M $CuSO_4$ solution in one container and zinc electrode is immersed in 1M $ZnSO_4$ Solution in another container. These two containers are connected by inverted U-tube containing a semi-solid paste of KCl , KNO_3 or NH_4Cl in gelatin or agar-agar called salt bridge.

Anodic half reaction



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

Cathodic half reaction



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

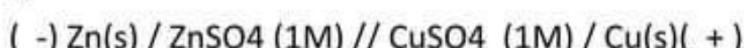
The overall cell reaction



Cell notation



or



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Emf of the cell is calculated as

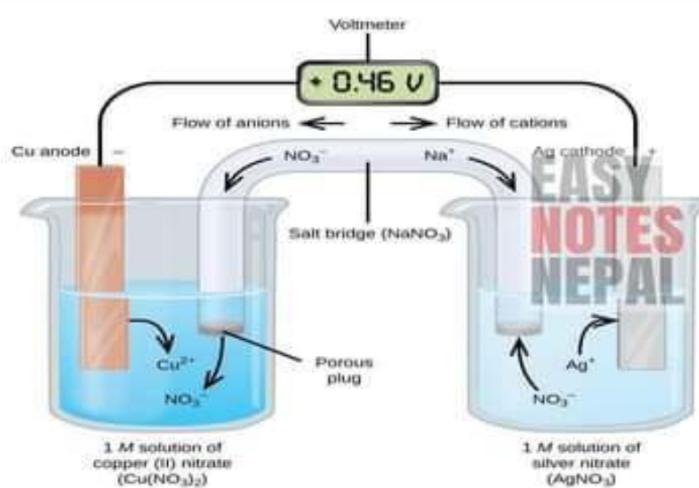
$$E^\circ \text{ Zn}^{++}/\text{Zn} = -0.76 \text{ V} \quad E^\circ \text{ Cu}^{++}/\text{Cu} = +0.34 \text{ V}$$

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{(\text{Red})\text{cathode}} - E^\circ_{(\text{Red})\text{anode}} \\ &= 0.34 - (-0.76) \\ &= 1.1 \text{ V} \end{aligned}$$

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Ag – Cu Cell



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2. To Determine anode and cathode in galvanic cell

- Electrode material having lower reduction potential gets easily oxidized and become anode
- While metal having higher reduction potential get easily reduced and become cathode
- ☐ In other words, elements lying above in ECS acts as anode and electrode lying below in series acts as cathode during construction of galvanic cell

For example-



$$E^\circ_{\text{red}} = -0.76$$



$$E^\circ_{\text{red}} = +0.34 \text{ volt}$$

If a galvanic cell of Zn and Cu is to be constructed , Zn becomes anode while Cu become cathode .

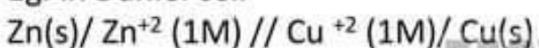
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3. To calculate emf of cell

Standard emf of cell is calculated from the following relation

$$E^\circ_{\text{cell}} = E^\circ_{\text{red (cathode)}} - E^\circ_{\text{red (anode)}}$$

Eg. in Daniel cell



$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{red (cathode)}} - E^\circ_{\text{red (anode)}} \\ &= E^\circ_{\text{Cu}^{++}/\text{Cu}} - E^\circ_{\text{Zn}^{++}/\text{Zn}} \\ &= 0.34 - (-0.76) \\ &= 1.1 \text{ V} \end{aligned}$$

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4. To predict whether a cell reaction is spontaneous or not

- If emf of cell reaction is positive , the cell reaction is feasible or spontaneous in given direction shown by net reaction i.e. it can take place
- If emf of cell reaction is negative , the cell reaction is not feasible or non-spontaneous in given direction shown by net reaction i.e. it cannot take place

Eg. in Daniel cell



$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{red (cathode)}} - E^\circ_{\text{red (anode)}} \\ &= E^\circ_{\text{Cu}^{++}/\text{Cu}} - E^\circ_{\text{Zn}^{++}/\text{Zn}} \\ &= 0.34 - (-0.76) \\ &= 1.1 \text{ V} \end{aligned}$$

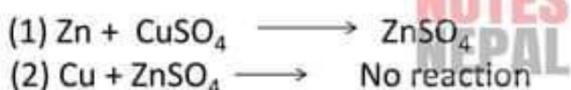
Since E°_{cell} is positive, the reaction is spontaneous in the direction of net reaction

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5. To predict whether a metal can or cannot displace other metals from their salt

- Metal having lower reduction potential can displace those metals having higher reduction potential from their salt.
- It means , metal lying above in electrochemical series can displace only those metals from their salts which lie below in ECS .

For example



Zn^{+2} has low tendency to get reduced or Zn has more tendency to get oxidised . In reaction (1) Zn displace Cu from Cu^{+2} or CuSO_4 because Zn has more tendency to get oxidised . In reaction (2) Zn is already in oxidised state and Cu can not displace it.

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Thus, in either case there is separation of charges between the metal rod and its ions in solution which leads to development of electrical double layer on metal electrode and electrolyte solution interface .

As a result , a potential difference exist between the metal and it's ions in solution interface .The potential difference between thus developed is called electrode potential.

Thus electrode potential is defined as potential difference set up between metal rod and its ions in solution due to separation of charges between them.

Simply it is the tendency of electrode to loose or gain electrons when it is in contact with the solution of it's ion .

Electrode potential depends on :

- i) Nature of metal electrode .
- ii) Concentration of metal ions in the solution .
- iii) Temperature of the solution .

Q. What is meant by single electrode potential? How is it measured? [1 + 1]

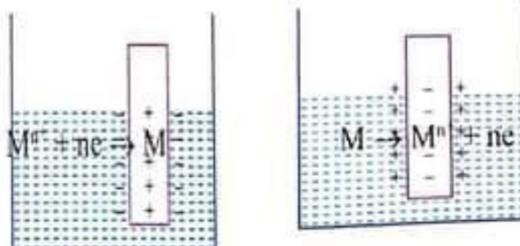
The potential difference developed at the solid – liquid interface when a metal rod is dipped in to electrolytic solution containing it's own metal ions is called electrode potential or single electrode potential . This arises due to the formation of electrical double layer between metal electrode and electrolyte solution interface .

Single electrode potential is measured with a reference electrode known as standard hydrogen electrode.

Q. How is single electrode potential originated ? [2marks]

When a metal electrode is dipped into electrolyte solution containing it's own metal ion then either the metal atom loses electrons on the electrode and positive metal ions pass into the solution and electrode develops negative charge or the metal ions of electrolyte accept electrons from electrode and deposit on the electrode and then electrode develops positive charge. During this process there is separation of charge on the electrode and electrolyte solution interface and single electrode potential is originated.

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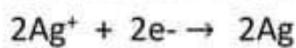
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- In the Cu – Ag cell, copper electrode is immersed in 1M $Cu(NO_3)_2$ solution in one container and silver electrode is immersed in 1M $AgNO_3$ solution in another container. These two containers are connected by salt bridge .

Anodic half reaction



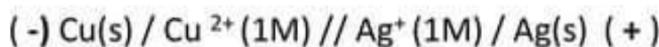
Cathodic half reaction



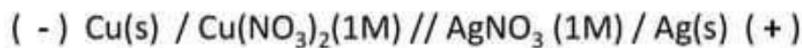
The overall cell reaction



Cell notation



or



$$E^\circ Ag^+ / Ag = 0.80 V$$

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

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Emf of the cell is calculated as

$$E^\circ Ag^+ / Ag = 0.80 V \quad E^\circ Cu^{2+} / Cu = + 0.34 V$$

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{(Red)cathode} - E^\circ_{(Red)anode} \\ &= 0.80 - (0.34) \\ &= 0.46 V \end{aligned}$$

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Salt bridge :

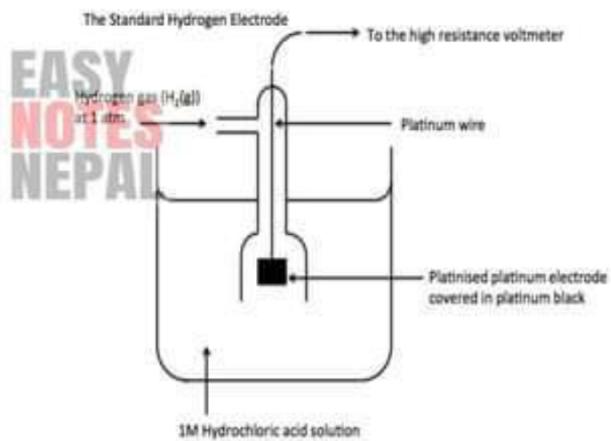
Salt bridge is a U-shaped glass tube filled with concentration solution of inert electrolyte like KCl , KNO₃ or NH₄NO₃ etc. in agar-agar. It connects electrolytic solution of two half cells and completes the cell circuit.

Functions of salt bridge :

- 1) It helps to complete the internal circuit of galvanic cell.
- 2) It helps to maintain the electrical neutrality in the two half cells with out direct mixing of electrolyte solution .

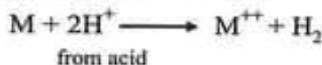
Standard hydrogen electrode [SHE] :

- ❖ SHE is electrode system in which Platinized platinum metal is immersed in 1M HCl solution at 25 °C and pure dry Hydrogen gas at 1 atmospheric pressure is bubbled over platinum metal.



6. To predict whether a metal can liberate hydrogen from acid or not:

Metals having strong tendency to lose electrons to form metal ions can displace H⁺ ions from acid solution. It means the metals having negative values of reduction potentials can liberate hydrogen from the acid.



Thus the metals like zinc, magnesium, nickel have negative E° values and hence they can liberate hydrogen from the acids. But the metals like copper, silver have positive E° values. It means they have electron accepting tendencies and hence their atoms can't donate electrons to H⁺ ions of the acid. Therefore, hydrogen gas is not liberated.

7. To predict the relative reactivity of metals

Greater the value of standard reduction potential of a given metal (M) smaller its tendency to lose electrons to change into metal cation (M⁺) and hence smaller its chemical reactivity. Thus, with the increase of standard reduction potential values on descending the electrochemical series, the chemical reactivity of the metal decreases in the same order.

Cell potential and Standard cell potential(Nernst equation)*

Walter Nernst derived the mathematical relationship to calculate half cell potential or single electrode potential (E) from the standard electrode potential and temperature of the cell. This relation is known as Nernst equation. It is given as

$$E = E^{\circ} - \frac{2.303RT}{nF} \log K$$

where,

E° = Standard electrode potential

R= Gas constant

T Kelvin temperature

N= Number of moles of electrons transferred in half cell reaction

F= faraday's constant

K = equilibrium constant

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Let us consider an oxidation half reaction when a metal electrode M gives M^{n+} ions as,



The Nernst equation takes the form

$$E = E^{\circ} - \frac{2.303RT}{nXF} \log \left[\frac{M^{n+}}{M} \right]$$

The concentration of solid metal [M] is taken as unity . So equation ii can be written as

$$E = E^{\circ} - \frac{2.303RT}{nXF} \log [M^{n+}]$$

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At $25^{\circ} C$, substituting the values of R, F, T , equation (iii) takes from

$$E = E^{\circ} - \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log [M^{n+}]$$

$$E = E^{\circ} - \frac{0.0591}{n} \log [M^{n+}]$$

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This is the relation for half cell in which oxidation occurs i.e. E is oxidation potential and E° is standard oxidation potential. To calculate the reduction potential, sign of E will be reversed.

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Standard electrode potential :

If the electrode potential is measured in standard conditions i.e. 1 molar concentration (1M) of electrolytic solution , temperature at 25°C and 1 atm pressure (in case of gas electrode) then it is called standard electrode potential . It is denoted by E° .

It is of two types

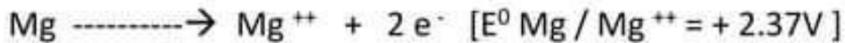
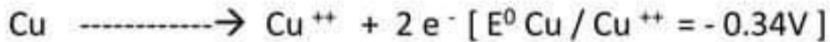


- 1) Standard oxidation electrode potential .
- 2) Standard reduction electrode potential .

Standard oxidation electrode potential :

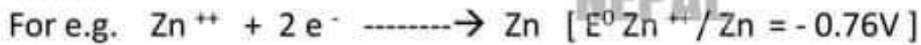
If electrode potential is developed due to oxidation reaction ,it is called oxidation potential. Oxidation potential at standard condition is called standard oxidation potential .

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Standard reduction electrode potential :

If electrode potential is developed due to reduction reaction ,it is called reduction potential. Reduction potential at standard condition is called standard reduction potential .



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Note :

- i) In IUPAC system , standard electrode potential means standard reduction electrode potential .
- ii) Standard reduction electrode potential value = - Standard oxidation electrode potential value.



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Electrochemical cell :

A device which converts electrical energy into chemical energy and chemical energy into electrical energy is called electrochemical cell .

There are two types of electrochemical cells.

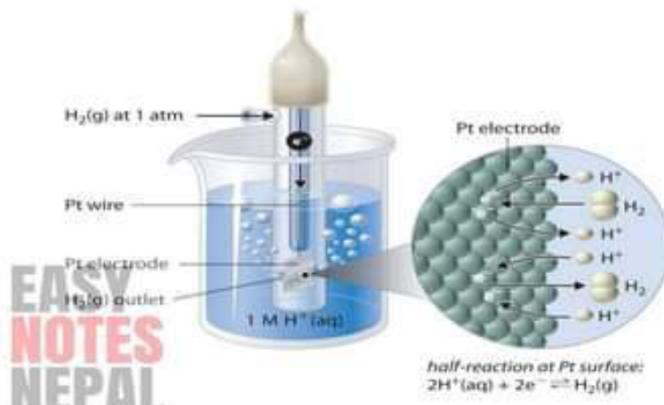
1) Electrolytic cell

2) Galvanic cell / Voltaic cell

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- It is a gas electrode. It is reversible to H⁺ ions of the solution
- Electrode potential of SHE is arbitrarily taken as zero



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- Hydrogen electrode is gas electrode. It is reversible to H⁺ ions of solution. A platinum foil is connected by a conducting wire and whole of this part is covered by glass jacket having an inlet . The platinized platinum foil is immersed in 1M HCl solution at 25°C . Pure and dry H₂ gas entered through the narrow inlet maintaining 1 atm pressure as shown above diagram .
- The hydrogen gas is easily absorbed by platinized platinum foil and released in the form of tiny bubbles as if the platinized platinum foil were the sources of hydrogen gas. This hydrogen gas is reversible to H⁺ ions of solution .
- It is used as reference electrode to measure the standard electrode potential of other electrodes. The potential value of SHE is assigned to be 0 V .

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This electrode is coupled with another electrode whose potential is to be determined because the potential value of SHE is assigned to be 0V .

Depending upon the nature of electrodes , SHE can be taken as anode or cathode half cell.

- If hydrogen electrode acts as anode half cell , the half cell notation is

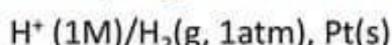


Oxidation half reaction is



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- If hydrogen electrode acts as cathode half cell, the half cell notation is



Reduction half reaction is



Measurement of standard electrode potential

- Electrode potential has to be measured against some reference standard electrode.
- The primary standard reference electrode against which all other potentials are measured is the standard hydrogen electrode.
- Standard electrode potential of an electrode is measured by coupling it with standard hydrogen electrode.
- Here measurement of standard electrode potential of Zn and copper electrodes is illustrated.

Relationship between cell potential and free energy

From thermodynamics , we know that maximum work done (W_{\max}) by system is equal to the decrease in Gibb's energy (G)

$$W_{\max} = -\Delta G \quad \dots\dots\dots \text{i}$$

From electrochemistry , the maximum work done by the system is equal to the product of charge and potential difference (emf or cell potential) i.e electrical work

$$W_{\max} = QE$$

$$W_{\max} = nFE \quad \dots\dots \text{ii}$$

n= no. of moles of electron

F = Faraday's constant

E= emf or cell potential of cell

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From equation i and ii

$$-\Delta G = nFE$$

$$\Delta G = -nFE$$

The standard cell potential (E°) is related to standard free energy change (ΔG°) through relationship

$$\Delta G^\circ = -nFE^\circ$$

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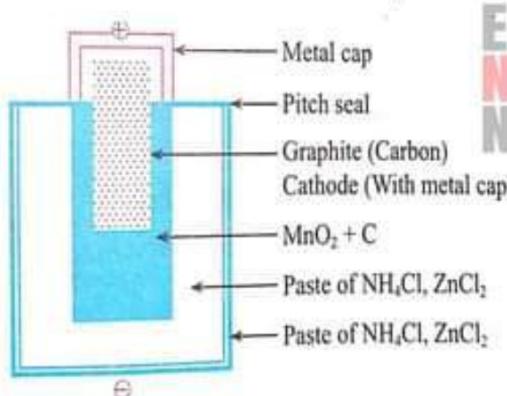
Some Commercial Batteries

- Battery is the assembly of electrochemical cells. There mainly two types of cell
 - 1. Primary cells
 - 2. Secondary cells
- In the primary cells , the reaction occurs only one and battery then becomes dead over a period of time and can not be used again
E.g. dry cell, mercury cell
- Secondary cells can be recharged by passing current through them so that they can be used again and again .
e.g. lead acid battery, nickel cadmium battery , Li-ion battery

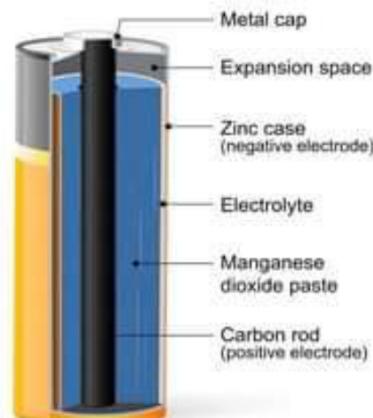
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Dry cell or Leclanche's cell

- ❖ It is the most familiar type of battery .
- ❖ In this cell anode consist of a zinc container and cathode is graphite rod surrounded by powdered MnO_2 and carbon. The space between the electrodes is filled with a moist paste of NH_4Cl and $ZnCl_2$.



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Difference between electrolytic cell and Galvanic cell.

Electrolytic cell

- 1) It converts electrical energy into chemical energy.
- 2) Redox reaction occurs non spontaneously.
- 3) Anode is represented by +ve sign and cathode is represented by - ve sign.
- 4) Salt bridge is not used.
- 5) Two electrodes are dipped in the same electrolytic solution with in a same container .

Galvanic cell

- 1) It converts chemical energy into electrical energy.
- 2) Redox reaction occurs spontaneously .
- 3) Anode is represented by – ve sign and cathode is represented by +ve sign.
- 4) Salt bridge is used .
- 5) Two electrodes are dipped in two different electrolytic solutions containing its own ion in two different container.

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Construction of Galvanic cell :

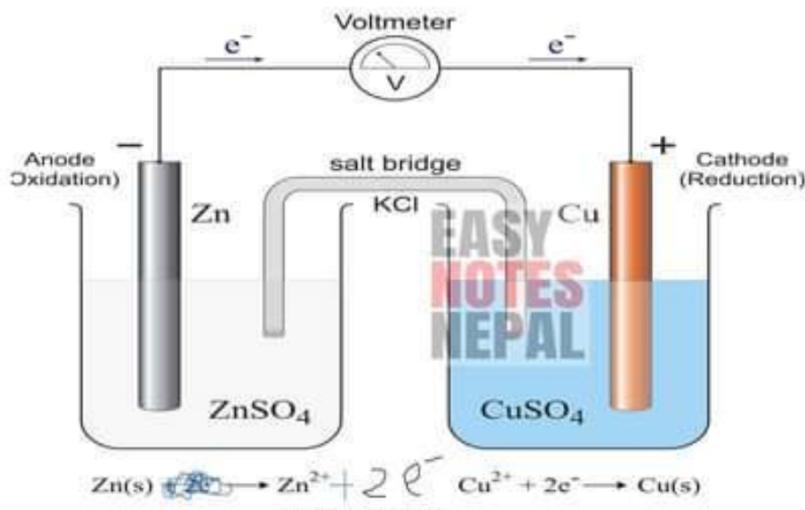


Fig: Daniel cell

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Cell notation or cell representation

For the symbolic representation of a galvanic cell, following rules should be followed.

- Electrode having higher reduction potential acts as cathode.
- Electrode having lower reduction potential acts as anode.
- Anode half cell is always written on the left and cathode half cell on the right from salt bridge.
- Anode is represented by negative and cathode by positive sign .
- Single vertical line (/) represent phase boundary , which separate the different form of same species.
- E.g. $\text{Zn(s) / Zn}^{2+}(\text{aq.})$ $\text{Cu}^{2+}(\text{aq.}) / \text{Cu (s)}$
- Double vertical line (//) represent the salt bridge which separate anode and cathode.

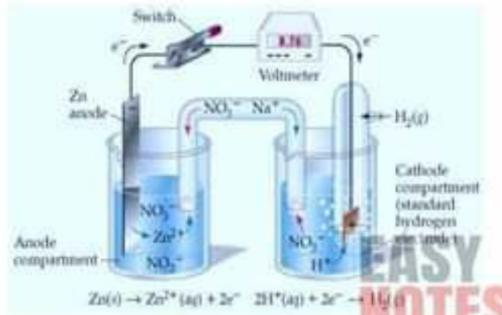
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- Concentration of ions are enclosed in the bracket with ions in respective side.
e.g. Zn^{++} (1M), Cu^{++} (0.5M)
- In case of gas, inert electrode like platinum is enclosed in bracket with gas in respective side.

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Measurement of electrode potential of Zn electrode



Cell notation of this combination is

$\text{Zn(s)}/\text{ZnSO}_4(\text{aq. } 1\text{M})/\text//\text{H}^+(\text{aq.})/\text{H}_2(\text{g, } 1\text{atm})\text{ Pt}$

Cell potential of this combination is measured 0.76 v

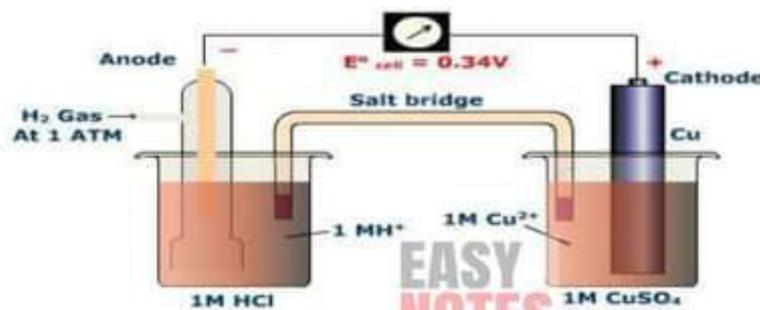
$$\text{E}^\circ_{\text{cell}} = \text{E}^\circ_{\text{cathode}} - \text{E}^\circ_{\text{anode}}$$

$$0.76 \text{ V} = 0 - \text{E}^\circ_{\text{anode}}$$

$$\text{E}^\circ_{\text{anode}} = -0.76 \text{ volt (reduction potential)}$$

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Measurement of standard electrode potential of Cu electrode



Cell notation of this combination is

$\text{Pt, H}_2(\text{g, } 1\text{ atm})/\text{H}^+(\text{aq. } 1\text{M})/\text//\text{CuSO}_4(\text{aq., } 1\text{M})/\text{Cu (S)}$

Cell potential of this combination is measured 0.76 v

$$\text{E}^\circ_{\text{cell}} = \text{E}^\circ_{\text{cathode}} - \text{E}^\circ_{\text{anode}}$$

$$0.34 \text{ V} = \text{E}^\circ_{\text{cathode}} - 0$$

$$\text{E}^\circ_{\text{cathode}} = 0.34 \text{ volt (reduction potential)}$$

$$= -0.34 \text{ volt (oxidation potential)}$$

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Calomel electrode

- The saturated calomel electrode (SCE) is a secondary reference electrode based on the reaction between elemental mercury and mercurous chloride (Hg_2Cl_2) i.e. calomel.

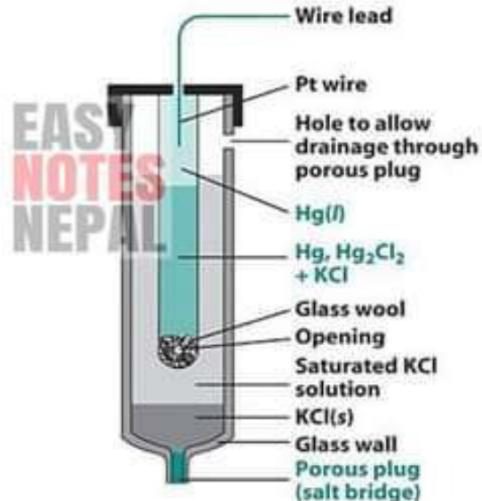


Fig: calomel electrode

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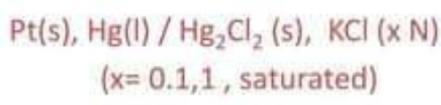
The central narrow tube of this electrode is filled with liquid mercury, mercurous chloride (Hg_2Cl_2) and saturated KCl solution into which platinum wire is dipped. The bottom of this electrode contains saturated KCl solution with some solid KCl which function as salt bridge because it connects the electrode to any other electrode solution through porous glass frit or fiber.

The calomel electrode is reversible, two types of reactions are possible depending upon the nature of electrode with which it coupled.

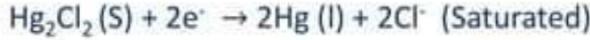
When it act as anode, half cell reaction is



Half cell notation is



When it act as cathode, the half cell reaction is

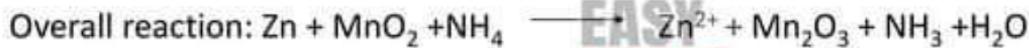
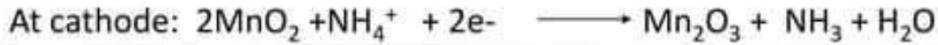


Half cell notation is



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- Dry cell have a potential approximately 1.25 to 1.5 V. The reaction that take place in dry cell is



- Thus produced NH_3 combines with $ZnCl_2$ to give $[Zn(NH_3)_2Cl_2]$ i.e.

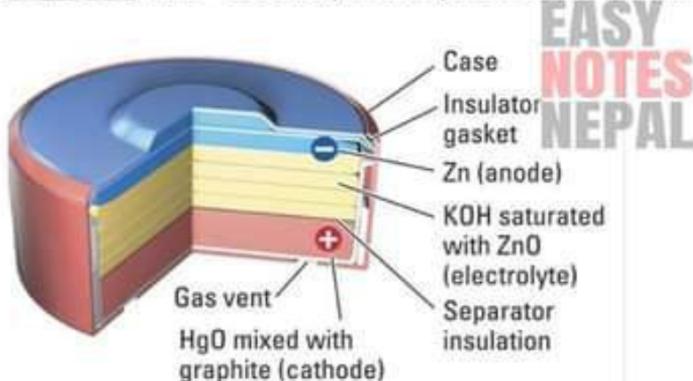


- If NH_3 does not combine with $ZnCl_2$, it would exert pressure so that it would be broken.
➤ Dry cells do not have an indefinite life as acidic NH_4Cl corrodes the zinc container even when not in use

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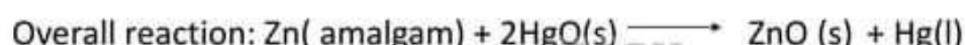
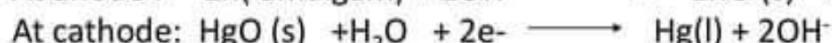
Mercury cell

- It is new type of cell which is used in small electrical circuits such as hearing aids, watches and camera.
- Here Zinc- mercury amalgam is used as anode and a paste of HgO and carbon as cathode. The electrolyte is a paste of KOH and ZnO .



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The reactions of cell is as follows :



- The cell potential is 1.35 V. The cell show constancy in potential throughout its life

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Lead acid battery

- ❖ It is the most important secondary cell.
- ❖ It is used in automobiles i.e. cars, buses, trucks, motorbikes, etc.
- ❖ Cathode plates (grids) coated with red brown lead dioxide (PbO_2) and anode plates are coated with spongy lead. The plates are immersed in dilute 40% H_2SO_4 .

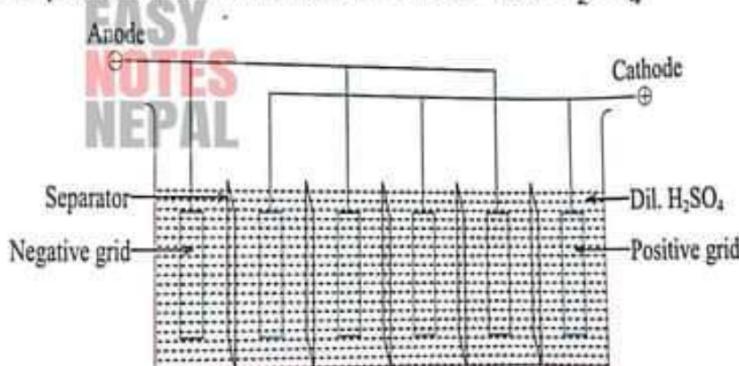


Fig: Lead storage battery

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Half cell

The electrode along with electrolytic solution is called half cell. Generally electrode contains the electrolytic solution of its own cation. There are two types of half cells.

Anodic half cell

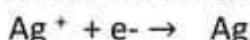
In this half cell oxidation occurs , hence , it also known as the oxidation half cell. It is represented on the left in cell notation with negative sign.



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Cathodic half cell

In this half cell reduction occurs hence it is also known as the reduction half cell. It is represented at the right of cell notation



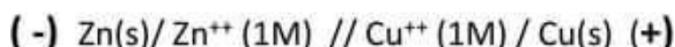
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➤ For example

1. Zn – Cu cell

$$E^\circ \text{Zn}^{++}/\text{Zn} = -0.76 \text{ V} \quad E^\circ \text{Cu}^{++}/\text{Cu} = +0.34 \text{ V}$$

Cell notation for Cu – Zn cell is



2. Cu- Ni cell

$$E^\circ \text{Ni}^{++}/\text{Ni} = -0.25 \text{ V} \quad E^\circ \text{Cu}^{++}/\text{Cu} = +0.34 \text{ V}$$

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Cell notation for Cu – Ni cell is



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3. Zn – Fe cell

$$E^\circ \text{Zn}^{++}/\text{Zn} = -0.76 \text{ V} \quad E^\circ \text{Fe}^{++}/\text{Fe} = -0.44 \text{ V}$$

Cell notation for Zn– Fe cell is



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Standard Electromotive force (emf) or cell potential of a cell

The difference between the electrode potentials of two half cells is known as emf of a cell. If it is calculated at standard condition then it is known as standard emf of cell.

The standard emf of an cell is calculated by a relation

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

Where,

$E^{\circ}_{\text{cathode}}$ = standard reduction potential developed at cathode

E°_{anode} = standard reduction potential developed at anode

Note

$$E^{\circ}_{\text{anode}} = - E^{\circ}_{\text{(ox)}_{\text{anode}}}$$

$E^{\circ}_{\text{(ox)}_{\text{anode}}}$ is standard oxidation potential of anode

Electrochemical Series (ECS)

- A series of electrode materials arranged on the basis of increasing standard reduction potential value is called electrochemical series.
- It is also called activity series or electromotive series.
- The electrochemical series is given below.

Electrode	Electrode reaction	E°_{red} (volts)
Li	$\text{Li}^+ + \text{e}^- \longrightarrow \text{Li}$	-3.05
K	$\text{K}^+ + \text{e}^- \longrightarrow \text{K}$	-2.93
Ba	$\text{Ba}^{+2} + 2\text{e}^- \longrightarrow \text{Ba}$	-2.90
Ca	$\text{Ca}^{+2} + 2\text{e}^- \longrightarrow \text{Ca}$	-2.87
Na	$\text{Na}^+ + \text{e}^- \longrightarrow \text{Na}$	-2.71
Mg	$\text{Mg}^{+2} + 2\text{e}^- \longrightarrow \text{Mg}$	-2.37
Al	$\text{Al}^{+3} + 3\text{e}^- \longrightarrow \text{Al}$	-1.66
Zn	$\text{Zn}^{+2} + 2\text{e}^- \longrightarrow \text{Zn}$	-0.76
Cr	$\text{Cr}^{+3} + 3\text{e}^- \longrightarrow \text{Cr}$	-0.74
Fe	$\text{Fe}^{+2} + 2\text{e}^- \longrightarrow \text{Fe}$	-0.44
Sn	$\text{Sn}^{+4} + 2\text{e}^- \longrightarrow \text{Sn}$	-0.14
Pb	$\text{Pb}^{+2} + 2\text{e}^- \longrightarrow \text{Pb}$	-0.13
H ₂ (Pt)	$2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$	0.00
Cu	$\text{Cu}^{+2} + 2\text{e}^- \longrightarrow \text{Cu}$	+0.34
Fe	$\text{Fe}^{+3} + \text{e}^- \longrightarrow \text{Fe}^{+2}$	+0.77
Ag	$\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}$	+0.8
Au	$\text{Au}^{+3} + 3\text{e}^- \longrightarrow \text{Au}$	+1.42
F ₂	$\text{F}_2 + 2\text{e}^- \longrightarrow 2\text{F}^-$	+2.87

Increasing oxidation potential →

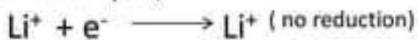
Increasing reduction potential →

Application of electrochemical series

1. To compare strength of oxidizing agent and reducing agent

❖ Greater the reduction potential of an electrode material, greater is its tendency to accept electrons to undergo reduction and hence act as strong oxidizing agent.

➤ For example,



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➤ The standard reduction potential of Li^+ is -3.35 and F_2 has 2.87.

➤ F_2 has the highest reduction potential and Li^+ ion has lowest reduction potential. This means that that F_2 is reduced most easily whereas Li^+ ions are reduced with greatest difficulty. In the other words, Fluorine is the strongest oxidizing agent whereas Li^+ ion is the weakest oxidizing agent.

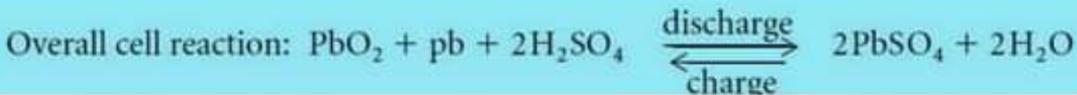
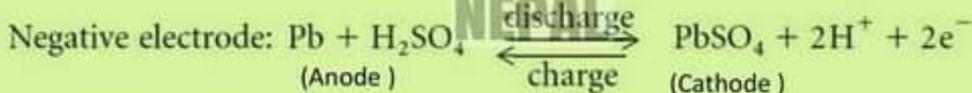
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- ❖ Similarly lower the reduction potential of an electrode material, greater is its tendency to lose electrons to undergo oxidation and hence act as strong reducing agent.
- Hence Li will be oxidized most easily and hence it is the best reducing agent whereas F^- is oxidized with greater difficulty and hence, it is weakest reducing agent

Element	Electrode reaction	E°/V
K	$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-3.045
Ca	$\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$	-2.925
Na	$\text{Na}^{+} + 2\text{e}^- \rightarrow \text{Na}$	-2.923
Mg	$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	-2.906
Al	$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-2.866
H ₂	$\text{H}_2 + 2\text{e}^- \rightarrow 2\text{H}^-$	-2.714
Pb	$\text{PbO}_2 + 2\text{e}^- \rightarrow \text{Pb} + 2\text{O}^{2-}$	-2.363
Cu	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	-1.662
Zn	$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.829
Fe	$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.763
Cr	$\text{Cr}^{3+} + 2\text{e}^- \rightarrow \text{Cr}$	-0.440
Pt	$\text{PtO}_2 + 2\text{e}^- \rightarrow \text{Pt} + 2\text{O}^{2-}$	-0.003
Sn	$\text{Sn}^{4+} + 2\text{e}^- \rightarrow \text{Sn}^{2+}$	0.310
Bi	$\text{Bi}^{3+} + 2\text{e}^- \rightarrow \text{Bi}$	0.280
H ₃	$\text{H}_3 + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	0.250
Pt	$\text{Pt}^{2+} + 2\text{e}^- \rightarrow \text{Pt}$	0.126
Fe	$\text{Fe}^{3+} + 2\text{e}^- \rightarrow \text{Fe}^{2+}$	0.038
H ₂	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{H}_2\text{O}$	0
Co	$\text{Co}^{3+} + 2\text{e}^- \rightarrow \text{Co}^{2+}$	+0.153
S	$\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \rightarrow 2\text{S}_2\text{O}_4^{2-}$	+0.170
Cr	$\text{Cr}^{3+} + 2\text{e}^- \rightarrow \text{Cr}^{2+}$	+0.337
I ₂	$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	+0.534
Pt	$\text{Pt}^{4+} + 2\text{e}^- \rightarrow \text{Pt}^{2+}$	+0.77
Ag	$\text{Ag}^{+} + \text{e}^- \rightarrow \text{Ag}$	+0.799
Hg	$\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}$	+0.854
H ₂	$\text{H}_2 + 2\text{e}^- \rightarrow 2\text{H}^-$	+1.066
O ₂	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	+1.220
O ₂	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{O}^{2-} + 2\text{H}_2\text{O}$	+1.330
Cl ₂	$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	+1.338
Au	$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	+1.498
Mn	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.510
F ₂	$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	+2.870

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- ❖ In each cell, the anode and cathode plates(grids) are arranged alternatively and separated from each other by separators.
- ❖ The commercial forms of lead storage batteries consist of six or twelve lead storage cells connected together.
- ❖ The reactions during discharge when current is drawn) and recharging as follows.

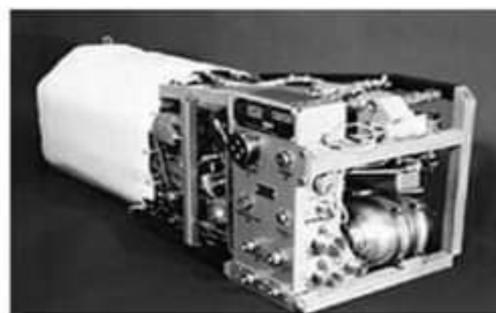
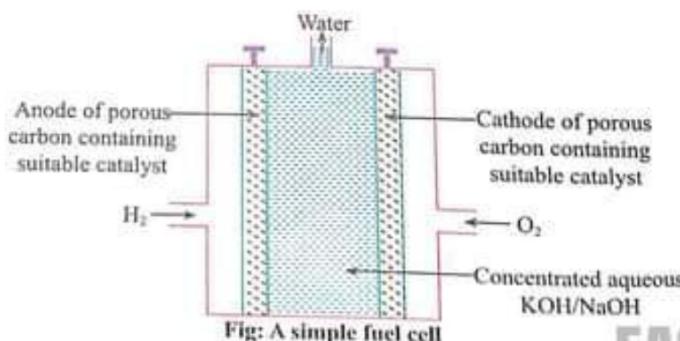


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Fuel Cells

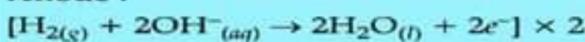
- A fuel cell is an electrochemical cell that converts the chemical energy of a fuel (like hydrogen, carbon monoxide or methane) and an oxidizing agent (often oxygen) into electricity through a pair of redox reactions
- H₂-O₂ fuel cell(or alkaline fuel cell) is the most successful fuel cell. It uses the reaction of hydrogen with oxygen to form water. This cell has been used for electric power in Apollo space programme.

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- In this cell, hydrogen and oxygen are bubbled through porous carbon electrode into concentrated aqueous sodium hydroxide. Catalyst are incorporated in the electrode. The electrode reactions are

Anode :



Cathode :



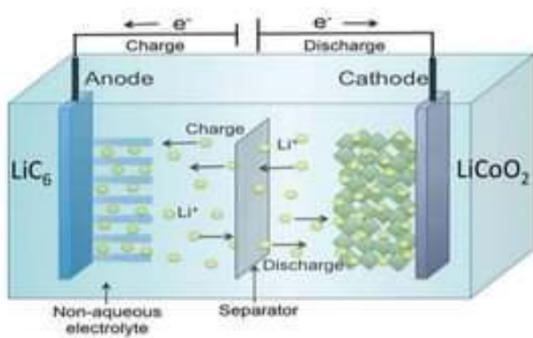
Net reaction :



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Lithium-ion batteries

- A lithium-ion battery or Li-ion battery is a type of rechargeable battery in which lithium ions move from the negative electrode through an electrolyte to the positive electrode during discharge and back when charging.
- Li-ion batteries use an intercalated lithium compound(like LiCoO₂) as a cathode (positive electrode) and typically graphite with lithium as a anode (negative electrode.)



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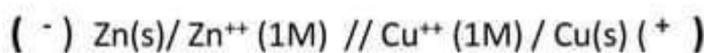
Fig: Li – ion battery

➤ For example

1. Zn – Cu cell

$$E^\circ \text{Zn}^{++}/\text{Zn} = -0.76 \text{ V} \quad E^\circ \text{Cu}^{++}/\text{Cu} = +0.34 \text{ V}$$

Cell notation for Cu – Zn cell is

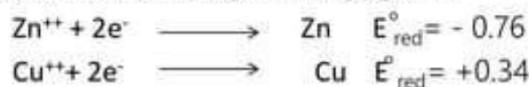


$$\begin{aligned}E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\&= 0.34 - (-0.76) \\&= 1.1 \text{ V}\end{aligned}$$

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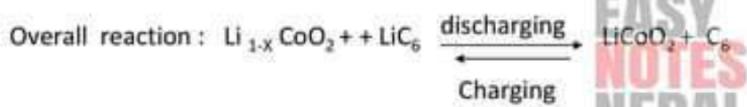
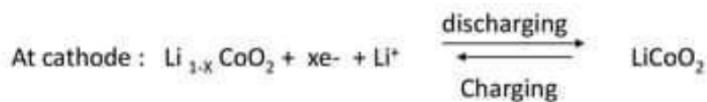
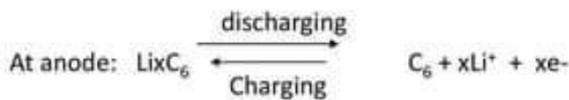
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Which one is strong oxidizing agent ?



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➤ Li-Ion batteries provide portable electricity, powering electronic gadgets such as mobile phones, laptops and tablets. Li-Ion batteries are also used to supply energy to medical equipment, electric vehicles and power tools.

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