

ELECTROCHEMISTRY



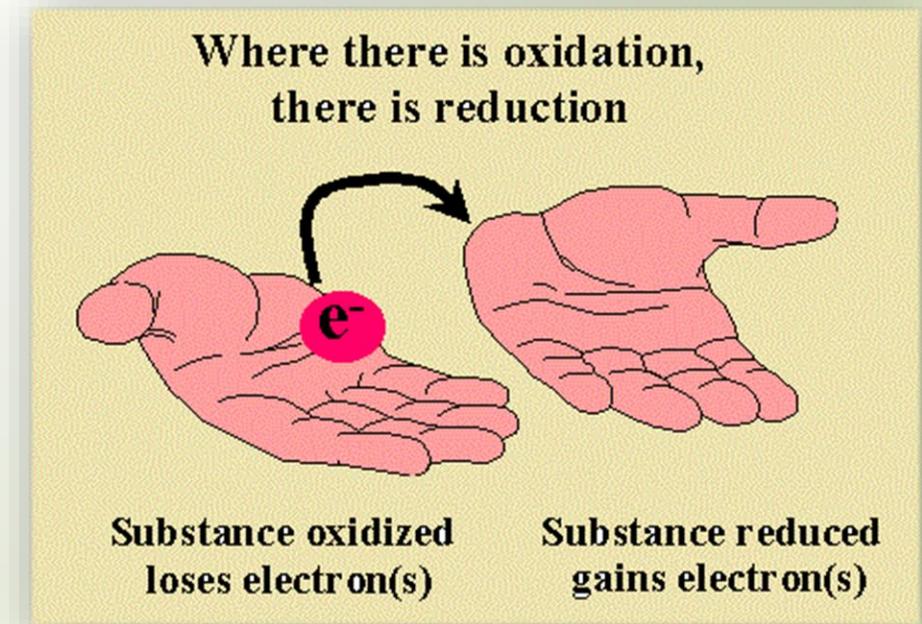
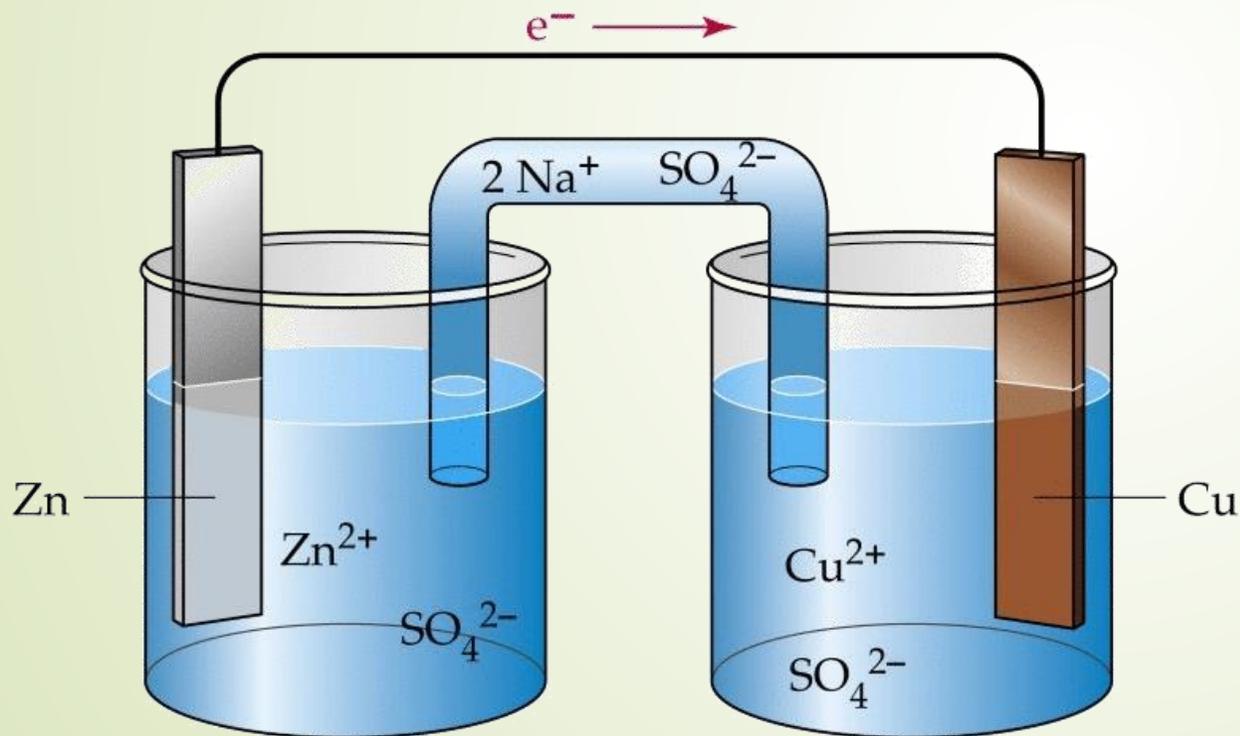
3. Electro-chemistry

- Introduction
- Describe an electrochemical cell
- Galvanic and Electrolytic cells
- Nernst equation for calculating the emf of galvanic cell
- Derive relation between Standard potential of the cell, Gibbs energy of cell reaction and its equilibrium constant
- Measurement of Conductivity of electrolytic solutions and calculation of their Molar conductivity
- Enunciate Kohlrausch law and learn its applications
- Construction of some primary and secondary batteries and fuel cells
- Corrosion as an electrochemical process

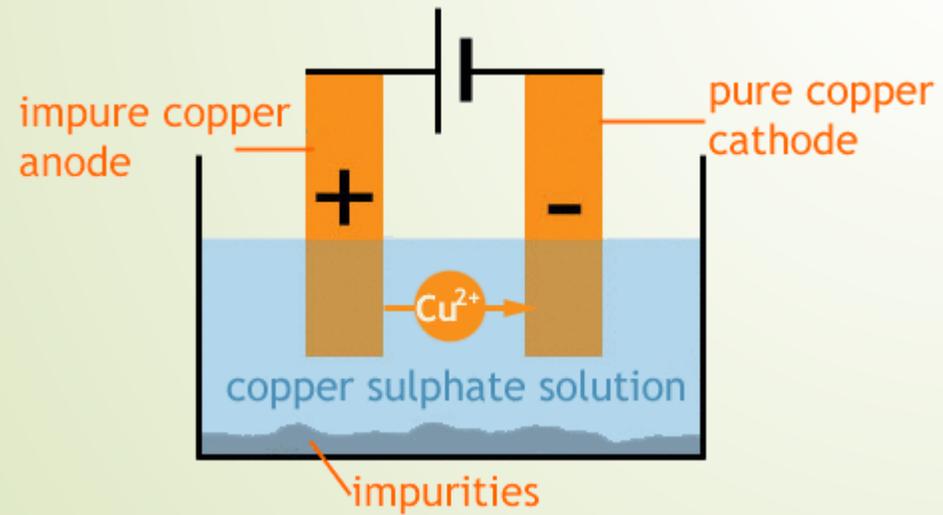
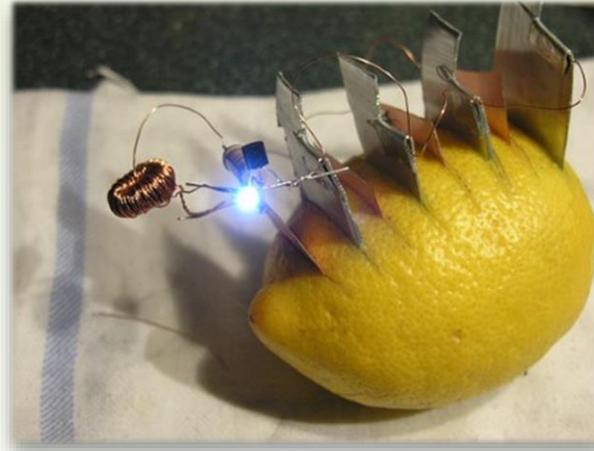
Electrochemistry- Intro

Study of production of electricity from energy released during spontaneous chemical reactions or the use of electrical energy to bring about non-spontaneous chemical transformations.

Electrochemistry deals with situations where redox reactions are separated in space or time , connected by an external source.



Why study Electrochemistry?



Spontaneous & non-spontaneous

Spontaneous (ΔG is – ive)

Having the potential to proceed without the assistance of external agency.

A spontaneous process is an irreversible process and may only be reversed by some external agency. E.g. Melting of ice

Non–spontaneous (ΔG is +ive)

Need assistance of external agency or source .

Reaction stops when source is removed. E.g. Hydrolysis of water.

Attaining stability

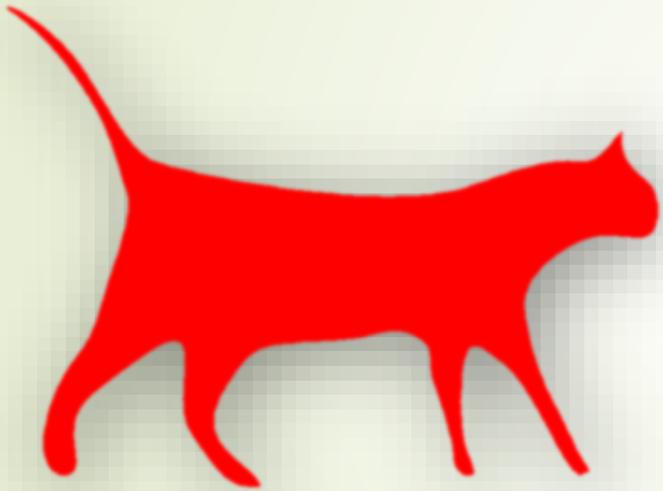
- History
- Rich gives to poor



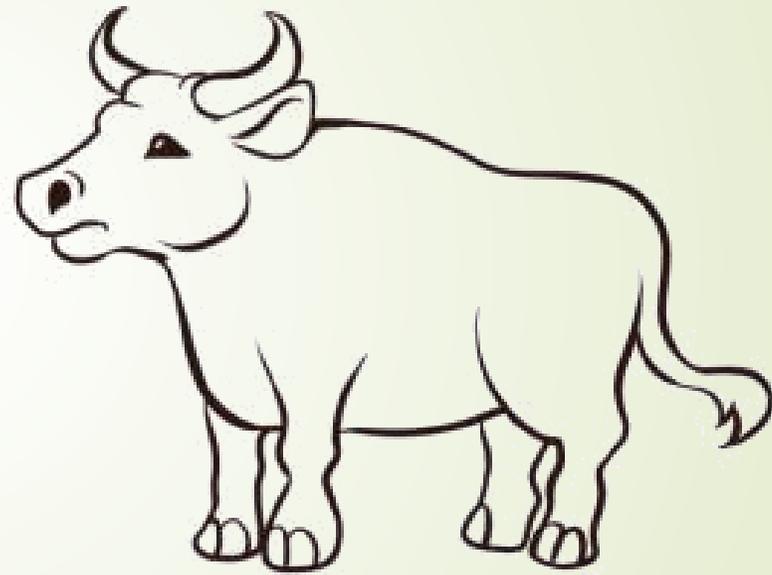
- Reactivity series

Potassium	Most reactive	K
Sodium		Na
Calcium		Ca
Magnesium		Mg
Aluminium		Al
Carbon		C
Zinc		Zn
Iron		Fe
Tin		Sn
Lead		Pb
Hydrogen		H
Copper		Cu
Silver		Ag
Gold		Au
Platinum		Pt
	Least reactive	

Oxidation-Reduction

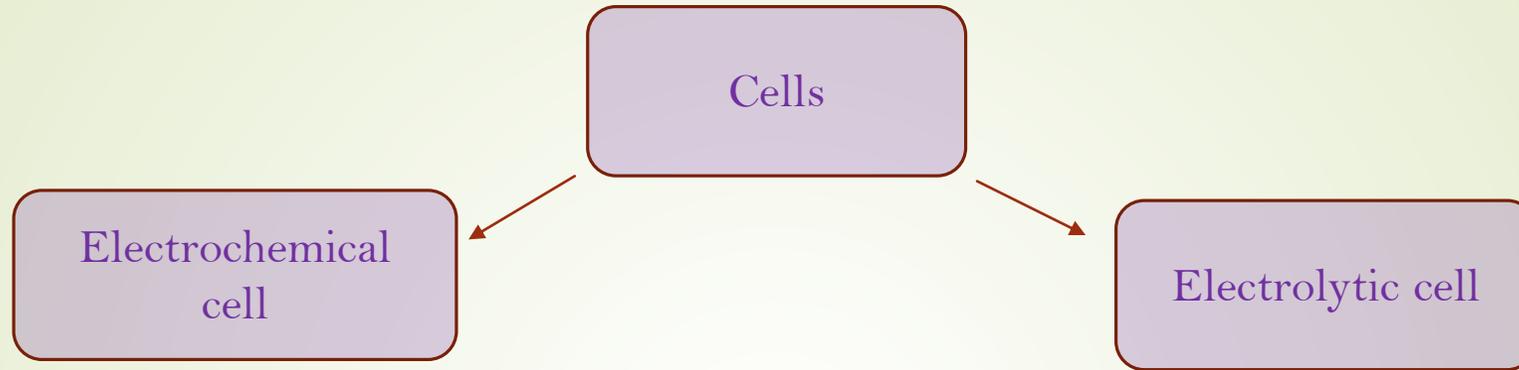


Red Cat

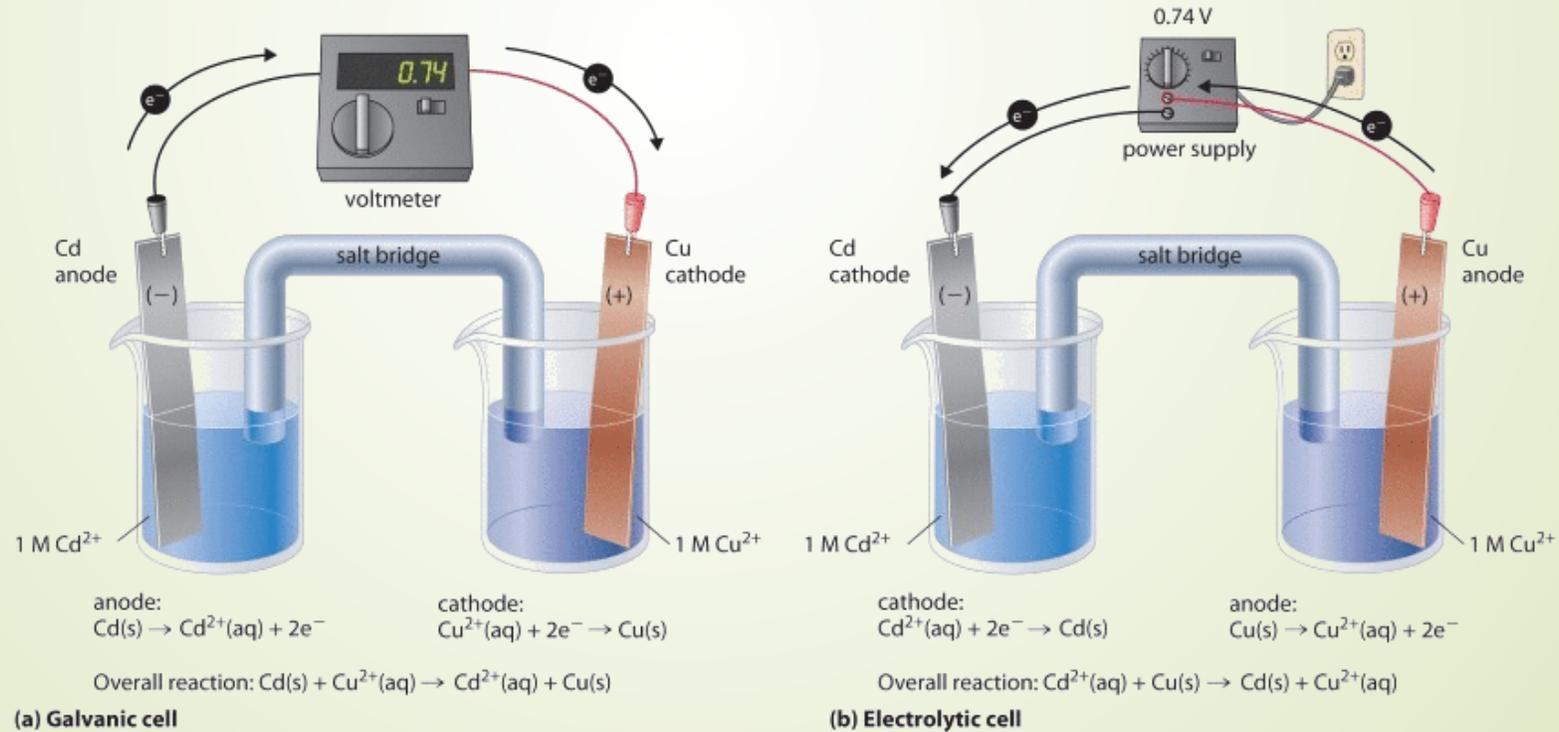


An Ox

Electrochemistry : Chart

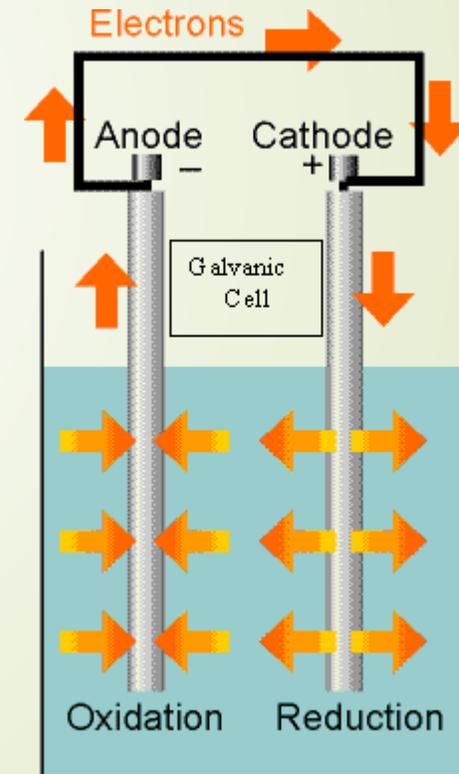
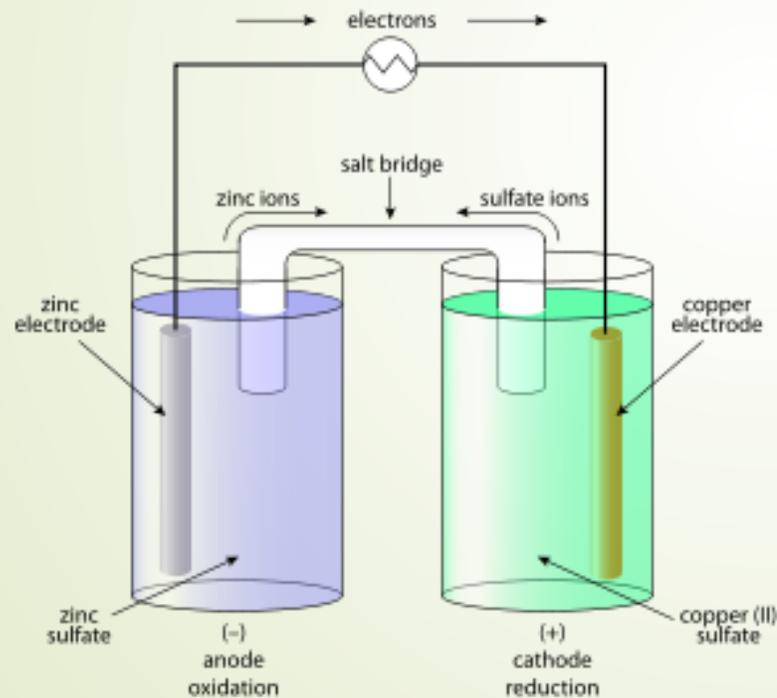


(Also known as **Galvanic** or **Voltaic cell**)



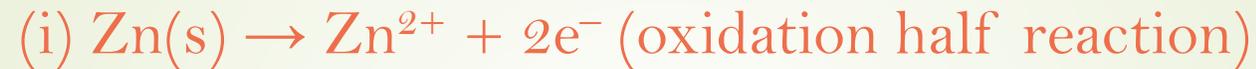
Galvanic cell or Voltaic cell

- A galvanic cell is an electrochemical cell that converts the chemical energy of a spontaneous redox reaction into electrical energy.
- In this device the Gibbs energy of the spontaneous redox reaction is converted into electrical work which may be used for running a motor or other electrical gadgets like heater, fan, geyser, etc.



Galvanic cell: Redox couples

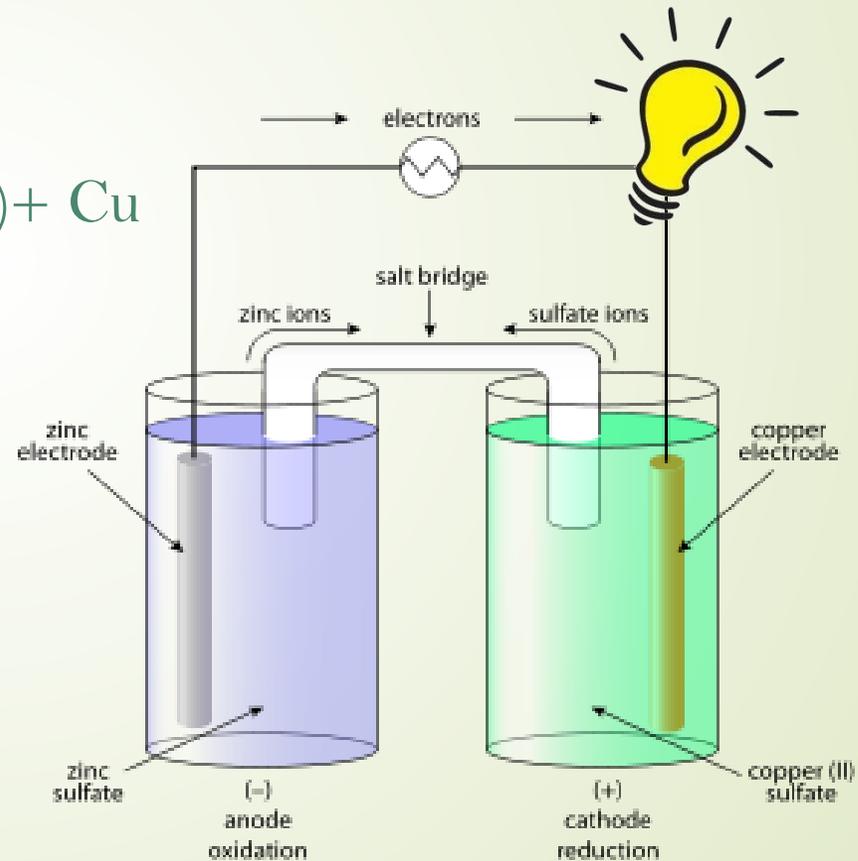
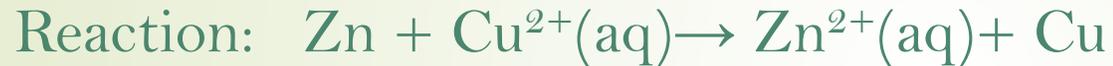
- This reaction (Daniel cell) is a combination of two half reactions whose addition gives the overall cell reaction:



- These two portions of the cell are also called **Half-cells or redox couples**.
- The copper electrode may be called the **Reduction half-cell** and the zinc electrode, the **Oxidation half-cell**.
- **A half-cell consists of a metallic electrode dipped into an electrolyte.**
- The two half-cells are connected by a metallic wire through a voltmeter and a switch externally & internally through a salt bridge.
- Sometimes, both the electrodes dip in the same electrolyte solution and in such cases we do not require a salt bridge.

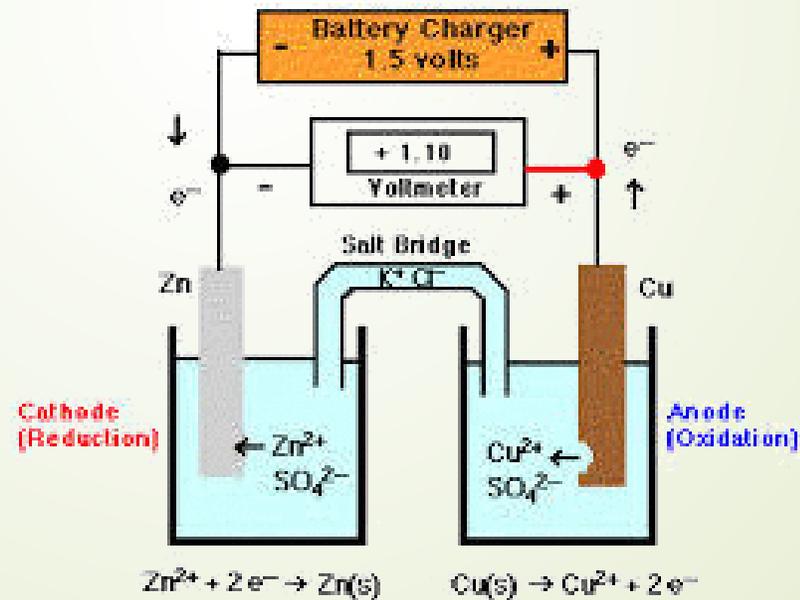
Daniel Cell (as a galvanic cell)

- This electrochemical or galvanic cell converts the chemical energy liberated during the redox reaction to electrical energy .
- It has an electrical potential equal to 1.1 V when concentration of Zn^{2+} and Cu^{2+} ions is 1 Molar.



Daniel cell (as a electrolytic cell)

- If an external opposite potential is applied in the galvanic cell and increased slowly, we find that the reaction continues to take place till the opposing voltage reaches the value 1.1 V , when, the reaction stops altogether and no current flows through the cell.
- Any further increase in the external potential again starts the reaction but in the opposite direction .
- It now functions as an electrolytic cell, a device for using electrical energy to carry non-spontaneous chemical reactions.

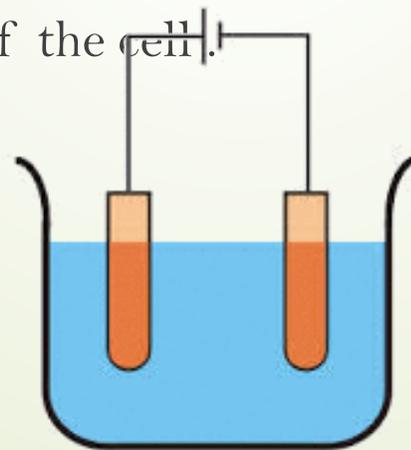


Electrode potential

- At equilibrium, there is a separation of charges and depending on the tendencies of the two opposing reactions, the electrode may be positively or negatively charged with respect to the solution.
- A potential difference develops between the electrode and the electrolyte which is called Electrode potential.
- When the concentrations of all the species involved in a half-cell is unity then the electrode potential is known as Standard electrode potential.
- According to IUPAC convention, standard reduction potentials are now called standard electrode potentials.
- In a galvanic cell, the half-cell in which oxidation takes place is called anode and it has a negative potential with respect to the solution.

Cell potential & Electromotive force

- There exists a potential difference between the two electrodes and as soon as the switch is in the 'on' position the electrons flow from negative electrode to positive electrode.
- The potential difference between the two electrodes of a galvanic cell is called the **Cell potential** and is measured in volts.
- The cell potential is the difference between the electrode potentials (reduction potentials) of the cathode and anode.
- The direction of current flow is opposite to that of electron flow.
- When no current is drawn through the cell, the cell potential is called the **Cell Electromotive force (emf)** of the cell.

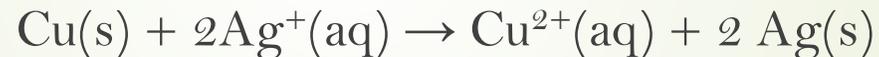


Representation of a cell

- It is convention that we keep the anode on the left & the cathode on the right while representing the galvanic cell.
- A galvanic cell is generally represented by putting a vertical line between metal and electrolyte solution and putting a double vertical line between the two electrolytes connected by a salt bridge.
- Under this convention the emf of the cell is positive and is given by the potential of the half-cell on the right hand side minus the potential of the half-cell on the left hand side.

$$(E_{\text{cell}} = E_{\text{right}} - E_{\text{left}})$$

Cell reaction:



Half-cell reactions:



Silver electrode acts as a cathode and copper electrode acts as an anode.

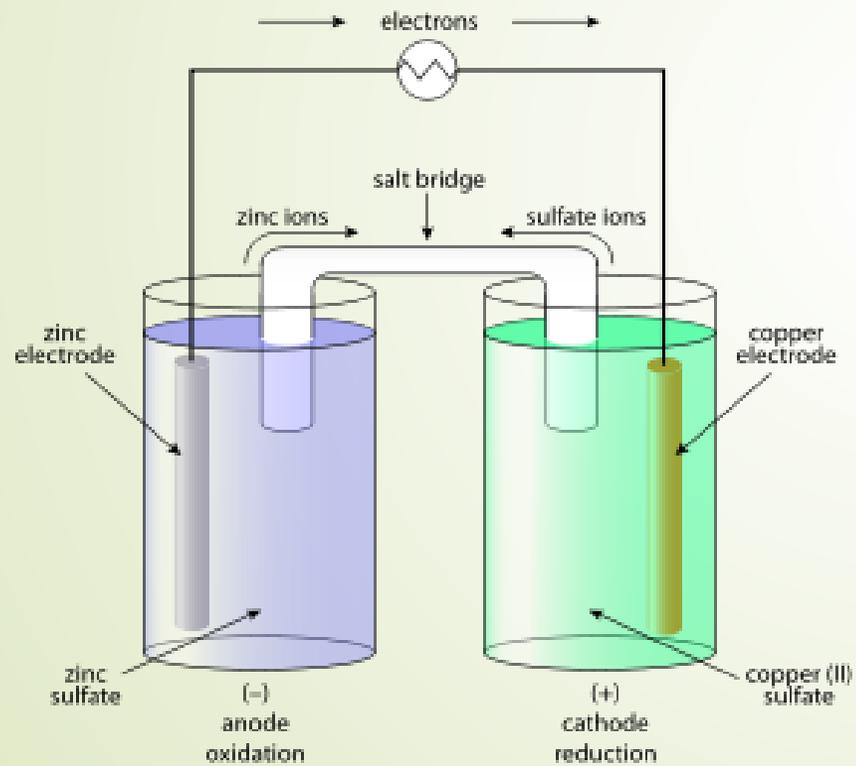
The cell can be represented as:



$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = E_{\text{Ag}^+ | \text{Ag}} - E_{\text{Cu}^{2+} | \text{Cu}}$$

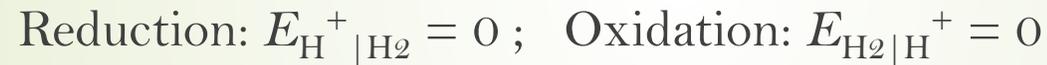


E.g.



Measurement of Electrode Potential

- The potential of individual half-cell cannot be measured.
- We can measure only the difference between the two half-cell potentials that gives the emf of the cell.
- If we arbitrarily choose the potential of one electrode (half-cell) then that of the other can be determined with respect to this.
- According to convention, a half-cell called standard hydrogen electrode is assigned a zero potential at all temperatures.

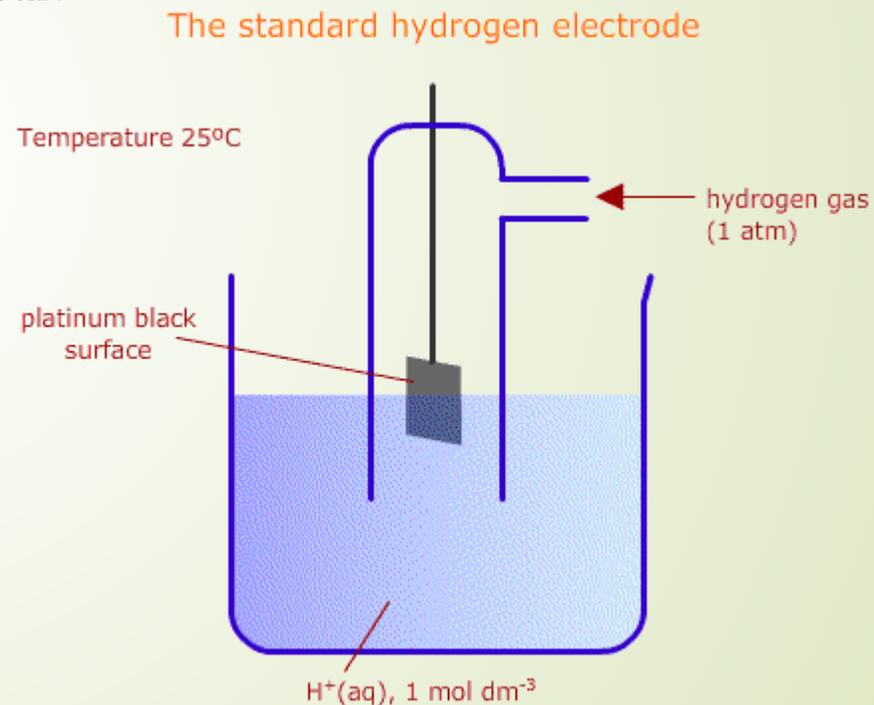


Standard Hydrogen Potential - Construction

- The standard hydrogen electrode consists of a platinum electrode coated with platinum black.
- The electrode is dipped in an acidic solution and pure hydrogen gas is bubbled through it.
- The concentration of both the reduced and oxidised forms of hydrogen is maintained at one molar & the pressure of hydrogen gas is one bar.



- At 298 K the emf of the cell, constructed by taking standard hydrogen electrode as anode (reference half-cell) and the other half-cell as cathode, gives the reduction potential of the other half-cell.



Using Standard Hydrogen Potential

- If the concentrations of the oxidized and the reduced forms of the species in the right hand half-cell are unity, then the cell potential is equal to standard electrode potential, E_R of the given half-cell.

$$E = E_R - E_L$$

As E_L for standard hydrogen electrode is zero, $E = E_R - 0 = E_R$

E.g. The measured emf of the cell: $\text{Pt(s)} \mid \text{H}_2(\text{g}, 1 \text{ bar}) \mid \text{H}^+(\text{aq}, 1\text{M}) \parallel \text{Cu}^{2+}(\text{aq}, 1\text{M}) \mid \text{Cu}$ is 0.34 V . It is also the value for the standard electrode potential of the half-cell corresponding to the reaction: $\text{Cu}^{2+}(\text{aq}, 1\text{M}) + 2\text{e}^- \rightarrow \text{Cu(s)}$

E.g. the measured emf of the cell: $\text{Pt(s)} \mid \text{H}_2(\text{g}, 1 \text{ bar}) \mid \text{H}^+(\text{aq}, 1 \text{ M}) \parallel \text{Zn}^{2+}(\text{aq}, 1\text{M}) \mid \text{Zn}$ is -0.76 V corresponding to the standard electrode potential of the half-cell reaction: $\text{Zn}^{2+}(\text{aq}, 1 \text{ M}) + 2\text{e}^- \rightarrow \text{Zn(s)}$

Note:

- The positive value of the standard electrode potential in the first case indicates that Cu^{2+} ions get reduced more easily than H^+ ions.
- The reverse process cannot occur, that is, hydrogen ions cannot oxidise Cu (or alternatively we can say that hydrogen gas can reduce copper ion) under the standard conditions described above. Thus, Cu does not dissolve in HCl.
- The negative value of the standard electrode potential in the second case indicates that hydrogen ions can oxidize zinc (or zinc can reduce hydrogen ions).
- **Metals like platinum** or gold are used as inert electrodes. They do not participate in the reaction but **provide their surface** for oxidation or reduction reactions and for the **conduction of electrons**.

Reduction potential values

- If the standard electrode potential of an electrode is greater than zero then its reduced form is more stable compared to hydrogen gas.
- Similarly, if the standard electrode potential is negative then hydrogen gas is more stable than the reduced form of the species.
- The standard electrode potential for fluorine is the highest indicating that fluorine gas (F_2) has the maximum tendency to get reduced to fluoride ions (F^-) and therefore fluorine gas is the strongest oxidising agent and fluoride ion is the weakest reducing agent.
- Lithium has the lowest electrode potential indicating that lithium ion is the weakest oxidising agent while lithium metal is the most powerful reducing agent in an aqueous solution.

Standard Reduction Potentials at 25 °C

	Reduction Half-Reaction	E° (V)	
Stronger oxidizing agent 	$F_2(g) + 2 e^- \longrightarrow 2 F^-(aq)$	2.87	Weaker reducing agent 
	$H_2O_2(aq) + 2 H^+(aq) + 2 e^- \longrightarrow 2 H_2O(l)$	1.78	
	$MnO_4^-(aq) + 8 H^+(aq) + 5 e^- \longrightarrow Mn^{2+}(aq) + 4 H_2O(l)$	1.51	
	$Cl_2(g) + 2 e^- \longrightarrow 2 Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e^- \longrightarrow 2 Cr^{3+}(aq) + 7 H_2O(l)$	1.33	
	$O_2(g) + 4 H^+(aq) + 4 e^- \longrightarrow 2 H_2O(l)$	1.23	
	$Br_2(aq) + 2 e^- \longrightarrow 2 Br^-(aq)$	1.09	
	$Ag^+(aq) + e^- \longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2 H^+(aq) + 2 e^- \longrightarrow H_2O_2(aq)$	0.70	
	$I_2(s) + 2 e^- \longrightarrow 2 I^-(aq)$	0.54	
	$O_2(g) + 2 H_2O(l) + 4 e^- \longrightarrow 4 OH^-(aq)$	0.40	
	$Cu^{2+}(aq) + 2 e^- \longrightarrow Cu(s)$	0.34	
	$Sn^{4+}(aq) + 2 e^- \longrightarrow Sn^{2+}(aq)$	0.15	
	$2 H^+(aq) + 2 e^- \longrightarrow H_2(g)$	0	
	$Pb^{2+}(aq) + 2 e^- \longrightarrow Pb(s)$	-0.13	
$Ni^{2+}(aq) + 2 e^- \longrightarrow Ni(s)$	-0.26		
$Cd^{2+}(aq) + 2 e^- \longrightarrow Cd(s)$	-0.40		
$Fe^{2+}(aq) + 2 e^- \longrightarrow Fe(s)$	-0.45		
$Zn^{2+}(aq) + 2 e^- \longrightarrow Zn(s)$	-0.76		
$2 H_2O(l) + 2 e^- \longrightarrow H_2(g) + 2 OH^-(aq)$	-0.83		
$Al^{3+}(aq) + 3 e^- \longrightarrow Al(s)$	-1.66		
$Mg^{2+}(aq) + 2 e^- \longrightarrow Mg(s)$	-2.37		
$Na^+(aq) + e^- \longrightarrow Na(s)$	-2.71		
$Li^+(aq) + e^- \longrightarrow Li(s)$	-3.04		
Weaker oxidizing agent			Stronger reducing agent

Uses of Electrochemical cells

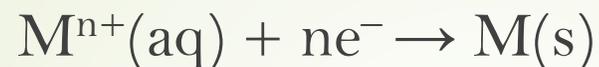
Electrochemical cells are extensively used for

1. Produce electricity
2. Determining the pH of solutions
3. Solubility product
4. Equilibrium constant and other thermodynamic properties
5. For potentiometric titrations

Exer. 1,2,3 & e.g

Nernst equation

- We had assumed that the concentration of all the species involved in the electrode reaction is unity. This need not be always true.
- Nernst showed that for the electrode reaction:



the electrode potential at any concentration measured with respect to standard hydrogen electrode can be represented by:

$$E_{(\text{M}^{n+}/\text{M})} = E_{(\text{M}^{n+}/\text{M})}^{\ominus} - \frac{RT}{nF} \ln \frac{[\text{M}]}{[\text{M}^{n+}]}$$

' R ' is gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$), ' F ' is Faraday constant (96487 C mol^{-1}), ' T ' is temperature in kelvin, ' n ' is no. of electrons and $[\text{M}^{n+}]$ is the concentration of the species, M^{n+} .

Nernst equation derivation

- For a general reaction of the type:



$$\Delta G = \Delta G^\circ + RT \ln Q$$

- In the cell only Electrical work done is done (no mechanical work is done).
- Electrical work done in one second is equal to electrical potential multiplied by total charge passed.

Work done , $W = -nFE_{(\text{cell})}$ [-ive as work is done by the system]

$$\Delta G = W = -nFE_{(\text{cell})}$$

Nernst equation: Daniel cell

In Daniell cell, the electrode potential for any given concentration of Cu^{2+} and Zn^{2+} ions,

$$E_{(\text{cell})} = E_{(\text{cell})}^{\ominus} - \frac{RT}{2F} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Cont.

By converting the natural logarithm in Equation to the base 10 and substituting the values of R , F and $T = 298 \text{ K}$.

$$E_{(\text{cell})} = E_{(\text{cell})}^{\ominus} - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

For a general electrochemical reaction of the type:



Nernst equation can be written as:

$$\begin{aligned} E_{(\text{cell})} &= E_{(\text{cell})}^{\ominus} - \frac{RT}{nF} \ln Q \\ &= E_{(\text{cell})}^{\ominus} - \frac{RT}{nF} \ln \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \end{aligned}$$

E.g

Equilibrium Constant from Nernst Equation

- If the circuit in Daniell cell is closed, reaction start taking place and as time passes, the concentration of Zn^{2+} keeps on increasing while the concentration of Cu^{2+} keeps on decreasing.
- At the same time voltage of the cell as read on the voltmeter keeps on decreasing.
- After some time, we shall note that there is no change in the concentration of Cu^{2+} and Zn^{2+} ions and at the same time, voltmeter gives zero reading. This indicates that equilibrium has been attained.
- In this situation the Nernst equation may be written as:

$$E_{(\text{cell})}^{\ominus} = \frac{2.303RT}{nF} \log K_C$$

Gibbs Energy of the Reaction

$$\Delta G = W = -nFE_{(\text{cell})}$$

Why voltage of battery doesn't drop after use?

Exer, e.g 3.6

Electrolytic solution

- An electrolyte solution is a solution that generally contains ions, atoms or molecules that have lost or gained electrons, and is electrically conductive.
- A **strong electrolyte** is a solute that completely, or almost completely, ionizes or dissociates in a solution. E.g NaCl, KCl, HCl
- A **weak electrolyte** is a solute that ionizes or dissociates negligibly in a solution. E.g CH_3COOH , ZnCl_2

Factors:

The conductivity of electrolytic (ionic) solutions depends on:

- (i) the nature of the electrolyte added
- (ii) size of the ions produced and their solvation
- (iii) the nature of the solvent and its viscosity
- (iv) concentration of the electrolyte
- (v) temperature (it increases with the increase of temperature).

Conductance of Electrolytic Solutions

- Conductance – Ease of flow of electric current through a body(metal or ionic solution).
- Resistance – Opposition to the flow of electric current through a body.
- The electrical resistance of any object is directly proportional to its length, L , and inversely proportional to its area of cross section, A .

$$\text{Resistance, } R = \rho L / A \text{ } (\Omega)$$

$$\text{Resistivity, } \rho = RA / L \text{ } (\Omega\text{m})$$

- Conductance, $G = \frac{1}{\text{Resistance}}$ and Conductivity, $k = \frac{1}{\text{Resistivity}}$

Units

Differences

Metallic Conductance	Electrolytic Conductance
1. Electrons are current carrier.	Ions are current carrier.
2. Happens in metal.	Happens in electrolytes.
3. Conductance decrease with increases in temp.	Conductance increases with increase in temp.
4. No change in chemical properties.	Chemical reaction takes place.
4. Does not involve transfer of matter	Involve transfer of ions in electrolyte
5. High conductivity	Low conductivity

Material	Conductivity/ S m ⁻¹	Material	Conductivity/ S m ⁻¹
Conductors		Aqueous Solutions	
Sodium	2.1×10 ³	Pure water	3.5×10 ⁻⁵
Copper	5.9×10 ³	0.1 M HCl	3.91
Silver	6.2×10 ³	0.01M KCl	0.14
Gold	4.5×10 ³	0.01M NaCl	0.12
Iron	1.0×10 ³	0.1 M HAc	0.047
Graphite	1.2×10	0.01M HAc	0.016
Insulators		Semiconductors	
Glass	1.0×10 ⁻¹⁶	CuO	1×10 ⁻⁷
Teflon	1.0×10 ⁻¹⁸	Si	1.5×10 ⁻²
		Ge	2.0

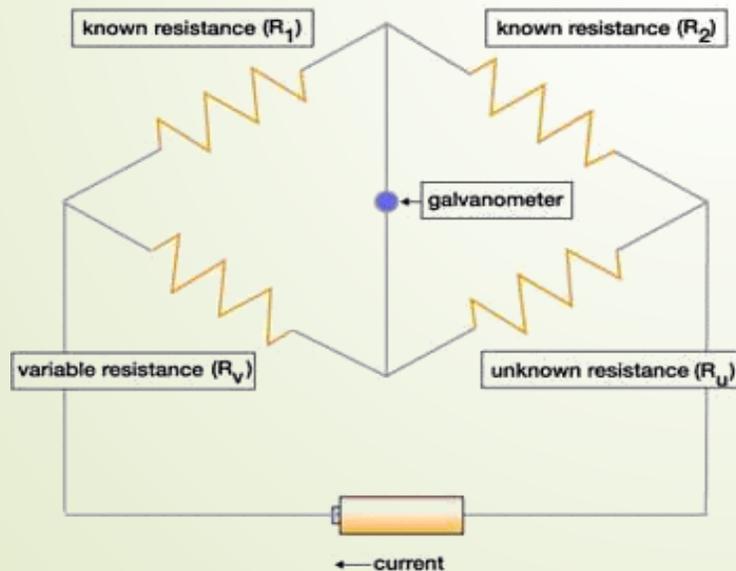
Measurement of the Conductivity of Ionic Solutions

- Measurement of an unknown resistance can be performed on a Wheatstone bridge.
- But for an ionic solution we face two problems:

Firstly, passing direct current (DC) changes the composition of the solution.

Secondly, a solution cannot be connected to the bridge like a metallic wire or other solid conductor.

- The first difficulty is resolved by using an alternating current (AC) source of power.
- Second problem is solved by using a specially designed vessel called conductivity cell.



Process

1. We find the cell constant, G^* , given by the equation:

$$G^* = \frac{L}{A} = R \kappa$$

2. Once the cell constant is determined, we can use it for measuring the resistance or conductivity of any solution. Unknown resistance $R = R_1 R_4 / R_3$

3. Once the cell constant and the resistance of the solution in the cell is determined, the conductivity of the solution is given by the equation:

$$\kappa = \frac{\text{cell constant}}{R} = \frac{G^*}{R}$$

Molar conductivity

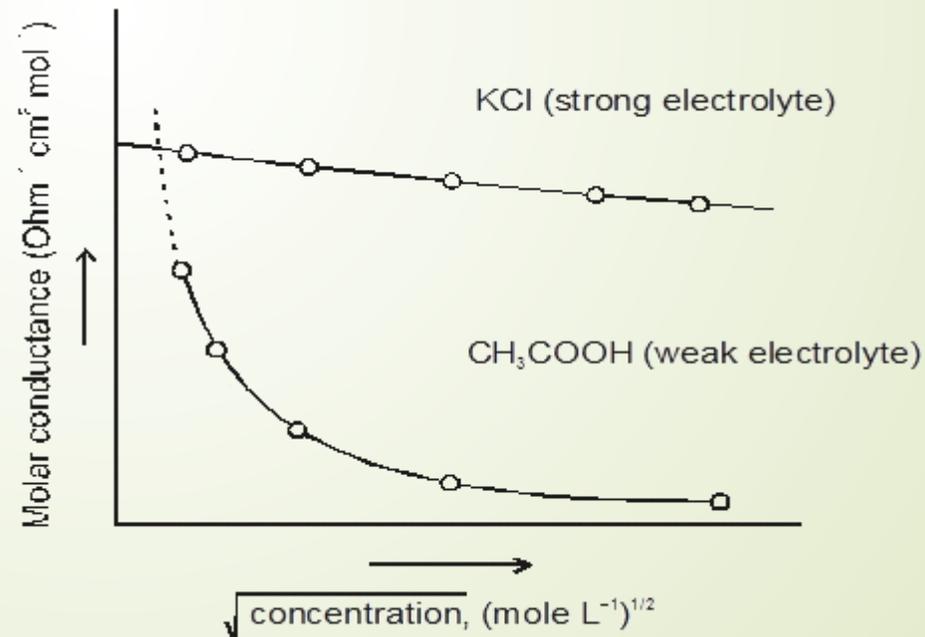
- The conductivity of solutions of different electrolytes in the same solvent and at a given temperature differs (due to charge and size of the ions, the concentration etc.).
- It is necessary to define a physically more meaningful quantity called molar conductivity denoted by the symbol Λ_m (Greek, lambda)

$$\text{Molar conductivity, } \Lambda_m = \kappa / c$$

- Molar conductivity increases with decrease in concentration. This is because the total volume, V , of solution containing one mole of electrolyte also increases.

Variation of Conductivity and Molar Conductivity with Concentration

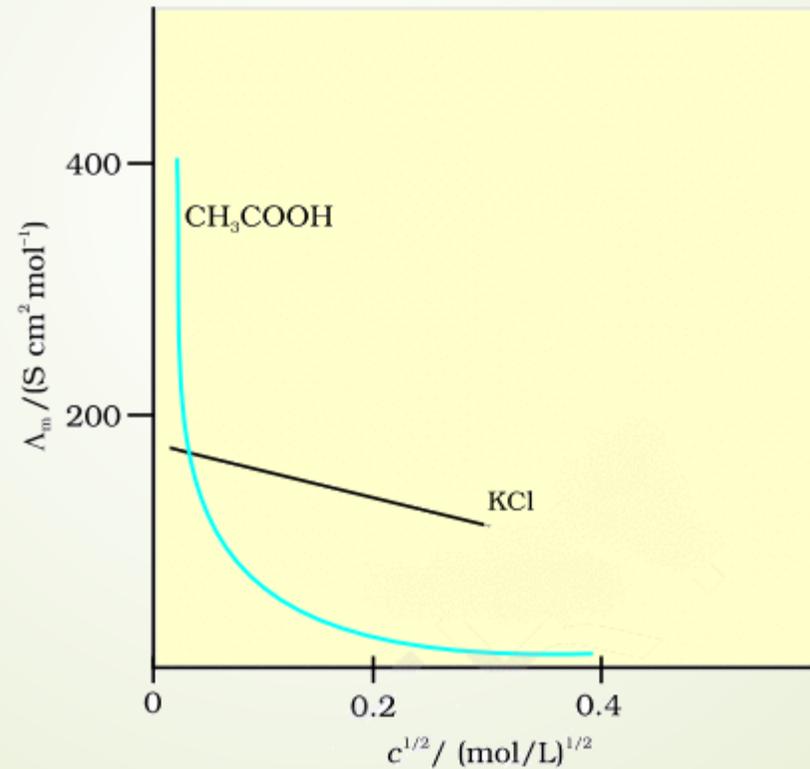
- Conductivity always **decreases with decrease in concentration** both, for weak and strong electrolytes, because the number of ions per unit volume that carry the current in a solution decreases on dilution.
- However, **molar conductivity** increases with dilution.
- As the total volume of solution containing one mole of electrolyte increases, the decrease in conductivity due to dilution is more than compensated by increase in its volume of solution that contains one mole of the electrolyte.



Limiting molar conductivity

When concentration approaches zero, the molar conductivity is known as limiting molar conductivity .

It is represented by the symbol Λ_m° .



Strong electrolytes

- For strong electrolytes, Λ_m increases slowly with dilution and can be represented by the equation:

$$\Lambda_m = \overset{\circ}{E}_m - A c^{1/2}$$

- We obtain a straight line with intercept equal to $\overset{\circ}{E}_m$ and slope equal to $-A$.
- The value of the constant A for a given solvent and temperature depends on the type of electrolyte i.e., the charges on the cation and anion produced on the dissociation of the electrolyte in the solution.
- Thus, NaCl, CaCl₂, MgSO₄ are known as 1-1, 2-1 and 2-2 electrolytes respectively. All electrolytes of a particular type have the same value for A .

- E.g.

Kohlrausch law of independent migration of ions(at infinite dilution)

- The limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.
- Thus, if $\lambda_{\text{Na}^+}^0$ and $\lambda_{\text{Cl}^-}^0$ are limiting molar conductivity of the sodium and chloride ions respectively, then the limiting molar conductivity for sodium chloride is given by the equation:

$$\Lambda_{m(\text{NaCl})}^0 = \lambda_{\text{Na}^+}^0 + \lambda_{\text{Cl}^-}^0$$

- In general, if an electrolyte on dissociation gives X cations and Y anions then its limiting molar conductivity is given by:

$$\Lambda_m^0 = X \lambda_+^0 + Y \lambda_-^0$$

Here, λ_+^0 and λ_-^0 are the limiting molar conductivities of the cation and anion respectively.

Weak electrolytes

- Weak electrolytes like acetic acid have lower degree of dissociation at higher conc. and hence for such electrolytes, the change in Λ_m with dilution is due to increase in the degree of dissociation and consequently the number of ions in total volume of solution that contains 1 mol of electrolyte.
- So \ddot{E}_m increases steeply on dilution, especially near lower concentrations. Therefore, \ddot{E}_m° cannot be obtained by extrapolation of Λ_m to zero concentration.
- At infinite dilution (i.e. 'c' \rightarrow zero) electrolyte dissociates completely ($\alpha = 1$), but at such low concentration the conductivity of the solution is so low that it cannot be measured accurately.
- Therefore, \ddot{E}_m° for weak electrolytes is obtained by using Kohlrausch law of independent migration of ions .
- At any concentration 'c', if ' α ' is the degree of dissociation then it can be approximated to the ratio of molar conductivity \ddot{E}_m at the concentration 'c' to limiting molar conductivity, \ddot{E}_m° .

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$$

Applications of Kohlrausch law

1. Find molar conductivity at infinite dilution, Λ_m° or Λ_m° .
2. Find dissociation constant, α .

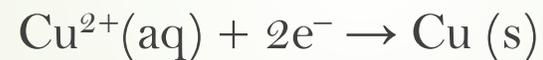
$$K_a = \frac{c\alpha^2}{(1-\alpha)} = \frac{c\Lambda_m^2}{\Lambda_m^{\circ 2} \left(1 - \frac{\Lambda_m}{\Lambda_m^\circ}\right)} = \frac{c\Lambda_m^2}{\Lambda_m^\circ (\Lambda_m^\circ - \Lambda_m)}$$

Electrolytic Cells and Electrolysis

- In an electrolytic cell external source of voltage is used to bring about a chemical reaction.
- For a non-spontaneous reaction (ΔG is +ive), external energy has to be supplied.

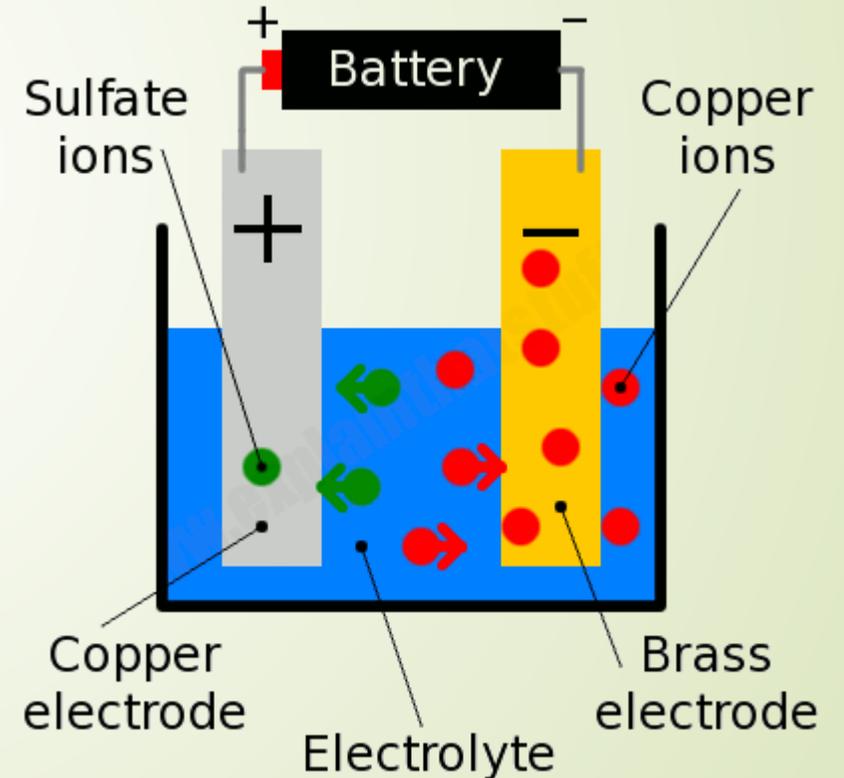
animation

E.g. At the anode, copper is converted into Cu^{2+} ions by the reaction:



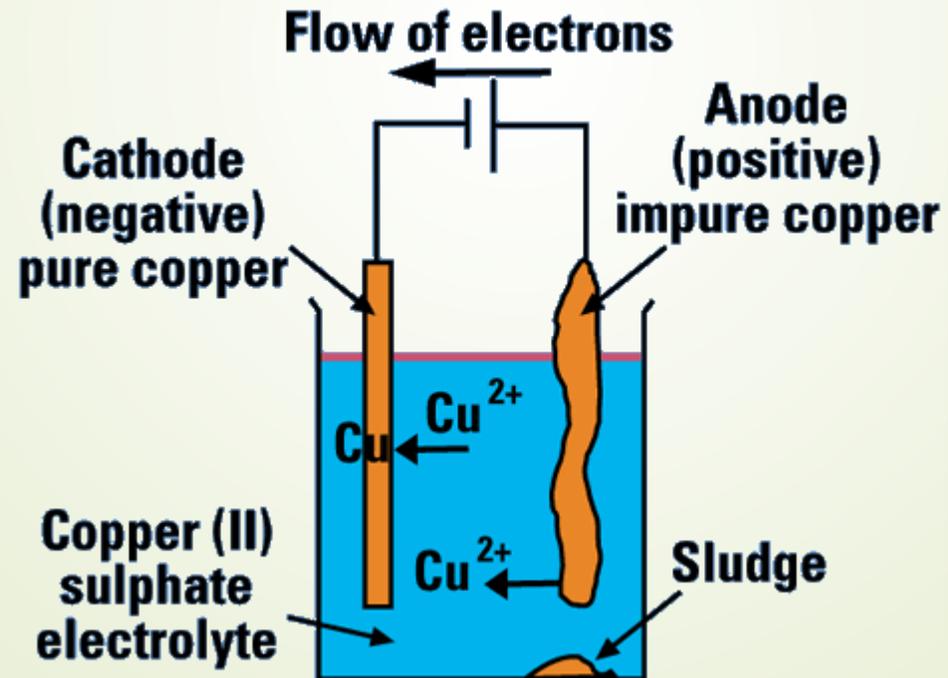
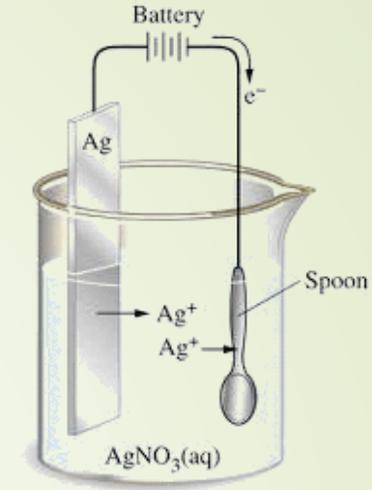
Copper metal is deposited on the cathode.

Thus copper is dissolved (oxidised) at anode and deposited (reduced) at cathode.



Applications:

1. Electrotyping
2. Purification of metal
3. Electroplating



Faraday's law of Electrolysis (Quantitative Aspect)

- (i) First Law: Amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt).
- (ii) Second Law: Amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights (Atomic Mass of Metal \div Number of electrons required to reduce the cation).

$$Q = i \times t \text{ (} Q \text{ is in coulombs when 'i' is in ampere and 't' is in second).}$$

The amount of electricity (or charge) required for oxidation or reduction depends on the stoichiometry of the electrode reaction.

For e.g. in the reaction:



One mole of the electron is required for the reduction of one mole of silver ions.

- For the electrode reactions:



- It is obvious that one mole of Mg^{2+} and Al^{3+} require 2 mol of electrons (2F) and 3 mol of electrons (3F) respectively.
- In commercial production of metals, current as high as 50,000 amperes are used that amounts to about 0.518 F per second.

E.g.

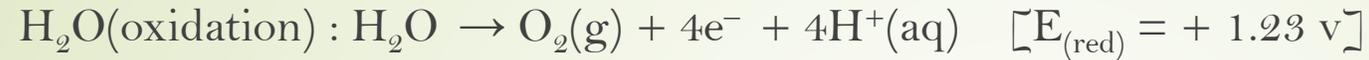
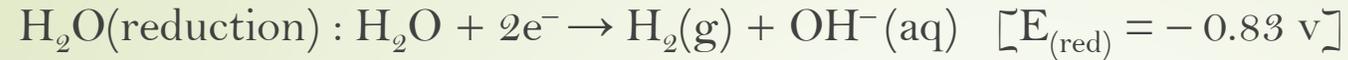
Products of electrolysis

- Products of electrolysis depend on:
 - the type of electrodes being used
 - the nature of material being electrolysed
- If the electrode is inert (e.g., platinum or gold), it does not participate in the chemical reaction and acts only as source or sink for electrons.
- The products of electrolysis depend on the different oxidizing and reducing species present in the electrolytic cell and their standard electrode potentials.

Cathode(reduction) – higher +ive potential of reduction potential will be chosen (or more –ive potential of oxidation potential)

Anode(oxidation) – lower +ive potential of reduction potential will be chosen (or more –ive potential of oxidation potential)

Water reduction/oxidation:



Overpotential

- Some of the electrochemical processes although feasible, are so slow kinetically that at lower voltages these do not seem to take place.
- Hence extra potential (called overpotential) has to be applied, which makes such reaction (process) relatively more difficult to occur . E.g. $\text{H}_2\text{O}(\text{oxid}) : [E_{(\text{oxid})} = -1.8 \text{ v}]$

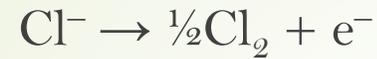
Examples

1. Molten NaCl -

Here we have only one cation (Na^+) which is reduced at the cathode



and one anion (Cl^-) which is oxidised at the anode

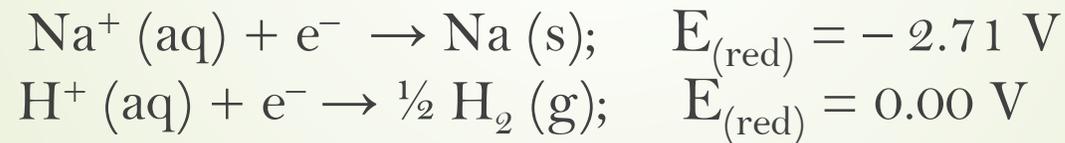


Hence the products of electrolysis are sodium metal and Cl_2 gas.

2. Aqueous NaCl solution -

In this case besides Na^+ and Cl^- ions we also have H^+ and OH^- ions along with the solvent molecules, H_2O .

At the cathode there is competition between the following reduction reactions:

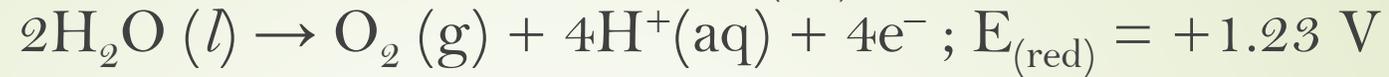
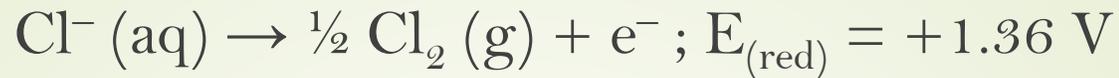


The reaction with higher value of E is preferred.

But H^+ (aq) is produced by the dissociation of H_2O : $\text{H}_2\text{O} (\text{l}) \rightarrow \text{H}^+ (\text{aq}) + \text{OH}^- (\text{aq})$

Therefore, the net reaction at the cathode : $\text{H}_2\text{O} (\text{l}) + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2(\text{g}) + \text{OH}^-$

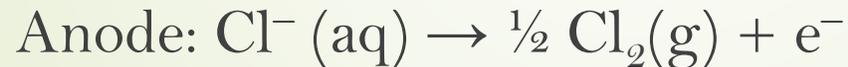
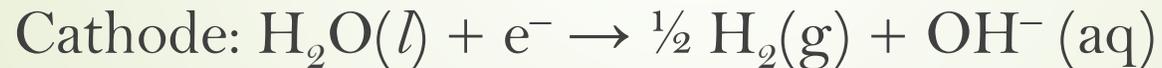
At the anode the following oxidation reactions are possible:



The reaction at anode with lower value of E is preferred and therefore, water should get oxidised in preference to $\text{Cl}^-(\text{aq})$.

However, on account of overpotential of oxygen, 1st reaction is preferred.

The net reactions may be summarised as:

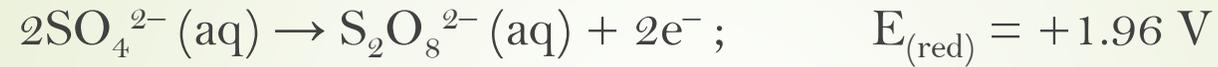


Net reaction:



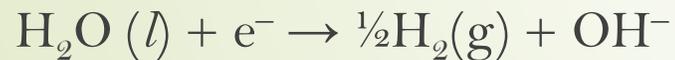
3. Electrolysis of H_2SO_4

The following processes are possible **at the anode**:



For dilute sulphuric acid, reaction 1st is preferred but at higher concentrations of H_2SO_4 , 2nd reaction is preferred.

At the cathode



Electrochemistry: Applications

1. Refining of metals
2. Extraction of active metals
3. Production of gases such as H_2 , O_2 , Cl_2 etc.
4. Electroplating
5. Electrotyping

Difference

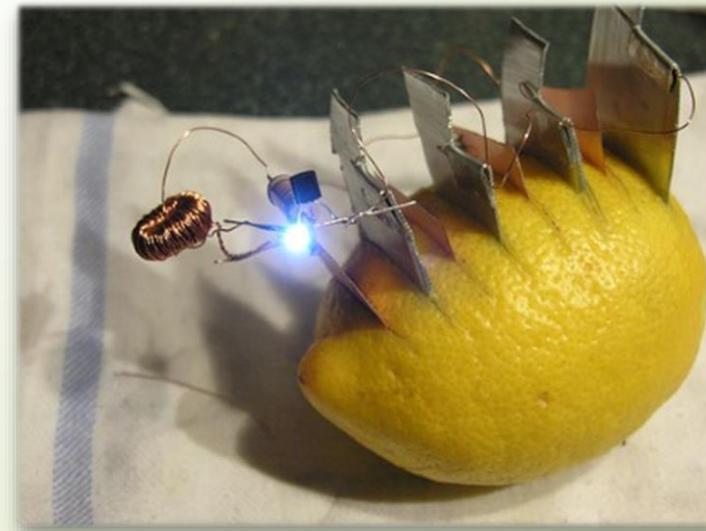
Galvanic cell	Electrolytic cell
1. Device to convert chemical energy to electrical energy	Device to convert electrical energy to chemical energy
2. Work is done by the cell	Work is done on the cell
3. Free energy of the system decrease $\Delta G < 0$	Free energy of the system increase $\Delta G > 0$
4. 2 electrodes are in separate half-cell	2 electrodes are in same cell
5. Reduction@ Cathode, Oxidation@ anode	same
6. Cathode bears +ive charge	Cathode bears -ive charge
7. Use in energy generation	Used in electrolysis, electroplating, refining of metals

Batteries

One or more than one cell connected in series(a galvanic cell) where the chemical energy of the redox reaction is converted into electrical energy.

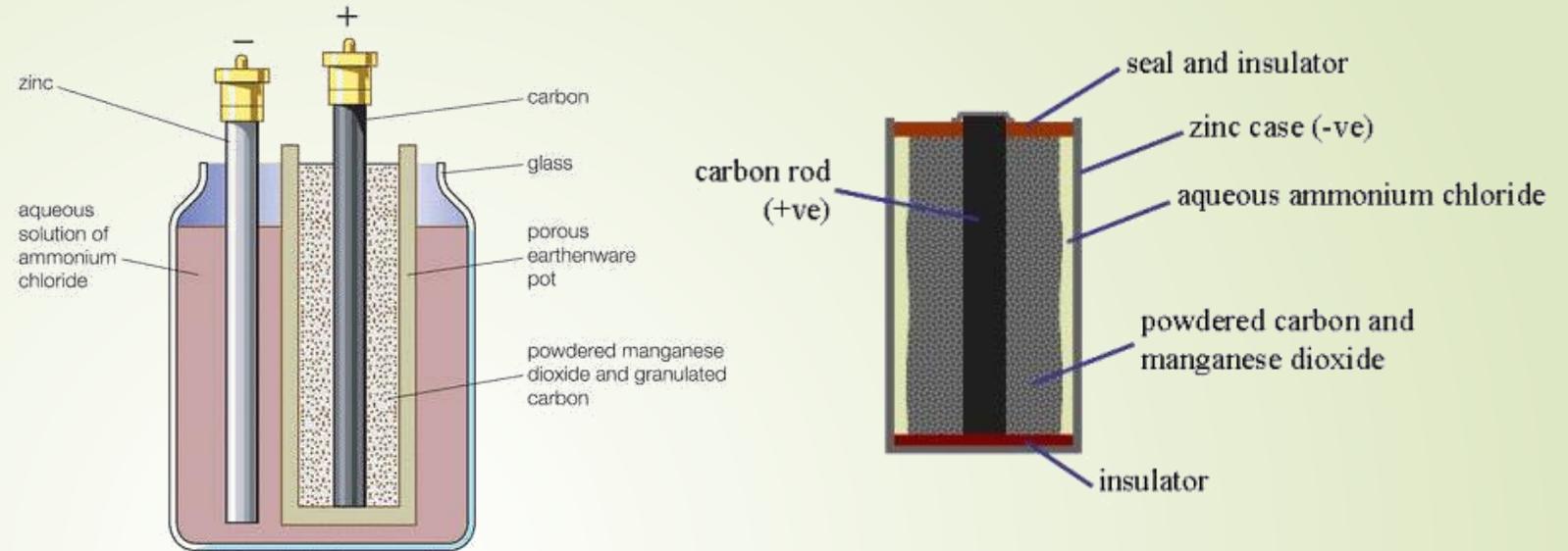
A battery should have the following advantages:

1. Reasonably light
2. Compact
3. Its voltage should not vary over use
4. Rechargeable
5. Last longer
6. Less environment pollution
7. Should be easily disposal after use



Battery types

- **Primary** – single use
- **Secondary**– Rechargable



Primary Cell:

- The most familiar example of this type is the **dry cell** (known as **Leclanche cell** after its discoverer) which is used commonly in our transistors and clocks.
- The cell consists of a zinc container that also acts as anode and the cathode is a carbon (graphite) rod surrounded by powdered manganese dioxide and carbon.

Leclanche cell

- The space between the electrodes is filled by a moist paste of ammonium chloride (NH_4Cl) and zinc chloride (ZnCl_2). The electrode reactions are complex, but they can be written approximately as follows :



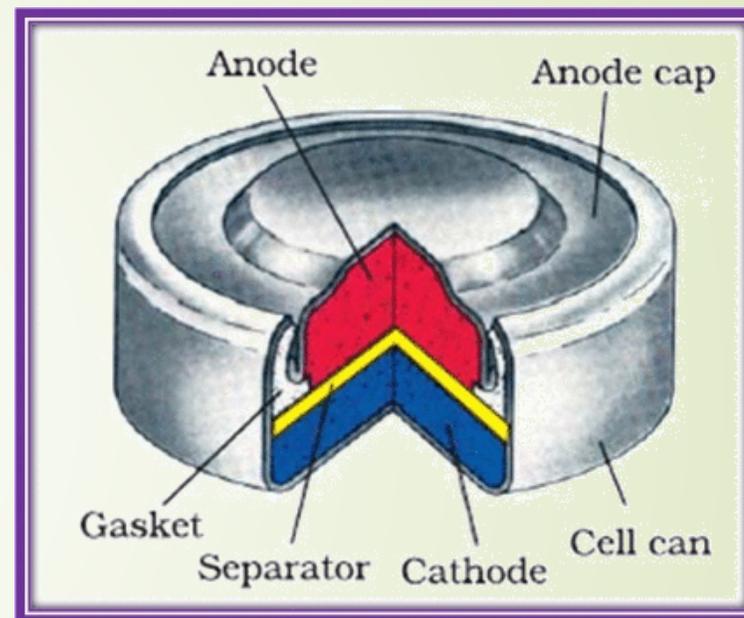
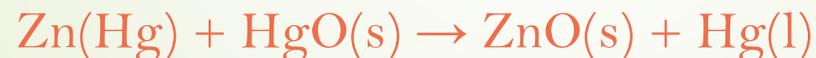
- In the reaction at cathode, manganese is reduced from the + 4 oxidation state to the +3 state.
- Ammonia produced in the reaction forms a complex with Zn^{2+} to give $[\text{Zn}(\text{NH}_3)_4]^{2+}$.
- The cell has a potential of nearly 1.5 V.

Mercury cell

- Suitable for low current devices like hearing aids, watches, etc. consists of zinc – mercury amalgam as anode and a paste of HgO and carbon as the cathode.
- The electrolyte is a paste of KOH and ZnO.
- The electrode reactions for the cell are given below:



The overall reaction is represented by :

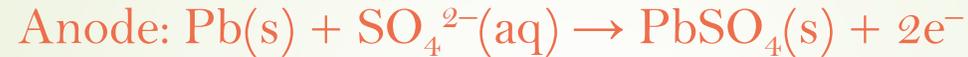


- The cell potential is approximately 1.35 V and remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its life-time.

Secondary cells

- A good secondary cell can undergo a large number of discharging and charging cycles. E.g. lead storage battery used in automobiles and invertors.
- It consists of a lead anode and a grid of lead packed with lead dioxide (PbO_2) as cathode. A 38% solution of sulphuric acid is used as an electrolyte.

- The cell reactions when the battery is in use are given below:



- Overall cell reaction consisting of cathode and anode reactions is:



- On charging the battery the reaction is reversed and $\text{PbSO}_4(s)$ on anode and cathode is converted into Pb and PbO_2 , respectively.

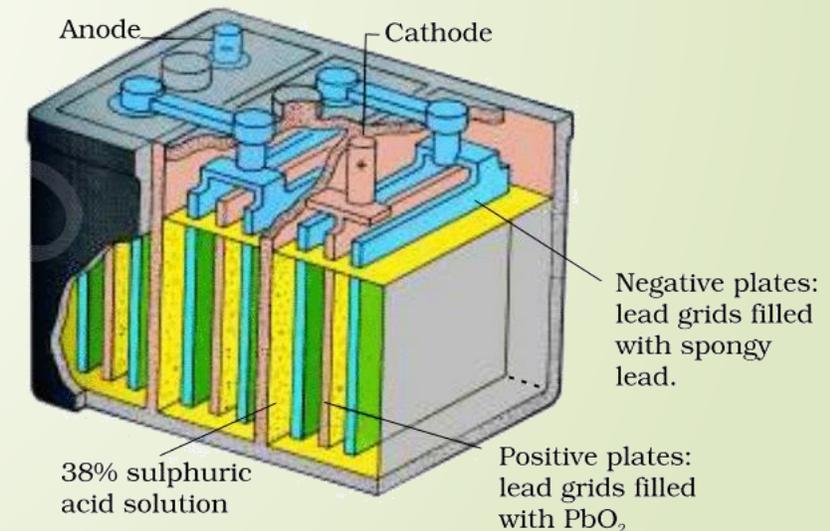


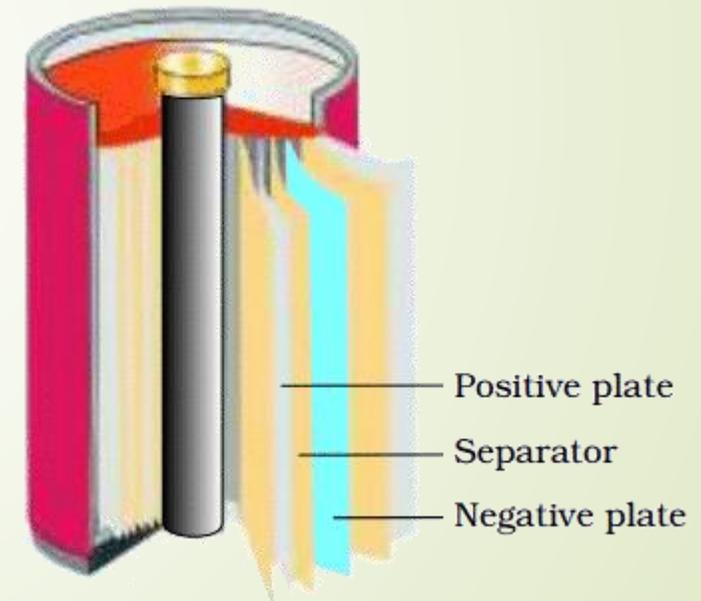
Fig. 3.10: The Lead storage battery.

Nickel-Cadmium Battery

- Another important secondary cell is the nickel-cadmium cell which has longer life than the lead storage cell but more expensive to manufacture.
- The overall reaction during discharge is:



- A rechargeable nickel-cadmium cell in a jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydroxide.

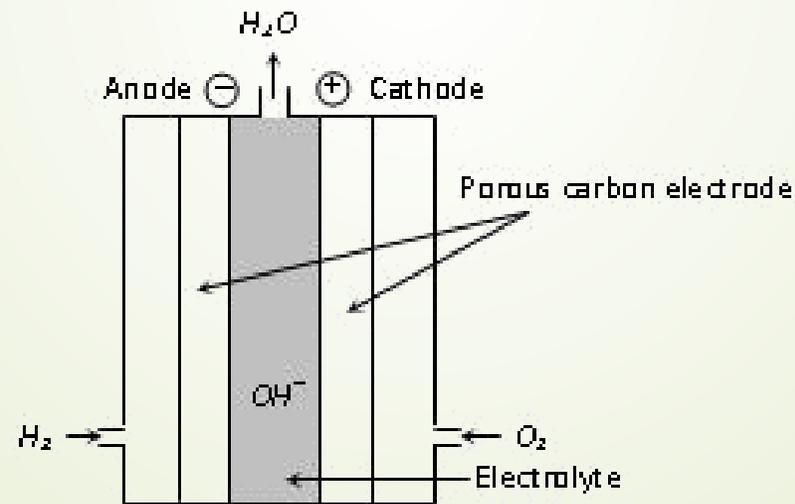


Fuel Cells

- Production of electricity by thermal plants is not a very efficient method and a source of pollution.
- In such plants, the chemical energy (heat of combustion) of fossil fuels (coal, gas or oil) is first used for converting water into high pressure steam, to run a turbine to produce electricity.
- We know that a galvanic cell directly converts chemical energy into electricity and is highly efficient.
- Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called Fuel cells.

Hydrogen- Oxygen fuel cell

- The cell was used for providing electrical power in the Apollo space programme. The water vapours produced during the reaction were condensed and added to the drinking water supply for the astronauts.
- In the cell, hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution.
- Catalysts like finely divided platinum or palladium metal are incorporated into the electrodes for increasing the rate of electrode reactions.



Cont.

- The electrode reactions are given below:



Overall reaction being:



- The cell runs continuously as long as the reactants are supplied.
- Fuel cells produce electricity with an efficiency of about 70 % compared to thermal plants whose efficiency is about 40%.
- These have been used in automobiles on an experimental basis.



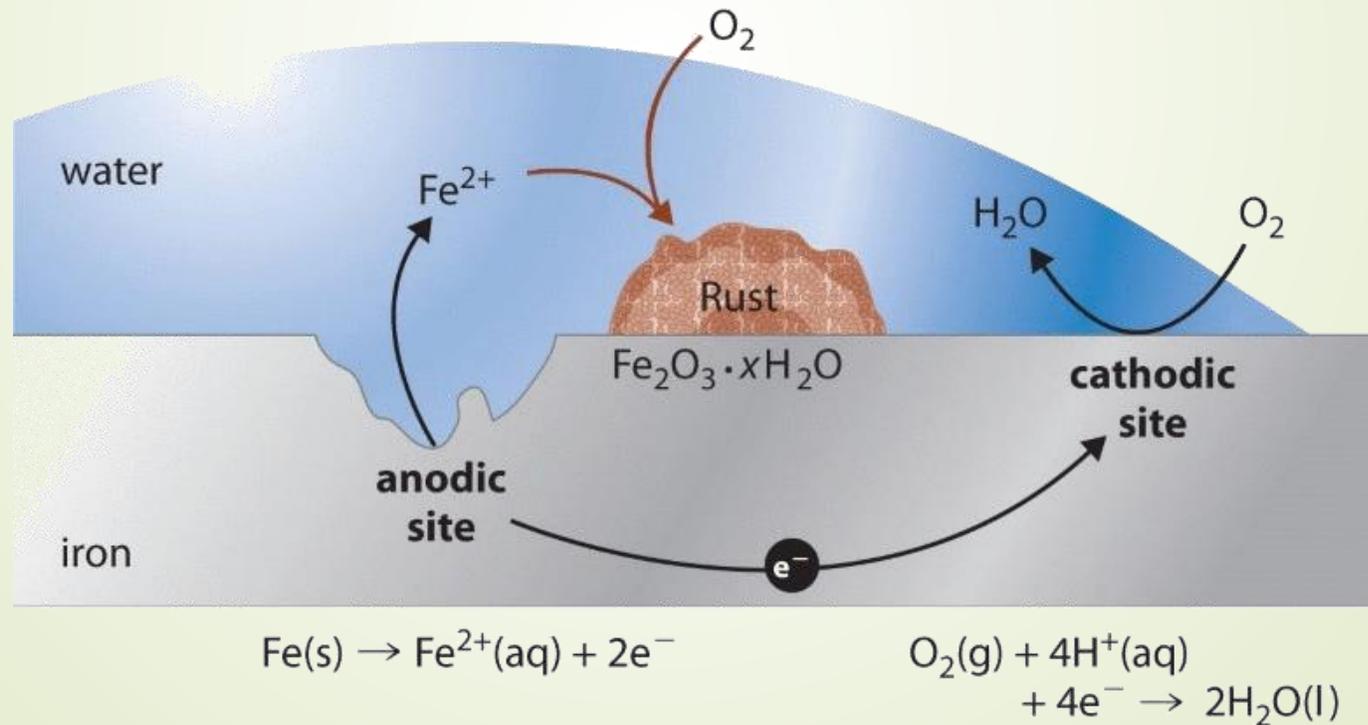
Corrosion

- Corrosion slowly coats the surfaces of metallic objects with oxides or other salts of the metal.
- The rusting of iron, tarnishing of silver, development of green coating on copper and bronze are some of the examples of corrosion.
- We lose crores of rupees every year on account of corrosion.
- In corrosion, a metal is oxidised by loss of electrons to oxygen and formation of oxides.



Corrosion : as a electrochemical process

- Corrosion of iron (commonly known as rusting) occurs in presence of water and air.
- At a particular spot of an object made of iron, oxidation takes place and that spot behaves as anode and we can write the reaction:

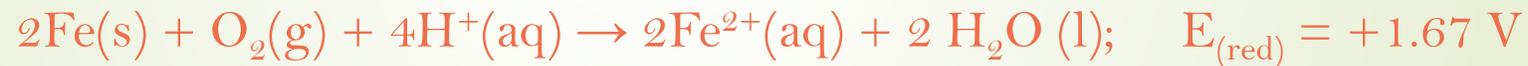


Cont.

- Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce O_2 in presence of H^+ (which is believed to be available from H_2CO_3 formed due to dissolution of carbon dioxide from air into water).
- Hydrogen ion in water may also be available due to dissolution of other acidic oxides from the atmosphere). This spot behaves as cathode with the reaction:



The overall reaction being:



- The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide ($Fe_2O_3 \cdot x H_2O$) and with further production of hydrogen ions.

Prevention of corrosion

Prevention of corrosion is of prime importance. It not only saves money but also helps in preventing accidents such as a bridge collapse or failure of a key component due to corrosion.

- One of the simplest methods of preventing corrosion is to prevent the surface of the metallic object to come in contact with atmosphere.
 - This can be done by covering the surface with paint or by some chemicals (e.g. bisphenol).
 - Another simple method is to cover the surface by other metals (Sn, Zn, etc.) .
- An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn, etc.) which corrodes itself but saves the object.

