Electrochemistry (BASIC INTRODUCTION)

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- **Electrolysis**
- **Faraday’s laws of electrolysis**
- **Conductance (Molar, specific and equivalent)**
- **Weak and strong electrolytes**
- **Kohlraush’s law**

- An electrolytic cell is an electrochemical cell that drives a non-spontaneous redox reaction through the application of electrical energy. They are often used to decompose chemical compounds, in a process called electrolysis—the Greek word lysis means to break up.
- An electrolytic cell has three component parts: an electrolyte and two electrodes (a cathode and an anode). The electrolyte (solution of water or other solvents in which ions are dissolved. Molten salts such as sodium chloride are also electrolytes. When driven by an external voltage applied to the electrodes, the ions in the electrolyte are attracted to an electrode with the opposite charge, where charge-transferring (also called faradaic or redox) reactions can take place. Only with an external electrical potential (i.e., voltage) of correct polarity and sufficient magnitude can an electrolytic cell decompose a normally stable, or inert chemical compound in the solution.
- In an electrolytic cell the negative electrode is called cathode and the positive electrode is called anode.

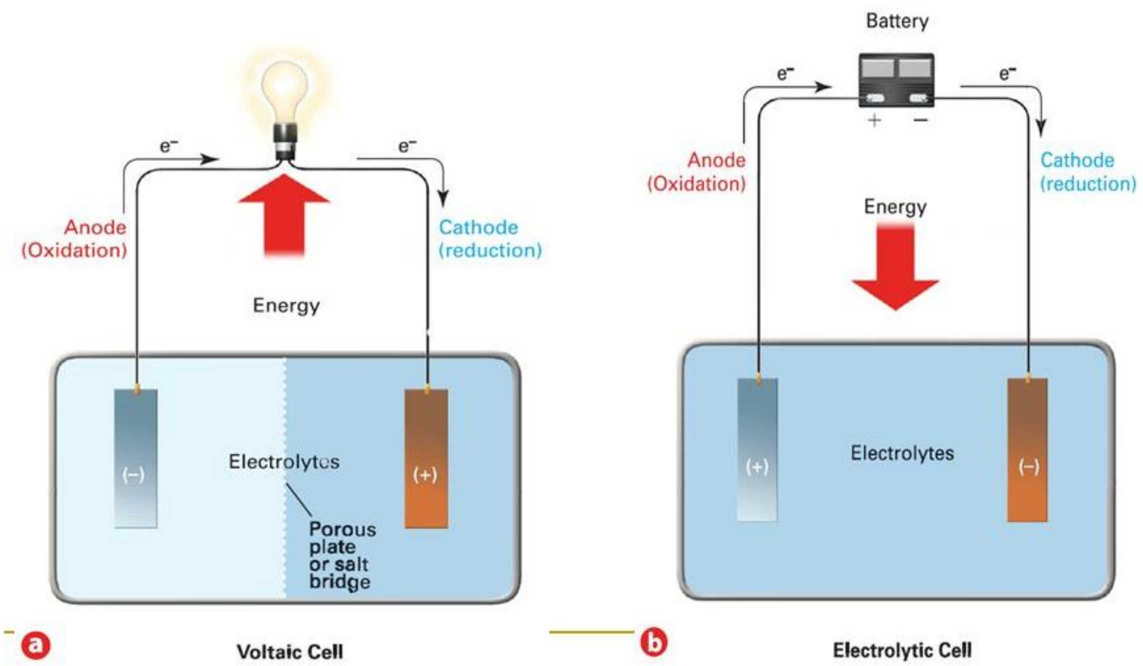


Image source: http://slideplayer.com/slide/8016149/25/images/12/Voltaic+Cells+-vs-+Electrolytic+Cells.jpg

Faraday's Law of electrolysis

1. The mass of elements produced at an electrode is proportional to the quantity of electricity Q passed through the solution. The SI unit of Q is Coulomb (C). The quantity of electricity can be expressed as :

Q= It (I is the current in Ampere and t is time in seconds)

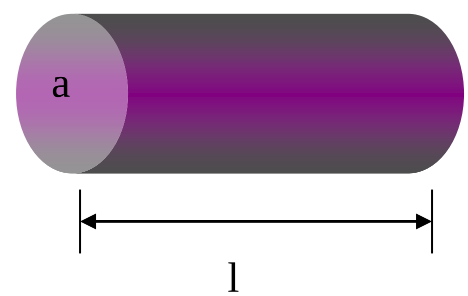
2. The mass of the element liberated at an electrode is proportional to the equivalent weight of the element.

Resistance

Resistance refers to the opposition to the flow of current.

For a conductor of uniform cross section(a) and length(l); Resistance R,

$$R \propto l \quad \text{and} \quad R \propto \frac{l}{a} \qquad \therefore R = \rho \frac{l}{a}$$



Where ρ is called resistivity or specific resistance.

ρ

Conductance

The reciprocal of the resistance is called conductance. It is denoted by C.

C=1/R

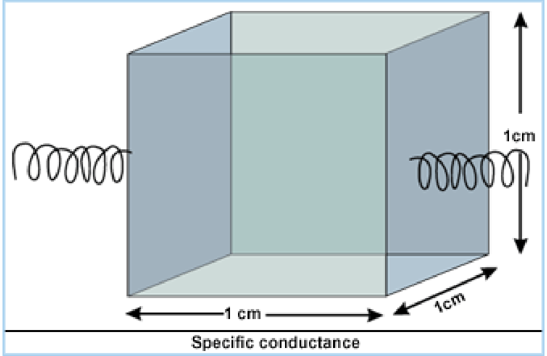
- **Conductors allows electric current to pass through them. Examples are metals, aqueous solution of acids, bases and salts etc. Unit of conductance is ohm^{-1} or mho or Siemen(S).**
- **Insulators do not allow the electric current to pass through them. Examples are pure water, urea, sugar etc.**

Specific Conductance

Conductance per unit volume of cell is known as specific conductance.

$$\therefore K = \frac{\ell}{a.R}$$

l/a is known as cell constant



Unit of specific conductance is ohm^{-1}cm^{-1}

SI Unit of specific conductance is **Sm^{-1}** where S is Siemen

Equivalent Conductance

It is the conductance of one gram equivalent of the electrolyte dissolved in V cc of the solution.

Equivalent conductance is represented by λ.

$$\lambda = \kappa \text{ x } V$$

$$\lambda = \frac{\kappa \; x \; 1000}{Normality}$$

Molar conductance

It is the conductance of a solution containing 1 mole of the electrolyte in V cc of solution. it is represented as m.

$$\mu = k \times V$$

$$\mu = \kappa \text{ x } 1000/M$$

Where V = volume solution in cc

μ = Molar conductance

κ = Specific conductance

M=molarity of the solution.

Relation between equivalent conductivity and molar conductivity

Molar conductivity = n- factor x equivalent conductivity

Electrolytes

Substances whose solution in water conducts electric current. Conduction takes place by the movement of ions.

Examples are salts, acids and bases.

Substances whose aqueous solution does not conduct electricity are called non electrolytes.

Examples are solutions of cane sugar, glucose, urea etc.

Types of Electrolytes

Strong electrolyte are highly ionized in the solution.

Examples are HCl, H_2SO_4, NaOH, KOH etc

Weak electrolytes are only feebly ionized in the solution.

Examples are H_2CO_3, CH_3COOH, NH_4OH etc

Difference between electronic & electrolytic conductors

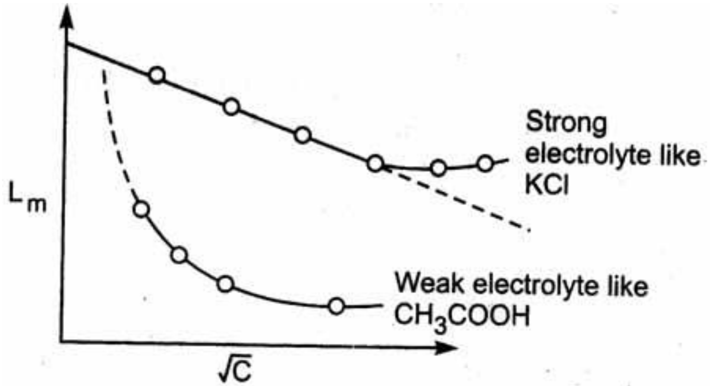
Electronic conductors	Electrolytic conductors
(1) Flow of electricity take place without the decomposition of substance.	(1)Flow of electricity takes place by the decomposition of the substance.
(2) Conduction is due to the flow of electron	(2) Flow of electricity is due to the movement of ions
(3) Conduction decreases with increase in temperature	(3) Conduction increases with increase in temperature

Effect of Dilution on Conductivity

Specific conductivity decreases on dilution.

Equivalent and molar conductance both increase with dilution and reaches a maximum value.

The conductance of all electrolytes increases with temperature.



http://www.sciencehq.com/wp-content/uploads/effect-of-dilution.jpg

Kohlrausch's Law

"Limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte."

$$\lambda_{\infty} = \lambda_a + \lambda_c$$

Where λ_a and λ_c are known as ionic conductance of anion and cation at infinite dilution respectively.

Application of Kohlrausch's law

1. **It is used for determination of degree of dissociation of a weak electrolyte.**

$$\alpha = \frac{\lambda_v}{\lambda_\infty}$$

Where, λ^{∞} **represents equivalent conductivity at infinite dilution.**

λ_v **represents equivalent conductivity at dilution v.**

2. **For obtaining the equivalent conductivities of weak electrolytes at infinite dilution.**