Ohm's Law

Ohms law discovered in 1825 state that the quantity of electricity flowing per second is determined by the difference in potential applied across the conductor and by the resistance offered by the conductor to the current .

E = I x R

Voltage = Current x Resistance

Georg Simon Ohm

Volts = Amperes x Ohms

Where : I is the current flow through a resistance R under applied potential E .

$$I \alpha E$$

$$I \alpha \frac{1}{R}$$

The electrolytic solutions like metallic conductors obey Ohm's law

Some definition of electrical unit

Ampere (amp) : is the invariable current of such strength that on passage through a water solution of silver nitrate it will deposit 1.118 mg of silver in 1.0 sec . Or ; Ampere is the amount of current produced by the force of one volt acting through a resistance of one ohm .

Ohm : is the resistance at $0.0^{o}C$ of a column of mercury of uniform cross section 106.3 cm long and containing 14.4521 g of mercury . Or ; is the electrical resistance between two point of a conductor when a constant potential difference of one volt applied and produces a current of one ampere .

Volt : is the potential difference required to send a current of 1.0 amp through a resistance of 1.0 ohm .

Coulomb : is the quantity of electricity transported by a current of 1.0 amp in 1.0 sec Since the quantity of electricity carried by a current must equal rate of transport times the time , the charge Q carried by a current (I) in (t) sec must be :

$$Q = I \cdot t$$

Faraday : is equal to 96490 absolute coulombs .

Electrical work (w) performed when a current of strength (I) passes for (t) sec through a resistance across which the potential drop (E) is given by Joule's law .

$$w = E.\,Q \rightarrow w = E.I.t$$

Joule : is the electrical unit of energy and is defined as the amount of work performed by a current of 1.0 amp flowing for 1.0 sec under a potential drop of 1.0 volt .

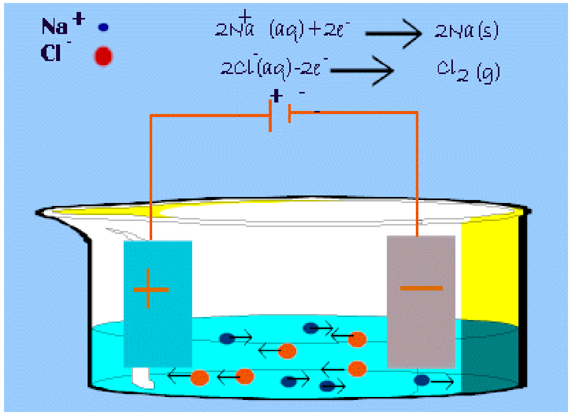
$$1.0 \text{ joule} = 1*10^{7} \text{ ergs} = 0.239 \text{ cal}$$

Watts :is a measure of power P , it is work performed at the rate of 1.0 joule per sec .or , is the rate at which work is done when one ampere of current flows through an electrical potential difference of one volt (1.0 w = 1.0 V.A)

$$P = E\,.Q \;/\; t$$

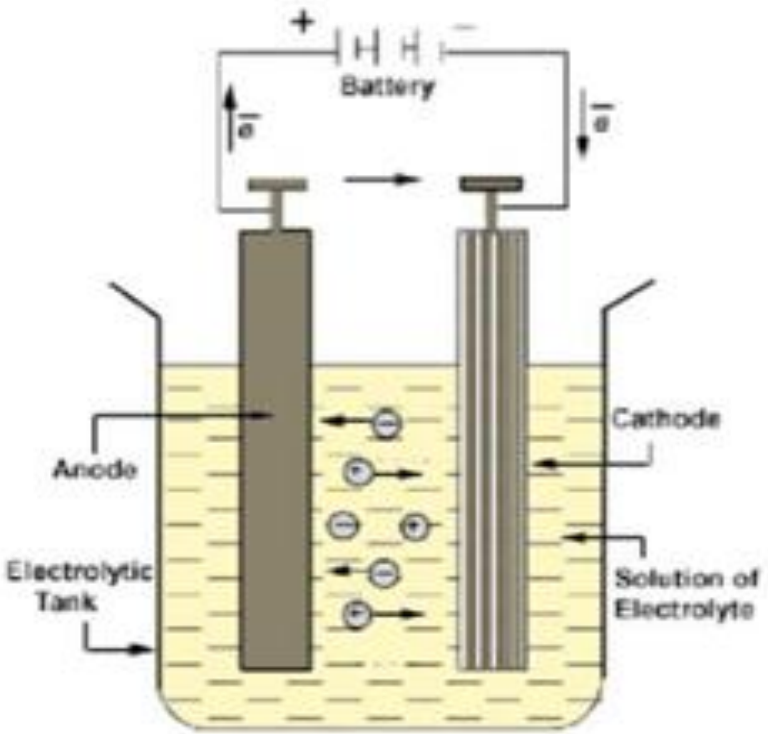
Ions : consist of atoms or group of atoms which have lost or gained electrons thus acquiring positive or negative charge respectively . The application of an electrical potential causes these charged particle of matter move , the positive ions in the direction of the current and the negative ions in the opposite direction .

Electrolytes : A solution in water or other solvents conduct electricity . Such solution exhibit the colligative behaviour (elevation boiling point , lowering freezing point , vapour pressure lowering and osmotic pressure) of solution of electrolytes all are higher than the corresponding effects for solution of non electrolytes of the same total concentration .



Electrolysis

The process of decomposition of an electrolyte by the passage of electricity is called electrolysis. In electrolysis electrical energy is used to cause a chemical reaction.



Classification of electrolytes :

Electrolytes can be classified to strong electrolytes (a solution which have a high degree of dissociation and are good conductance) , and weak electrolytes (exhibits poor conductance low degree of dissociation)

-Strong electrolytes can be subdivided to :

(1-1) type ; ex : HC l , NaCl .

(1-2) type ; ex : K_2SO_4 , H_2SO_4 .

(2-1) type ; ex : $Mg(NO_3)_2$, $BaCl_2$.

(2-2) type ; ex : $MgSO_4$, $CuSO_4$.

(3-1) type ; such as potassium ferricyanied $K_3Fe(CN)_6$

Theory of electrolytic dissociation :

The colligative properties of electrolytes and the fact that solution of electrolytes conduct electricity led S. Arrhenius to propose in 1887 his theory of electrolytic dissociation .

Arrhenius postulated that electrolytes in solution are dissociated into electrically charged particles , called ions in such a manner that the total charge on the positive ions is equal to the total charge on the negative ions . The net result is , therefore , that the solution as a whole is neutral in spite of the presence of electrically charged particles in it .

Arrhenius pointed out further that an electrolyte in solution need not necessarily be completely dissociated into ions; instead it may be only partially dissociated to yield ions in equilibrium with unionized molecules of the substance . It may then be anticipated from the laws of chemical equilibrium that the extent of dissociation will vary with concentration, becoming greater as the concentration of dissolved substance becomes lower.

In view of this , complete dissociation may be expected to take place only in infinitely dilute solutions .

$$AB \leftrightarrow A^{+} + B^{-}$$

At finite concentration the electrolyte will be only partially ionized to a degree dependent on the nature of the substance and the concentration .

The idea of partial electrolytic dissociation was employed by Arrhenius to explain the colligative behaviour of solutions of electrolytes .

colligative properties of dilute solution depend on the number of particles , irrespective of kind . When a substance in solution dissociates into ions , the number of particles in solution is increased , so there is an increase in the colligative effects .

In terms of this theory any observed values (for example) of molal F.P depressions higher than for a nonelectrolyte and lower than the limits of complete dissociation are be accounted for partial dissociation of the electrolyte , so it is possible to calculate the degree of ionization of an electrolyte .

The values of α (degree of ionization) obtained by this method agree quite well for weak electrolytes , but for strong electrolytes the agreement is not what is to be expected from the measurements .

The Arrhenius interpretation concentrate about number of ions and he ignore the mobility of ions.

The Arrhenius suggestion are only apply on weak electrolytes because the strong electrolytes are completely dissociate at high concentration

Factors affecting degree of ionization:

The degree of ionization depends on polarity and strength of bond and extent of solvation of ions formed

i) Nature of electrolyte : the value of α depends on the nature of electrolyte .

ii) Nature of solvent α for polar solvent is greater than that for non-polar solvents .

iii) Dilution : increasing the dilution α increases , it is found that an infinite dilution weak electrolytes ionize almost completely .

iv) Temperature : α depends on temp , when temp. Increases the kinetic energy of molecule increases which in turn decreases the ionic force of attraction between ions as a result more and more ions are formed .

v) Common ion effect : the suppression of ionization of weak electrolytes in the presence of strong electrolytes having one ion common to both is known as common ion effect .

Arrhenius Theory of Electrolytic Dissociation

- Two methods can be used to determine the degree of dissociation:

- First method: the degree of dissociation can be determined from conductance measurements. Equivalent conductance at infinite dilution Λ_o was a measure of the complete dissociation of the solute into its ions and that Λ_c represented the number of solute particles present as ions at concentration c.

- Hence the fraction of solute molecules ionized, or the degree of dissociation, can be expressed by the equation

$$\alpha = \frac{\Lambda_c}{\Lambda_o}$$

in which Λ_c / Λ_o is known as the conductance ratio

Arrhenius Theory of Electrolytic Dissociation

- Second method to find α : The van't Hoff factor i can be connected with the degree of dissociation α in the following way:

$$\alpha = \frac{i-1}{v-1}$$

where v is the number of ions produced from the electrolyte ionization e.g. for NaCl v=2, for $CaCl_2$ v=3

- The cryoscopic method is used to determine i from the expression

$$i = \frac{\Delta T_f}{k_f m}$$

Arrhenius Theory of Electrolytic Dissociation

Example: The equivalent conductance of acetic acid at 25°C and at infinite dilution is 390.7 mho cm^2/Eq.

The equivalent conductance of a 5.9*10^{-3} M solution of acetic acid is 14.4 mho cm^2/Eq. What's the degree of dissociation of acetic acid at this concentration?

Answer:

$$\alpha = \frac{\Lambda_c}{\Lambda_o}$$

= 14.4/390.7

= 0.037 or 3.7%

Arrhenius Theory of Electrolytic Dissociation

Example: Calculate the degree of ionization of 0.1 m acetic acid providing that its freezing point is -0.188°C.

Answer: Acetic acid dissociates into two ions, so v = 2.

To calculate i:

$$i = \frac{\Delta T_f}{k_f m}$$

= 0.188/ (1.86*0.1)= 1.011

It is possible now to calculate the degree of ionization:

$$\alpha = \frac{i - 1}{v - 1}$$

= (1.011-1)/ (2-1) = 0.011 or 1.1%

Faraday’s law of electrolysis:

Michael Faraday , on the basis of his research .he found that , during electrolysis , the quantities of substances liberated at electrodes depend upon the following three factors :

i- The quantity of current passed .

ii – Time duration of passing the current at a uniform rate .

iii – Charge on the ions being deposited .

Faraday’s law applies to molten electrolytes as well as to solutions of electrolytes and independent of temperature , pressure , or the nature of the solvent ,as long as the latter can promote ionization of the solute .

Faraday's First Law of Electrolysis

"The mass of an element liberated on an electrode during electrolysis is directly proportional to the quantity of electricity, Q, which passes through the solution of an electrolyte".

$$w \alpha Q$$

Q = I.t

W is the mass or amount of a substance deposited or liberated , and Q is the quantity of electricity .
if I is the current in amperes which passes for t seconds , then :

$$w \alpha I.t$$

If Q is the quantity of electricity then according to the Faraday's 1st law ;

$$Q = I \cdot T$$

The larger unit of the quantity of electricity is called Faraday .

one Faraday = 96500 coulombs

The quantity of a substance, which is deposited when one Faraday (96500 coulombs) of electricity is passed through an electrolyte is called one 'Gram Chemical Equivalent' of that substance.

Faraday's Second Law of Electrolysis

According to the 2nd law of Faraday, "The masses of different substances deposited or liberated, when same quantity of electricity is passed through different electrolytes, connected in series are proportional to their '*chemical equivalent masses*'.

$W \propto e$

When the same quantity of electricity is passed through them , then the masses of Ag , Cu and Al deposited would be directly proportional to their chemical equivalent masses .

$$\frac{w_1}{w_2} = \frac{E_1}{E_2} = \frac{z_1 It}{z_2 It}$$

$$\frac{w_1}{w_2} = \frac{z_1}{z_2}$$

According to Faraday , if exactly 96500 coulombs of electric charge is passed then the mass of Ag deposited would be equal to 108g (108/1) that of copper is 31.75g (63.5/2) , and Al is 9.0g (27/3) which are their equivalent mass s of an element .

$$\text{Eq. Mass of an element} = \frac{\text{Atomic mass of an element}}{\text{valency of the element}}$$

The current of 96500 coulombs is called one Faraday (F)

Faraday is defined as

the quantity of charge which deposits or liberates exactly one gram equivalent of a substance.

Electrochemical equivalent:

Electrochemical equivalent of a substance may be defined as "*The amount (or weight) of the substance deposited or liberated, when one coulomb of electric charge is passed through an electrolyte*".

$$w \alpha e$$

e is equivalent weights

ē is the electro chemical equivalent

$$w = \frac{I.t.e}{F} = I.t.\overline{e}$$

$$\overline{e} = \frac{e}{F} = \frac{e}{96500}$$

Z = ē

w= z.l.t

-How many coulombs are required for the following reduction :

1- 1.0 mole of Al^{+3} to Al

2- 1.0 mole of Cu^{+2} to Cu

-Calculate the chemical equivalent of Cu^{+2}, Ag^{+1}, H^{+}. If you know the atomics weights of the cations respectively are 63.6, 107.9, and 1.008 ?

Calculate the weight of silver deposited when a current of 0.2 amp flowing for 30 min ?

$$w = \frac{I.t.e}{F} = \frac{0.5 \times 30 \times 60 \times 107.87}{96500}$$

$$w = 0.4024g$$

A current of 0.5 ampere was passed through a solution of $CuSO_4$ for one hour. Calculate the mass of copper metal deposited on the cathode.
Electrochemical equivalent of Cu=0.000329 g/C = 3.29×10^{-4} g/C or 3.294×10^{-7} Kg/C

Electrochemical equivalent of Cu = (63.54/ 2 * 96500) = $3.29*10^{-4}$ g/C

W = z . I .t = ē .I .t

w = $3.294*10^{-7}$ * 0.5 * (1* 60* 60)

= $5.929*10^{-4}$ Kg/C

When an aqueous solution of copper sulphate is electrolysed, copper is deposited at the cathode.

$$Cu^{2+}_{(aq)} + 2e^{-} \longrightarrow Cu_{(s)} \quad \text{(at cathode)}$$

If a constant current was passed for 5 hours and 404 mg of Cu was deposited. Calculate the current passed through $CuSO_4$.

g	F
63.5	2
0.404	x

$$x = \frac{2 * 0.404}{63.5} = 0.01272F$$

1.0 F = 96500 coulomb

∴ 0.01272 F = 0.01272 * 96500 = 1227.48 coulomb

Q = I.t

I = Q /t → I = 1227.48 /(5 *3600) = 0.068 amper

1. A compound whose aqueous solution is decomposed into its components when electricity is passed through it is called

A. non-electrolyte.
B. electrolyte.
C. acid.
D. salt.

2. The unit used for the quantity of electricity, in SI system, is

A. ohm.
B. ampere.
C. coulomb.
D. gram/equivalent.

3. What mass of calcium is collected on cathode when 1F of electricity is passed through its solution?

A. 40g
B. 20g
C. 10g
D. 5g

-$Ni(NO_3)_2$ solution is electrolyzed between pt electrodes using a current of 5.0 Ampere for 30 minutes. What is the Weight of Ni will be produced at the cathode? If you know the atomic Weight of Ni =58.69

-The current passage was 15A through silver nitrate solution for 10 sec that required to precipitate 9.9gm silver. What is the current efficiency? If you know the atomic Weight of Ag= 108 .

-The current passage was 0.1A through $CuSO_4$ solution for 10 min at 25C^o, if used pt electrode as cathode. If you know the atomic Weight of Cu= 63.5.

Calculate (1)copper weight at cathode?

(2) the Oxygen volume is evolved at anode at 740 mmHg?