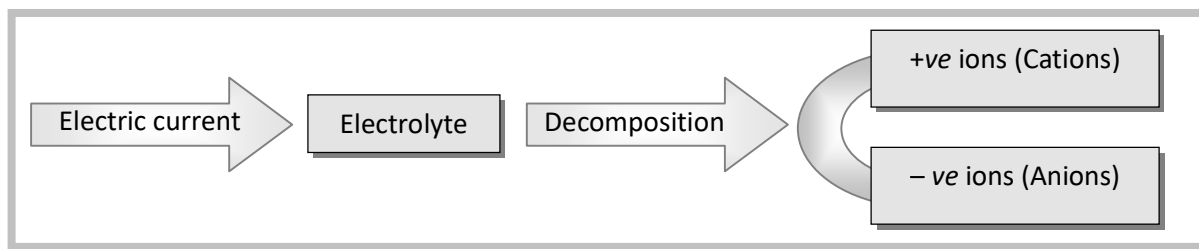


## Electrolytes and Electrolysis.

(1) **Definition:** "The substances whose aqueous solution undergo decomposition into ions when electric current is passed through them are known as **electrolytes** and the whole process is known as **electrolysis** or **electrolytic decomposition**."



Solutions of acids, bases, salts in water and fused salts etc. are the examples of electrolytes. Electrolytes may be **weak** or **strong**. Solutions of cane sugar, glycerin, alcohol etc., are examples of **non-electrolytes**.

(2) **Electrolytic cell or Voltmeter:** The device in which the process of electrolysis or electrolytic decomposition is carried out is known as **electrolytic cell** or **voltmeter**. Following are the important characteristics of voltmeter,

(i) Voltmeter consist of a vessel, two electrodes and electrolytic solution.

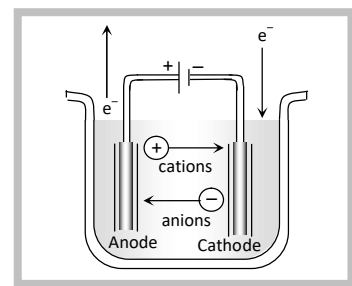
(ii) Voltmeter convert **electrical energy into chemical energy** i.e., electrical energy is supplied to the electrolytic solution to bring about the redox reaction (i.e., electrolysis) which is **non-spontaneous** and takes place only when electrical energy is supplied.

(iii) In voltmeter, both the electrodes are suspended in only one of the electrolytic solution or melt of the electrolyte in the same vessel.

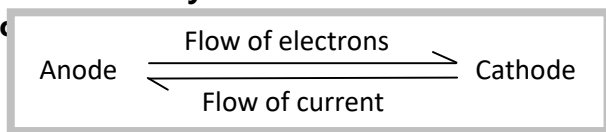
(iv) The electrodes taken in voltmeter may be of the same or different materials.

(v) The electrode on which oxidation takes place is called **anode** (or +ve pole) and the electrode on which reduction takes place is called **cathode** (or -ve pole)

(vi) During electrolysis in voltmeter **cations are discharged on cathode** and **anions on anode**.



(vii) In voltmeter, outside the **electrolyte** electrons flow from **anode to cathode** and **current** flow from **cathode to anode**



(viii) For voltameter,  $E_{\text{cell}} = -ve$  and  $\Delta G = +ve$ .

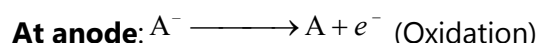
### (3) Mechanism of electrolysis

(i) The net chemical change that takes place in the cell is called the **cell reaction**, which is non-spontaneous in case of electrolytic cell.

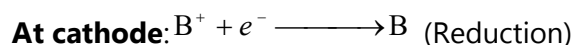
(ii) The mechanism of electrolysis can be easily explained on the basis of **ionization theory** according to which, the electrolytes are present in the form of ions in solution and the function of electricity is only to direct these ions to their respective electrodes.

(iii) During electrolysis cations move towards the cathode (-vely charged) while anions move towards the anode (+vely charged).

(iv) The anions on reaching the anode give up their electrons and converted into the neutral atoms.



On the other hand cations on reaching the cathode take up electrons supplied by battery and converted to the neutral atoms.



This overall change is known as **primary change** and products formed is known as **primary products**.

(v) The primary products may be collected as such or they undergo further change to form molecules or compounds. These are called **secondary products** and the change is known as **secondary change**.

(vi) The products of electrolysis depend upon,

(a) Nature of electrolyte,

(b) Concentration of electrolyte,

(c) Charge density flown during electrolysis,

(d) Nature of electrodes used,

- Electrodes which do not take part in chemical change involved in a cell are known as **inert electrode**. E.g. Graphite, Platinum.

- Electrodes which take part in chemical change involved in a cell knows as **active electrode**. E.g. Hg, Au, Cu, Fe, Zn and Ni electrode etc.

(e) Over voltage: For metal ions to be deposited on the cathode during electrolysis, the voltage required is almost the same as the standard electrode potential. However for liberation of gases, some extra voltage is required than the theoretical value of the standard electrode potential ( $E^0$ ). This extra voltage required is called **over voltage or bubble voltage**.

(vii) The deposition of different ions at the electrodes takes place only for the time of electricity is passed and stops as soon as electricity is switched off.

Note: The electrolyte as a whole remains neutral during the process of electrolysis as equal number of charges are neutralized at the electrodes.

If the cathode is pulled out from the electrolytic solution of the cell then there will be no passage of current and ions will show simply diffusion and state moving randomly.

If electrode is active at cathode, metal goes on depositing on cathode and at anode metal is dissolved.

#### (4) Preferential discharge theory

(i) According to this theory "If more than one type of ion is attracted towards a particular electrode, then the ion is discharged one which requires least energy or ions with lower discharge potential or which occur low in the electrochemical series".

(ii) The potential at which the ion is discharged or deposited on the appropriate electrode is termed the **discharge or deposition potential**, (D.P.). The values of discharge potential are different for different ions.

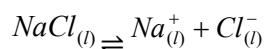
(iii) The decreasing order of discharge potential or the increasing order of deposition of some of the ions is given below,

**For cations:**  $Li^+, K^+, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Zn^{2+}, Fe^{2+}, Ni^{2+}, H^+, Cu^{2+}, Hg^{2+}, Ag^+, Au^{3+}$ .

**For anions:**  $SO_4^{2-}, NO_3^-, OH^-, Cl^-, Br^-, I^-$ .

(5) **Electrolysis and electrode processes:** The chemical reactions which take place at the surface of electrode are called **electrode reactions or electrode processes**. Various types of electrode reactions are described below,

(i) **Electrolysis of molten sodium chloride:** Molten sodium chloride contains  $Na^+$  and  $Cl^-$  ions.



On passing electricity,  $Na^+$  ions move towards cathode while  $Cl^-$  ions move towards anode. On reaching cathode and anode following reactions occur.

**At cathode:**  $Na^+_{(l)} + e^- \rightarrow Na_{(l)} \downarrow$  (Reduction, primary change)

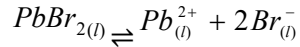
**At anode:**  $Cl^-_{(l)} - e^- \rightarrow \dot{Cl}$  (Oxidation, primary change)

$\dot{Cl} + \dot{Cl} \rightarrow Cl_{2(g)} \uparrow$  (Secondary change)

**Overall reaction:**  $2Na^+_{(l)} + 2Cl^-_{(l)} \xrightarrow{\text{Electrolysis}} 2Na_{(l)} + Cl_{2(g)}$

The sodium obtained at the cathode is in the molten state.

(ii) **Electrolysis of molten lead bromide:** Molten lead bromide contains  $Pb^{2+}_{(l)}$  and  $Br^-$  ions.



On passing electricity,  $Pb^{2+}$  ions move towards cathode while  $Br^{-}$  ions move towards anode. On reaching cathode and anode following reactions occur,

**At cathode:**  $Pb_{(l)}^{2+} + 2e^{-} \rightarrow Pb_{(l)} \downarrow$  (Reduction, primary change)

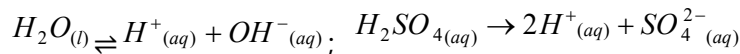
**At anode:**  $Br_{(l)}^{-} - e^{-} \rightarrow \dot{B}r$  (Oxidation, primary change)

$\dot{B}r + \dot{B}r \rightarrow Br_{2(g)} \uparrow$  (Secondary change)

**Overall reaction:**  $Pb_{(l)}^{2+} + 2Br_{(l)}^{-} \xrightarrow{\text{Electrolysis}} Pb_{(l)} + Br_{2(g)}$

The lead obtained at the cathode is in the molten state.

(iii) **Electrolysis of water:** Water is only weakly ionized so it is bad conductor of electricity but the presence of an acid ( $H_2SO_4$ ) increases the degree of ionization of water. Thus, in solution, we have three ions, i.e.,  $H^{+}$ ,  $OH^{-}$  and  $SO_4^{2-}$  produced as follows,



When electric current is passed through acidified water,  $H^{+}$  ions move towards cathode,  $OH^{-}$  and  $SO_4^{2-}$  ions move towards anode. Now since the discharge potential of  $OH^{-}$  ions is much lower than that of  $SO_4^{2-}$  ions, therefore,  $OH^{-}$  ions are discharged at anode while  $SO_4^{2-}$  ions remain in solution. Similarly,  $H^{+}$  ions are discharged at the cathode. The reactions, occurring at the two electrodes may be written as follows,

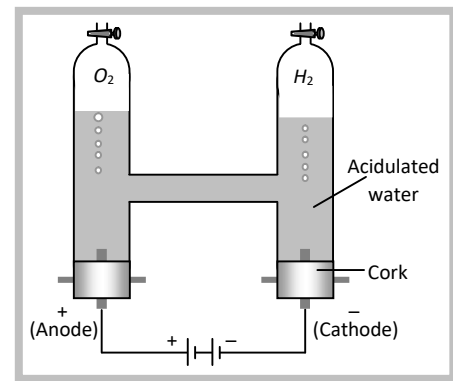
**At cathode:**  $H^{+}_{(aq)} + e^{-} \rightarrow H$ . (Reduction, primary change)

$\dot{H} + \dot{H} \rightarrow H_{2(g)}$  (Secondary change)

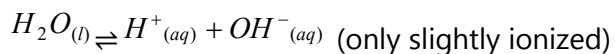
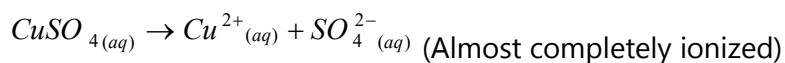
**At anode:**  $OH^{-}_{(aq)} + e^{-} \rightarrow OH$  (Oxidation, primary change)

$4OH \rightarrow 2H_2O_{(l)} + O_2$  (Secondary change)

**Overall reaction:**  $4H^{+}_{(aq)} + 4OH^{-}_{(aq)} \rightarrow 2H_{2(aq)} + 2H_2O_{(l)} + O_{2(g)}$ .



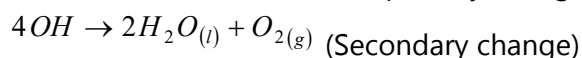
(iv) **Electrolysis of aqueous copper sulphate solution using inert electrodes:** Copper sulphate and water ionize as under,



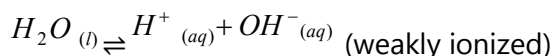
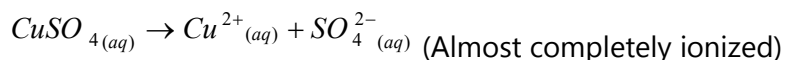
On passing electricity,  $Cu^{2+}_{(aq)}$  and  $H^+_{(aq)}$  move towards the cathode while  $SO_4^{2-}$  ions and  $OH^-$  ions move towards the anode. Now since the discharge potential of  $Cu^{2+}$  ions is lower than that of  $H^+$  ions, therefore,  $Cu^{2+}$  ions are discharged at cathode. Similarly,  $OH^-$  ions are discharged at the anode. The reactions, occurring at the two electrodes may be written as follows,

**At cathode:**  $Cu^{2+} + 2e^- \rightarrow Cu$  (Reduction, primary change)

**At anode:**  $4OH^- - 4e^- \rightarrow 4OH$  (Oxidation, primary change)



(v) **Electrolysis of an aqueous solution of copper sulphate using copper electrode:** Copper sulphate and water ionize as under:



On passing electricity,  $Cu^{2+}$  and  $H^+$  move towards cathode while  $OH^-$  and  $SO_4^{2-}$  ions move towards anode. Now since the discharge potential of  $Cu^{2+}$  ions is lower than that of  $H^+$  ions, therefore,  $Cu^{2+}$  ions are discharged in preference to  $H^+$  ions at cathode. **Unlike electrolysis of  $CuSO_4$  using platinum electrodes**, no ions are liberated here, instead, anode itself undergoes oxidation (i.e., loses electrons) to form  $Cu^{2+}$  ions which go into the solution. This is due to the reason that Cu is more easily oxidized than both  $OH^-$  and  $SO_4^{2-}$  ions. The reactions, occurring at the two electrodes may be written as follows,

**At cathode:**  $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$  (Reduction, primary change).

**At anode:**  $Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$  (Oxidation, primary change).

Products of electrolysis of some electrolytes

Electrolyte	Electrode	Product at cathode	Product at anode
Aqueous $\text{NaOH}$	Pt or Graphite	$\text{H}_2$	$\text{O}_2$
Fused $\text{NaOH}$	Pt or Graphite	$\text{Na}$	$\text{O}_2$
Aqueous $\text{NaCl}$	Pt or Graphite	$\text{H}_2$	$\text{Cl}_2$
Fused $\text{NaCl}$	Pt or Graphite	$\text{Na}$	$\text{Cl}_2$
Aqueous $\text{CuCl}_2$	Pt or Graphite	$\text{Cu}$	$\text{Cl}_2$
Aqueous $\text{CuCl}_2$	Cu electrode	$\text{Cu}$	$\text{Cu}$ oxidized to $\text{Cu}^{2+}$ ions
Aqueous $\text{CuSO}_4$	Pt or Graphite	$\text{Cu}$	$\text{O}_2$
Aqueous $\text{CuSO}_4$	Cu electrode	$\text{Cu}$	$\text{Cu}$ oxidized to $\text{Cu}^{2+}$ ions
Dilute $\text{H}_2\text{SO}_4$	Pt electrode	$\text{H}_2$	$\text{O}_2$
Conc. $\text{H}_2\text{SO}_4$	Pt electrode	$\text{H}_2$	Peroxodisulphuric acid ( $\text{H}_2\text{S}_2\text{O}_8$ )
Aqueous $\text{AgNO}_3$	Pt electrode	$\text{Ag}$	$\text{O}_2$
Aqueous $\text{AgNO}_3$	Ag electrode	$\text{Ag}$	$\text{Ag}$ oxidized to $\text{Ag}^+$ ions
Acidified water	Pt electrode	$\text{H}_2$	$\text{O}_2$
Fused $\text{PbBr}_2$	Pt electrode	$\text{Pb}$	$\text{Br}_2$

Note: Alkali metals, alkaline earth metals and other metals having  $E^0$  lower than hydrogen cannot be obtained during electrolysis of their aqueous salt solutions because of their strong electropositive nature. The electrolysis of aqueous solution of electrolytes is somewhat more complex because of the ability of water to be oxidized as well as reduced.

(6) **Application of electrolysis:** Electrolysis has wide applications in industries. Some of the important applications are, as follows,

(i) Production of hydrogen by electrolysis of water.

(ii) Manufacture of heavy water ( $D_2O$ ).

(iii) **Electrometallurgy:** The metals like Na, K, Mg, Al, etc., are obtained by electrolysis of fused electrolytes.

Fused electrolyte	Metal isolated
$NaCl + CaCl_2 + KF$	Na
$CaCl_2 + CaF_2$	Ca
$Al_2O_3 + \text{rhyolite}$	Al
$MgCl_2 + NaCl + CaCl_2$	Mg
$NaOH$	Na
$KCl + CaCl_2$	K

(iv) **Manufacture of non-metals:** Non-metals like hydrogen, fluorine, chlorine are obtained by electrolysis.

(v) **Electro-refining of metals:** It involves the deposition of pure metal at cathode from a solution containing the metal ions. Ag, Cu etc. are refined by this method.

(vi) **Electrosynthesis:** This method is used to producing substances through non-spontaneous reactions carried out by electrolysis. Compounds like NaOH, KOH,  $Na_2CO_3$ ,  $KClO_3$ , white lead,  $KMnO_4$  etc. are synthesized by this method.

(vii) **Electroplating:** The process of coating an inferior metal with a superior metal by electrolysis is known as electroplating. The aim of electroplating is, to prevent the inferior metal from corrosion and to make it more attractive in appearance. The object to be plated is made the cathode of an electrolytic cell that contains a solution of ions of the metal to be deposited.

For electroplating	Anode	Cathode	Electrolyte
With copper	Cu	Object	$CuSO_4 + \text{dilute } H_2SO_4$
With silver	Ag	Object	$K[Ag(CN)_2]$
With nickel	Ni	Object	Nickel ammonium sulphate
With gold	Au	Object	$K[Au(CN)_2]$
With zinc	Zn	Iron objects	$ZnSO_4$

With tin	Sn	Iron objects	SnSO <sub>4</sub>
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**Thickness of coated layer:** Let the dimensions of metal sheet to be coated be ( $a \text{ cm} \times b \text{ cm}$ ).

Thickness of coated layer =  $c \text{ cm}$

Volume of coated layer =  $(a \times b \times c) \text{ cm}^3$

Mass of the deposited substance = Volume  $\times$  density =  $(a \times b \times c) \times dg$

$$\therefore \boxed{(a \times b \times c) \times d = \frac{I \times t \times E}{96500}}$$

Using above relation we may calculate the thickness of coated layer.

Note: Sometimes radius of deposited metal atom is given instead of density.

For example, radius of silver atom =  $10^{-8} \text{ cm}$ ; Atomic mass of Ag = 108

$$\text{Mass of single silver atom} = \frac{108}{6.023 \times 10^{23}} \text{ g}$$

$$\text{Volume of single atom} = \frac{4}{3} \times \pi R^3 = \frac{4}{3} \times 3.14 \times (10^{-8})^3 \text{ cm}^3$$

$$\text{Density of Ag} = \frac{\text{Mass of single atom}}{\text{Volume of single atom}} = \frac{108 / 6.023 \times 10^{23}}{\frac{4}{3} \times 3.14 \times (10^{-8})^3} = 42.82 \text{ g / cm}^3$$