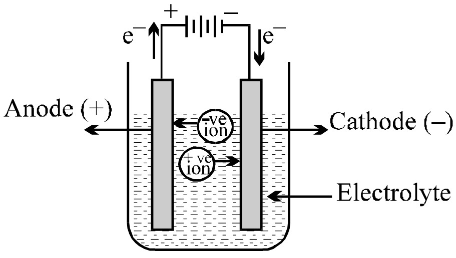
# ELECTROCHEMISTRY

## ELECTROLYSIS

The process of chemical decomposition of an electrolyte by the passage of electricity is called electrolysis or electrolytic dissociation. It is carried out in **electrolytic cell** where electrical energy is converted into chemical energy. For electrolysis two suitable electrodes are immersed in the solution of an electrolyte. When an electric potential is applied between the electrodes, the positive ions move towards the cathode and negative ions move towards the anode. The gain of electrons (decrease in oxidation number) means reduction takes place at the cathode and loss of electrons (increase in oxidation number) means oxidation takes place at anode.



Electrolytic cell

There are two aspects of electrolysis :

### (A) Qualitative aspects of electrolysis :-

In qualitative aspect products formed at electrode are identified. At electode product formation depends up on the following :

(i) Nature of electrolyte

(ii) Nature of electrodes : The metal strip at which current enters is called **anode**; anode is positively charged in electrolytic cell. On the other hand, the electrode at which current leaves is called **cathode**. Cathode is negatively charged. There are two types of electrodes

(a) Attackable : The attackable electrodes participate in the electrode reaction. They are made up of reactive metals like Zn, Cu, Ag etc in their respective solutions. In such electrodes, atom of the metal gets oxidised into the corresponding cation, which is passed into the solution. Thus, such anode gets dissolved and their mass decreases.

- If electrode is active at cathode, metal goes on depositing and at anode metal is dissolved. The process is called electroplating.

(b) Non - attackable : Non-attackable electrodes do not participate in the electrode reaction as they are made up of unreactive elements like Pt, graphite etc. Such electrodes do not dissolve and their mass remain same.

- Among the two cations, that cation is discharged at the cathode which has higher reduction potential. Among the two anions, that anion will be discharged at the anode which has lower reduction potential or higher oxidation potential.
- The discharge of $NO_3^-$, $PO_4^{3-}$ and $SO_4^{2-}$ ions at anode does not commonly take place from aqueous solution.

(iii) Concentration of electrolytic solution.

**Examples of electrolysis :**

### (a) Electrolysis of Molten Sodium Chloride

$$NaCl_{(molten)} \longrightarrow Na^+ + Cl^-$$

Reaction at anode (oxidation) : $2Cl^- \longrightarrow Cl_2(g) + 2e^-$

Reaction at cathode (reduction) : $2Na^+ + 2e^- \longrightarrow 2Na(s)$

### (b) Electrolysis of Sodium Chloride Solution

On electrolysis of aqueous solution of NaCl, the possible species involved in half-reactions are $Na^+$, $Cl^-$ and $H_2O$.

The possible cathode half-reactions are

$Na^+(aq) + e^- \longrightarrow Na(s) \qquad E° = -2.71V$

$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \qquad E° = -0.83V$

Under the standard conditions, $H_2O$ is to be reduced in preference to $Na^+$ and Hydrogen is evolved at the cathode.

The possible anode half-reactions are

$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^- \qquad E° = -1.36V$

$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad E° = -1.23V$

Under the standard-state conditions, $H_2O$ is to be oxidized in preference to $Cl^-$. But since electrode potentials, depend on concentrations it turns out that when the solution is concentrated enough in $Cl^-$, $Cl_2$ is the product; but in dilute solution, $O_2$ is the product. **Starting with very dilute NaCl solutions, the oxidation potential of $Cl^-$ is very negative, so $H_2O$ is oxidised in preference to $Cl^-$. But as the NaCl concentration increase, the oxidation potential of $Cl^-$ increases until eventually $Cl^-$ is oxidized in preference to $H_2O$. The product changes from $O_2$ to $Cl_2$.**

The half-reactions and cell reaction for the electrolysis of aqueous sodium chloride to chlorine and hydroxide ion are as follows:

$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \qquad$ (cathode)

$2\,Cl^-(aq) \longrightarrow Cl_2(g) + 2e^- \qquad$ (anode)

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$2H_2O(l) + 2Cl^-(aq) \longrightarrow H_2(g) + Cl_2(g) + 2OH^-(aq)$

Because the electrolysis started with sodium chloride, the cation in the electrolyte solution is $Na^+$. On evaporation of the electrolyte solution, sodium hydroxide NaOH is obtained.

**(c) Electrolysis of Molten lead bromide using inert (pt/graphite) electrodes.**

**Cathode (reduction) :** $Pb^{2+} + 2e^- \rightarrow Pb(s) \qquad E^0 = -0.13\text{ V}$

**Anode (oxidation) :** $2Br^- \rightarrow Br_2(g) + 2e^- \qquad E^0 = -1.09\text{ V}$

Overall reaction $Pb^{+2} + 2Br^- \rightarrow Pb(s) + Br_2(g)$

$E_{cell} = -0.13 - 1.09 = -1.22\text{ V}$

$E_{ext} > 1.22\text{ V}$

**(d) Electrolysis of aq $CuSO_4$ using inert (pt/graphite) electrode**

**Cathode (reduction) :** $Cu^{2+} + 2e^- \rightarrow Cu(s) \qquad E^0 = 0.34\text{ V}$

$2H_2O(\ell) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E^0 = -0.83V$

At cathode reduction of $Cu^{2+}$ (aq) will be preferred over reduction of water as its standard reduction potential is more, than that of water.

Thus reaction at cathode : $Cu^{2+} + 2e^- \rightarrow Cu(s)$

**Anode (oxidation) :** $2\,SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \qquad E^0 = -1.96\text{ V}$

$2H_2O(\ell) \rightarrow O_2(g) + 4H^+ + 4e^- \qquad E^0 = -1.23\text{ V}$

At anode oxidation of water is preferred over oxidation of sulphate ion as its standard oxidation potential is more, than that of sulphate ion.

Thus reaction at anode : $2H_2O(\ell) \rightarrow O_2(g) + 4H^+ + 4e^-$

After electrolysis solution will become acidic (pH < 7)

**(e) Electrolysis of aq. $CuSO_4$ using Cu electrode.**

**Cathode (reduction) :** $Cu^{2+} + 2e^- \rightarrow Cu \qquad E^0 = +0.34\text{ V}$

$2H_2O(\ell) + 2e^- \rightarrow H_2(g) + 2OH^- E^0 = -0.83\text{ V}$

At cathode reduction of $Cu^{2+}$ (aq) will be preferred over reduction of water as its standard reduction potential is more, than that of water.

Thus reaction at cathode :

$$Cu^{2+} + 2e^- \rightarrow Cu(s)$$

**Anode (oxidation) :** $SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$ $E^0_{OX} = -1.96$ V

$2H_2O(\ell) \rightarrow O_2(g) + 2H^+ + 4e^-$ $E^0 = -1.23$ V

$Cu(s) \rightarrow Cu^{2+} + 2e-$ $E^0 = -0.34$ V

At anode oxidation of copper solid is preferred over oxidation of water and sulphate ion, as its standard oxidation potential is more than that of water and sulphate ion.

Thus reaction at anode :

$$Cu(s) \rightarrow Cu^{2+} + 2e-$$

It is an example of electrolytic refining and there will be no change in the pH and concentration of electrolyte.

**(f) Electrolysis of dilute $H_2SO_4$ :**

**Cathode (reduction)** $2H^+ + 2e^- \rightarrow H_2(g)$ E° = 0

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-$ E° = –0.83 V

due to less availability of $H^+$ ions, it will not participate in formation of $H_2$ gas therefore reduction of water will take place.

**Anode (oxidation)** $SO_4^{-2} \rightarrow S_2O_8^{-2} + 2e^-$ E° = –1.96 V

$2H_2O(l) \rightarrow O_2(g) + 2H^+ + 4e^-$ E° = –1.23 V

oxidation of water is preferred over oxidation of sulphate ion as its standard oxidation potential is more, than that of sulphate ion.

**(g) Electrolysis of concentrated $H_2SO_4$**

**Cathode (reduction)** $2H^+ + 2e^- \rightarrow H_2(g)$ E° = 0

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-$ E° = –0.83 V

due to reduction of $H^+$ ions, formation of $H_2$ gas takes place.

**Anode (oxidation)** $SO_4^{-2} \rightarrow S_2O_8^{-2} + 2e^-$ E° = –1.96 V

$2H_2O(l) \rightarrow O_2(g) + 2H^+ + 4e^-$ E° = –1.23 V

due to oxidation of $SO_4^{2-}$ ions, formation of persulphate ion ($S_2O_8^{-2}$) takes place.

## (B) QUANTITATIVE ASPECTS OF ELECTROLYSIS

1 mole electron = $N_A$ electron = 96500 coulomb = 1 Faraday

$$\underset{1\,mol}{Na^+}(aq) + \underset{1F}{e^-} \rightarrow \underset{1\,mol}{Na}(s)$$

$$\underset{1\,mol}{Cu^{+2}}(aq) + \underset{2F}{2e^-} \rightarrow \underset{1\,mol}{Cu}(s)$$

Therefore, $\underset{1\,mol}{M^{+n}}(aq) + \underset{nF}{ne^-} \rightarrow \underset{1\,mol}{M}(s)$

nF charge discharges = 1 mol of $M^{+n}$ ion

$\therefore$ 1 F charge discharges $= \frac{1}{n}$ mol of $M^{+n}$ ion

$= \frac{1}{n} \times n$ = 1 g equivalent of $M^{+n}$ ion

Hence $\boxed{1 \text{ mole } e^- = 1\text{ F} = 1 \text{ g equivalent}}$

## FARADAY'S LAWS OF ELECTROLYSIS

**(a) First law of electrolysis :**

Amount of substance deposited or liberated at an electrode is directly proportional to amount of charge passed through the solution.

$W \propto Q$

W = amount of substance deposited, Q = charge in coulomb

$W = ZQ$

$Z$ = electrochemical equivalent

when $Q = 1$ coulomb, then $W = Z$

Thus, amount of substance deposited or liberated by 1 coulomb charge is called **electrochemical equivalent.**

Let I ampere current is passed till 't' seconds .

Then, $Q = It \quad \therefore \quad W = ZIt$

1 Faraday = 96500 coulomb = Charge on one mole electrons

***One faraday is the charge required to liberate or deposit one gram equivalent of a substance at corresponding electrode***.

Let 'E' is equivalent weight then 'E' gram will be liberated by 96500 coulomb.

$\therefore$ 1 Coulomb will liberate $\frac{E}{96500}$ gram ;

By definition, $Z = \frac{E}{96500} \quad \therefore \quad W = \frac{EIt}{96500} \quad \boxed{\frac{W}{E} = \frac{It}{96500} = \text{number of g eq} = \text{number of faraday}}$

**(b) Second law of electrolysis :**

When same amount of charge is passed through different electrolyte solutions connected in series then weight of substances deposited or liberated at electrodes are in ratio of their respective equivalent weights.

i.e. $\frac{W_1}{W_2} = \frac{E_1}{E_2}$

## POINTS TO REVISE

### PRODUCTS OF ELECTROLYSIS OF SOME ELECTROLYTES

| S. No. | Electrolyte | Electrode | Product obtained at anode | Product obtained at cathode |
|---|---|---|---|---|
| (i) | Aqueous NaCl | Pt or Graphite | $Cl_2$ | $H_2$ |
| (ii) | Fused NaCl | Pt or Graphite | $Cl_2$ | Na |
| (iii) | Aqueous NaOH | Pt or Graphite | $O_2$ | $H_2$ |
| (iv) | Fused NaOH | Pt or Graphite | $O_2$ | Na |
| (v) | Aqueous $CuSO_4$ | Pt or Graphite | $O_2$ | Cu |
| (vi) | Aqueous $CuSO_4$ | Copper | Cu oxidises to $Cu^{+2}$ Ions | Cu |
| (vii) | Aqueous $CuCl_2$ | Copper | Cu oxidises to $Cu^{+2}$ ions | Cu |
| (viii) | Aqueous HCl | Pt or Graphite | $Cl_2$ | $H_2$ |
| (ix) | Dilute $H_2SO_4$ | Pt or Graphite | $O_2$ | $H_2$ |
| (x) | Conc. $H_2SO_4$ | Pt or Graphite | $S_2O_8^{-2}$ | $H_2$ |
| (xi) | Aqueous $AgNO_3$ | Pt of Graphite | $O_2$ | Ag |
| (xii) | Dilute NaCl | Pt or Graphite | $O_2$ | $H_2$ |

- For electrolysis $\Delta G$ = +ve, So it is non-spontaneous process.
- In electrolytic cell D.C. current is used.

## ELECTROCHEMICAL SERIES

Arrangement of different elements on the basis of their SRP values is known as electrochemical series or activity series.

| Electrode | Reaction | SRP (at 298 K) |
|---|---|---|
| Li | $Li^+ + e^- \rightarrow Li(s)$ | – 3.05 V |
| K | $K^+ + e^- \rightarrow K(s)$ | – 2.93 V |
| Ba | $Ba^{+2} + 2e^- \rightarrow Ba$ | – 2.91 V |
| Ca | $Ca^{+2} + 2e^- \rightarrow Ca(s)$ | – 2.87 V |
| Na | $Na^+ + e^- \rightarrow Na(s)$ | – 2.71 V |
| Mg | $Mg^{+2} + 2e^- \rightarrow Mg(s)$ | – 2.36 V |
| Al | $Al^{3+} + 3e^- \rightarrow Al$ | – 1.66 V |
| Mn | $Mn^{+2} + 2e^- \rightarrow Mn$ | – 1.18 V |
| $H_2O$ | $H_2O(l) + e^- \rightarrow \frac{1}{2}H_2 + OH^-$ | – 0.828 V |
| Zn | $Zn^{+2} + 2e^- \rightarrow Zn(s)$ | – 0.76 V |
| Cr | $Cr^{+3} + 3e^- \rightarrow Cr(s)$ | – 0.74 V |
| Fe | $Fe^{2+} + 2e^- \rightarrow Fe$ | – 0.44 V |
| Cd | $Cd^{+2} + 2e^- \rightarrow Cd(s)$ | – 0.40 V |
| Co | $Co^{2+} + 2e^- \rightarrow Co$ | – 0.28 V |
| Ni | $Ni^{+2} + 2e^- \rightarrow Ni(s)$ | – 0.25 V |
| Sn | $Sn^{+2} + 2e^- \rightarrow Sn(s)$ | – 0.14 V |
| Pb | $Pb^{+2} + 2e^- \rightarrow Pb(s)$ | – 0.13 V |
| $H_2$ | $2H^+ + 2e^- \rightarrow H_2(g)$ | 0.00 V |
| Cu | $Cu^{2+} + 2e^- \rightarrow Cu(s)$ | 0.34 V |
| $I_2$ | $I_2 + 2e^- \rightarrow 2I^-$ | 0.54 V |
| Fe | $Fe^{3+} + e^- \rightarrow Fe^{2+}$ | 0.77 V |
| Hg | $Hg_2^{2+} + 2e^- \rightarrow Hg(l)$ | 0.79 V |
| Ag | $Ag^+ + e^- \rightarrow Ag$ | 0.80 V |
| Hg | $Hg^{2+} + 2e^- \rightarrow Hg(l)$ | 0.85 V |
| $Br_2$ | $Br_2 + 2e^- \rightarrow 2Br^-$ | 1.09 V |
| Pt | $Pt^{+2} + 2e^- \rightarrow Pt$ | 1.20 V |
| $O_2$ | $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O(\ell)$ | 1.23 V |
| $Cl_2$ | $Cl_2 + 2e^- \rightarrow 2Cl^-$ | 1.36 V |
| Au | $Au^{+3} + 3e^- \rightarrow Au(s)$ | 1.40 V |
| $F_2$ | $F_2 + 2e^- \rightarrow 2F^-$ | 2.87 V |

## APPLICATIONS OF ELECTROCHEMICAL SERIES

### (i) Oxidising and reducing power –

$$\text{Oxidising power} \quad \alpha \quad \text{SRP} \quad \alpha \quad \frac{1}{\text{SOP}}$$

$$\text{Reducing power} \quad \alpha \quad \text{SOP} \quad \alpha \quad \frac{1}{\text{SRP}}$$

**(ii) Reactivity of metals –**

$$\text{Reactivity of metal} \quad \alpha \quad \text{SOP} \quad \alpha \quad \frac{1}{\text{SRP}}$$

- In ECS reactivity of metal decreases from top to bottom.
- Li is most reactive metal.

**(iii) Reactivity of non-metals –**

$$\text{Reactivity of non-metal} \quad \alpha \quad \text{SRP} \quad \alpha \quad \frac{1}{\text{SOP}}$$

- In ECS reactivity of non-metal increases from top to bottom.
- $F_2$ is most reactive non-metal.

**(iv) Displacement reactions in solution –**

More reactive metal / non-metal displaces less reactive metal / non-metal in their solution.

- $Cu + 2\,AgNO_3 \rightarrow Cu(NO_3)_2 + 2\,Ag$

  $Ag + Cu(NO_3)_2 \rightarrow$ No reaction
- $2\,KI + Cl_2 \rightarrow 2\,KCl + I_2$

  $I_2 + 2\,KCl \rightarrow$ No reaction

**(v) Metal above hydrogen displaces $H_2$ from dilute acid solution.**

- $Zn + H_2SO_4(aq) \rightarrow ZnSO_4 + H_2(g)$

  $Cu + H_2SO_4(\text{dilute}) \rightarrow$ No reaction