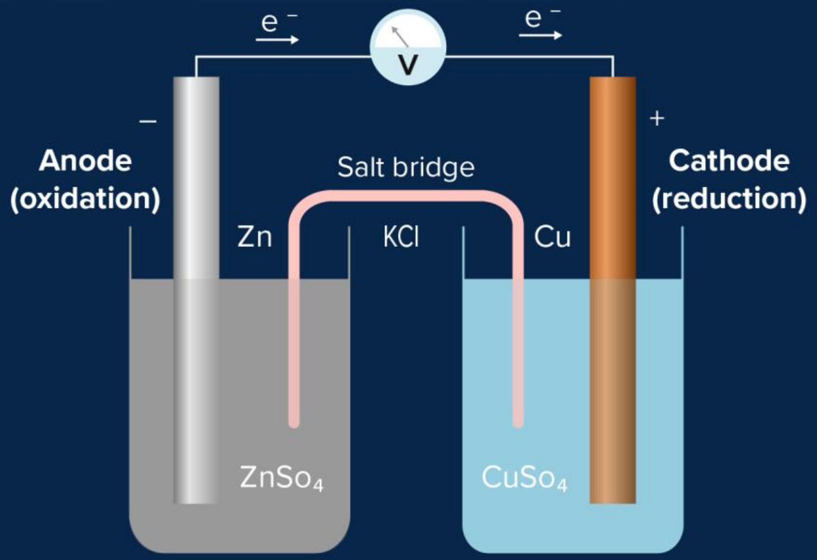
ELECTROCHEMISTRY- L3



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

$Zn(s) \mid ZnSO_4\,(aq) \parallel CuSO_4\,(aq) \mid Cu(s)$

CHEMISTRY

ANOOP SIR

ANOOP SIR
CHEMISTRY

PUSHPENDU SIR
ZOOLOGY

MRINAL SIR
PHYSICS

PANKHURI MA'AM
BOTANY

AKASH SIR
PHYSICS

SACHIN SIR
ZOOLOGY

MISSION MBBS

BIO की रण NEETi

CHEMISTRY SUPER 30

PHY की रण NEETi

MON - SAT | 12 PM - 8 PM

Aakash Live Webinars

Aakash + BYJU'S

6 Months NEET Strategy till May 2023

20th November, 2022

12:30 pm

Dr. Sachin Kapur

Biology Expert - NEET

ANTHE

AAKASH NATIONAL TALENT HUNT EXAM

Your Gateway To Success

For Class VII to XII

Current Students & Passouts

Aakash
+ BYJU'S

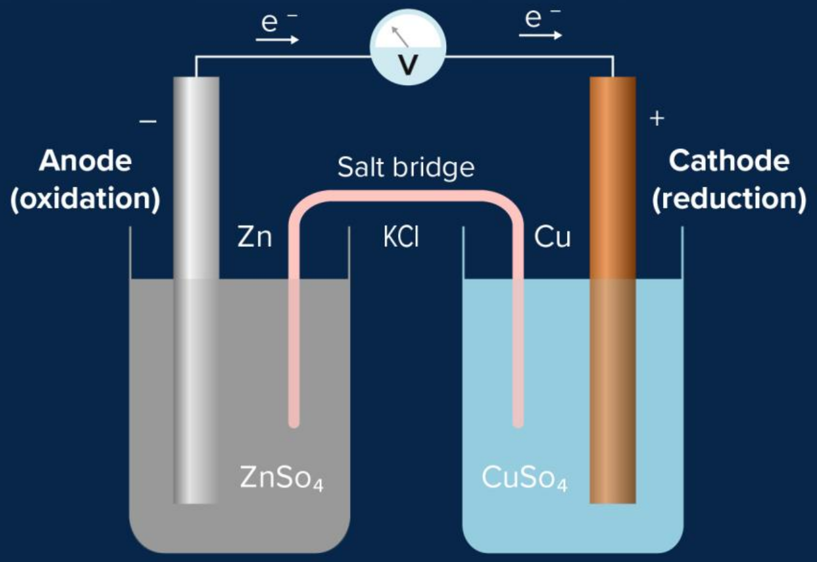
NEET

STUDENTS' SURVEY

LINK IN DESCRIPTION

https://t.me/neetaakashdigital

ELECTROCHEMISTRY- L3



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

$Zn(s) \mid ZnSO_4\,(aq) \parallel CuSO_4\,(aq) \mid Cu(s)$

CHEMISTRY

ANOOP SIR

Electrolytic cell and Electrolysis

Electrical energy is used to do the chemical reations with ΔG positive.

The electrode at which reduction takes place is cathode.
In electrolysis, cathode is negative. So cation (positive ion) moves towards cathode and is reduced there.

The electrode at which oxidation takes place is the anode.
In electrolysis, anode is positive. So anion (negative ion) moves towards anode and is oxidised there.

In case we have more than one kind of anion & cation, there is a preference to discharge.

Electrolytic cell and Electrolysis

Preferential discharge series → conditional → change in conditions can and will change the order

Conditions → 1 molar conc of each ion, 298 K temp, Pt electrodes, aq. solution.

cathodic (cation) discharge series.

Late Prof B.C.S Mazintl Had cup Made of Silver plated with gold

Li K Ba Ca Na Mg Al | Zn Fe Ni Sn Pb [H] Cu Hg Ag Pt Au

↓ $[H]_{H_2O}$ (below Al | Zn)

↑ 1 Molar (below [H])

↑ first to discharge (below Au)

last to discharge (below Li)

Release of hydrogen from water requires an extra potential (over potential)

Electrolytic cell and Electrolysis

A solution in water contains $\underline{Ag^+}$, Cu^{2+}, Mg^{2+} & Hg^{2+}. Give the order of discharg of metals on cathode.

$\underline{Ag}$ $\underline{Hg}$ $Cu \rightarrow H_2$ Mg will not be released → aq medium

Anionic discharge series → oxygen also needs an over potential

$F^-, SO_4^{2-}, NO_3^-, PO_4^{3-} \rightarrow$ are not oxidized in aq medium in dilute solution

$H_2O \longrightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$

$Cl^- \rightarrow \frac{1}{2}Cl_2$ $Br^- \rightarrow \frac{1}{2}Br_2$, $I^- \rightarrow \frac{1}{2}I_2$

If we consider just the electrode potentials, Oxygen should be released before Cl_2

Electrolytic cell and Electrolysis

Effect of change in conc of solution -

dil H_2SO_4 → aq medium

$2H_2SO_4 \longrightarrow 2H^+ + 2HSO_4^-$

Electrolysis (Pt electrode)

(cathode) (anode -

cation	Anion
H^+	HSO_4^-
H^+	~~OH^-~~
H_2	O_2

H_2SO_4

Electrolytic cell and Electrolysis

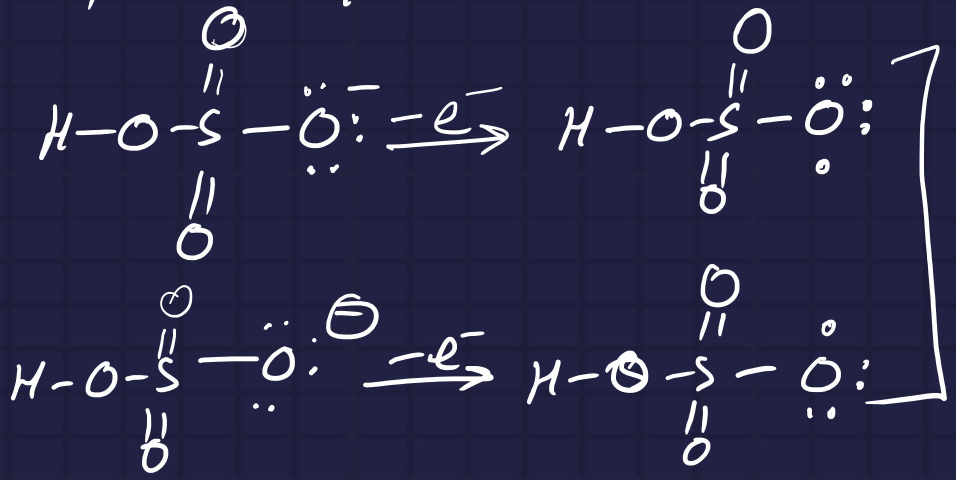
Conc H_2SO_4 (50%)

$$2H_2SO_4 \longrightarrow 2H^+ + 2HSO_4^-$$

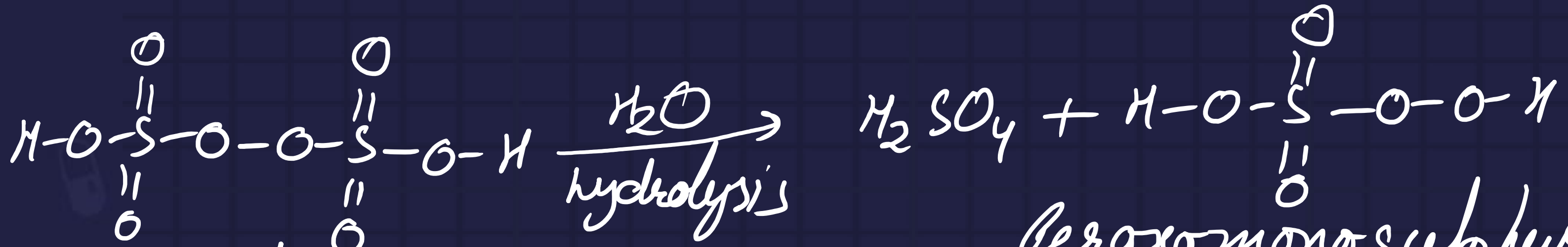
cation	Anion
H^+	HSO_4^-
H^+	OH^-

H_2

$H_2S_2O_8$



$$\left[\begin{array}{l} H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\ddot{\underset{..}{O}}:^{-} \xrightarrow{-e^-} H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\dot{\underset{.}{O}}: \\ H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\ddot{\underset{..}{O}}:^{\ominus} \xrightarrow{-e^-} H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\dot{\underset{..}{O}}: \end{array}\right]$$



$$H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-H \xrightarrow[\text{hydrolysis}]{H_2O} H_2SO_4 + H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-O-H$$

peroxodisulphuric acid

Marshall's Acid

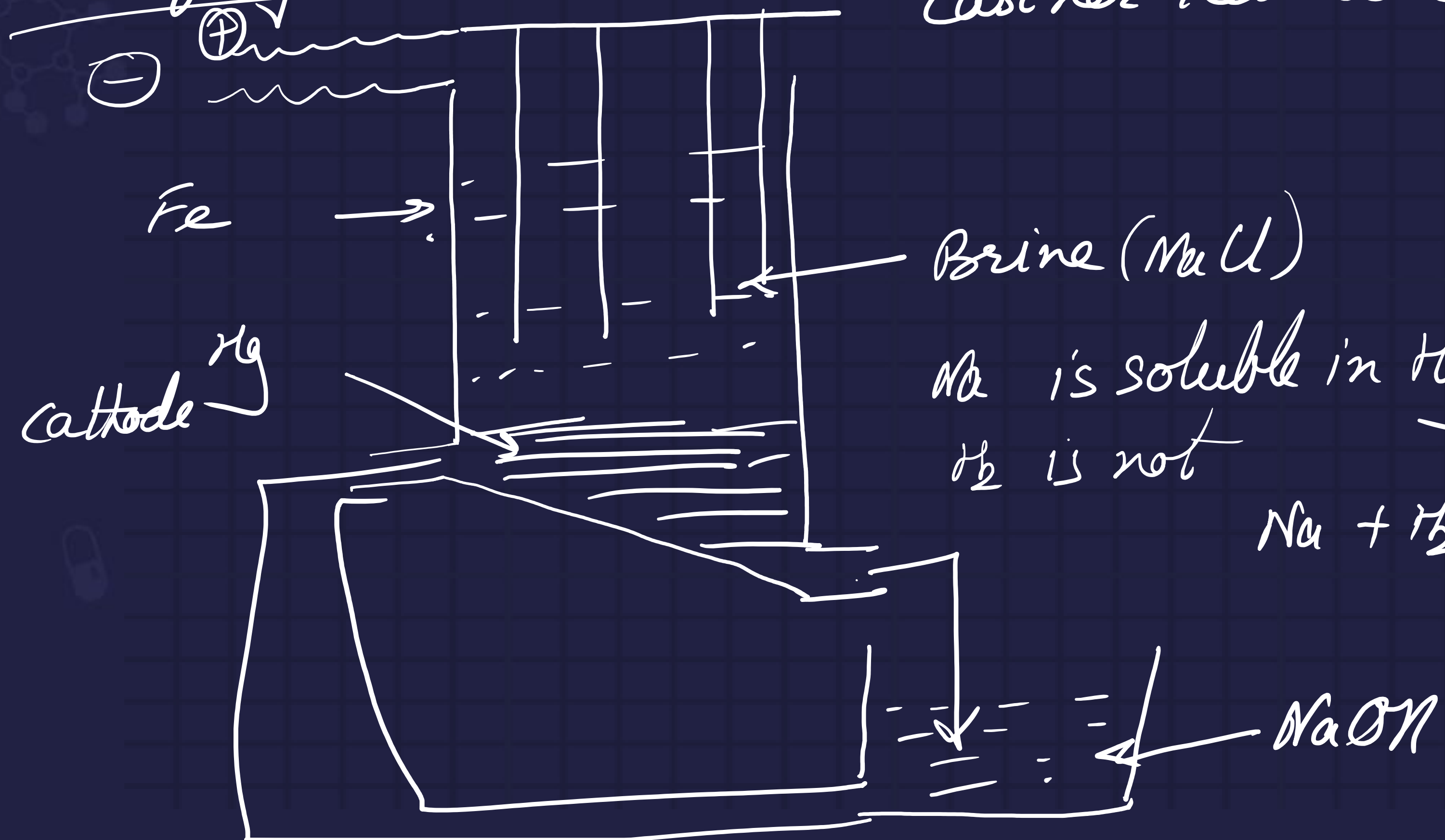
Peroxomonosulphuric acid

caro's acid

Electrolytic cell and Electrolysis

$H_2SO_5 + H_2O \rightarrow H_2SO_4 + \underline{\underline{H_2O_2}}$

Change of electrode: → mercury cathode cell
Castner Kellner cell



Na is soluble in Hg
H_2 is not

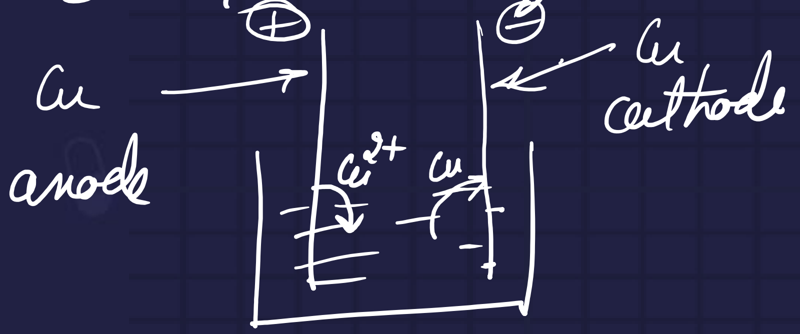
$Na + H_2O \rightarrow NaOH + \frac{1}{2}H_2$

Electrolytic cell and Electrolysis

Inert electrode → provides surface for the reaction (reduction or oxidation not redox) to take place, helps in conduction of electrons, can catalyse the reaction but is not consumed → Pt, Hg, graphite

Reactive electrode → Most often anode of the same metal of which salt is taken as electrolyte

$CuSO_4$ electrolysed with Cu electrodes .



anode will be consumed
cathode will become thick
electrolyte concentration will not change .

Electrolytic cell and Electrolysis

$CuSO_4$ electrolysed with Pt electrodes

cathode	anode
$\cancel{Cu^{2+}}$	SO_4^{2-}
H^+	$\cancel{OH^-}$

Cu

O_2

H_2SO_4

Qualitative aspect of Electrolysis

Electrolytic cell and Electrolysis

Quantitative aspects of Electrolysis.

Faraday's laws of Electrolysis.

1. Equivalent → amount of electrolyte which shows a change when 1 Faraday charge (1 mol electrons) is passed

Amount of substance changed, deposited or released

2. Electrochemical equivalent, z → The amount which shows a change when 1 coulomb charge is passed.

$$z = \frac{Eq}{96487} \simeq \frac{Eq}{96500}$$

Electrolytic cell and Electrolysis

Faraday's first law of electrolysis

Amount of substance (electrolyte) which shows a change, deposition or release is directly proportional to the charge passed.

$$m \propto Q$$

$$m \propto It$$

$$m = zIt = \frac{Eq}{96500} It$$

Second law → If same charge is passed through different electrolytes then the ratio of masses of substance changed (deposited, released) is same as the ratio of their equivalents.

Electrolytic cell and Electrolysis

$m_1 : m_2 : m_3$

$= Z_1 : Z_2 : Z_3$

$= E_{q_1} : E_{q_2} : E_{q_3}$

Electrolytic Cell and Electrolysis

Electrolytic Cell

An electrolytic cell is an electrochemical cell in which a **non-spontaneous reaction** is driven by an external source of current.

It converts **electrical** energy into **chemical** energy.

Electrolytic Cell

Cell reaction: $2H_2O\ (\ell) \longrightarrow 2H_2\ (g) + O_2\ (g)$ $E_{cell} = -1.23\ V$

The spontaneous process is actually the **reverse reaction** (i.e., formation of H_2O from H_2 and O_2).

For this at pH = 7, $\mathbf{E_{cell} = 1.23\ V}$.

Electrolytic Cell

In order to drive the **electrolysis of H_2O**, the electrical power source must be able to supply a **minimum** of 1.23 V.

Electrolysis

Electrolysis is a process of oxidation and reduction **due to current** in the electrolytic solution.

An electrolyte is a combination of **cations and anions,** which can conduct electricity in fused state or in aqueous solution.

Construction of Electrolytic Cell

Construction of Electrolytic Cell

Source of current

↓

External battery

Construction of Electrolytic Cell

Cathode is attached to the negative terminal of the battery.

Reduction occurs at the cathode.

So, the cathode acts as a **negative** electrode.

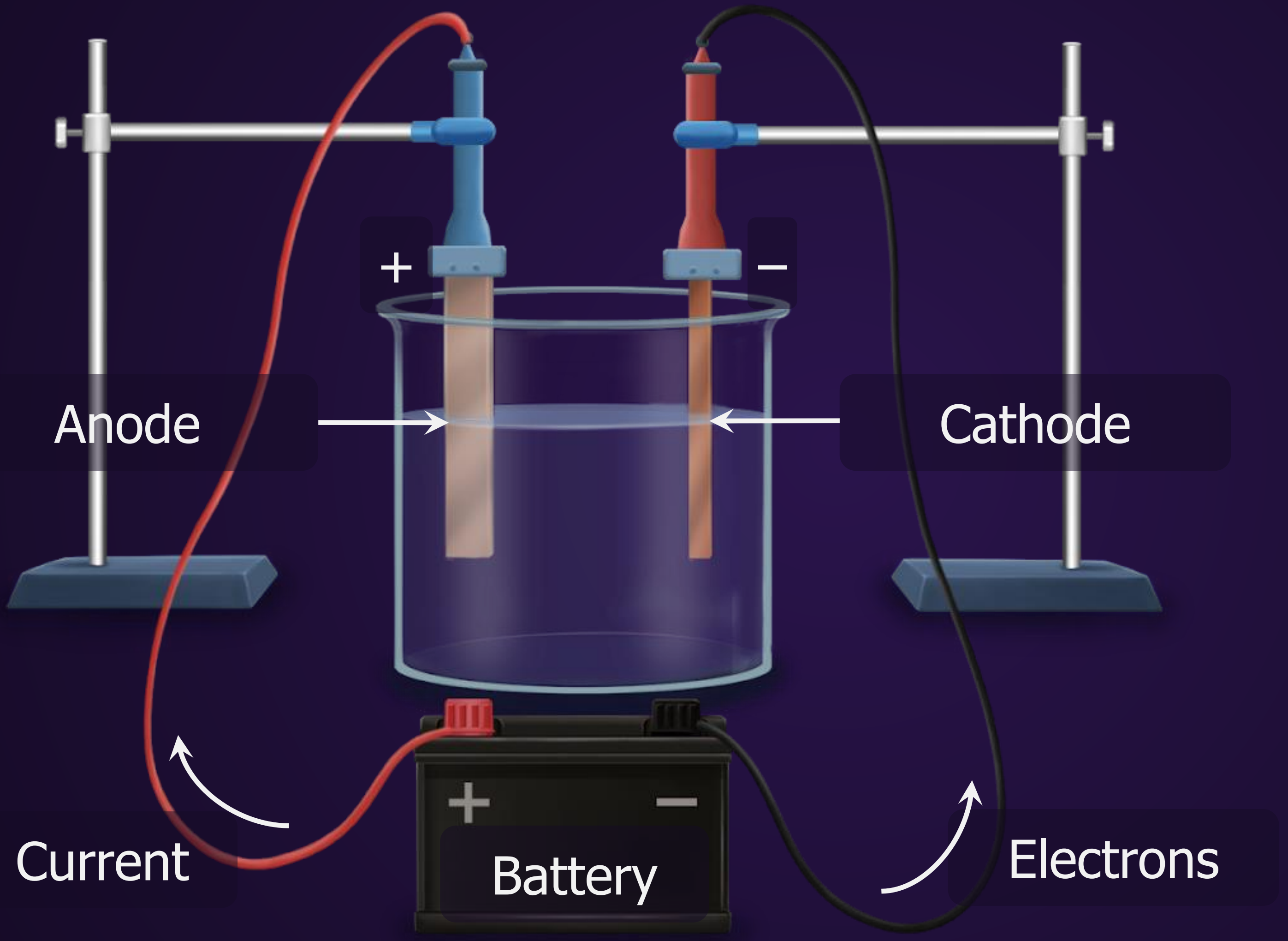
Construction of Electrolytic Cell

Anode is attached to the positive terminal of the battery.

Oxidation occurs at the anode.

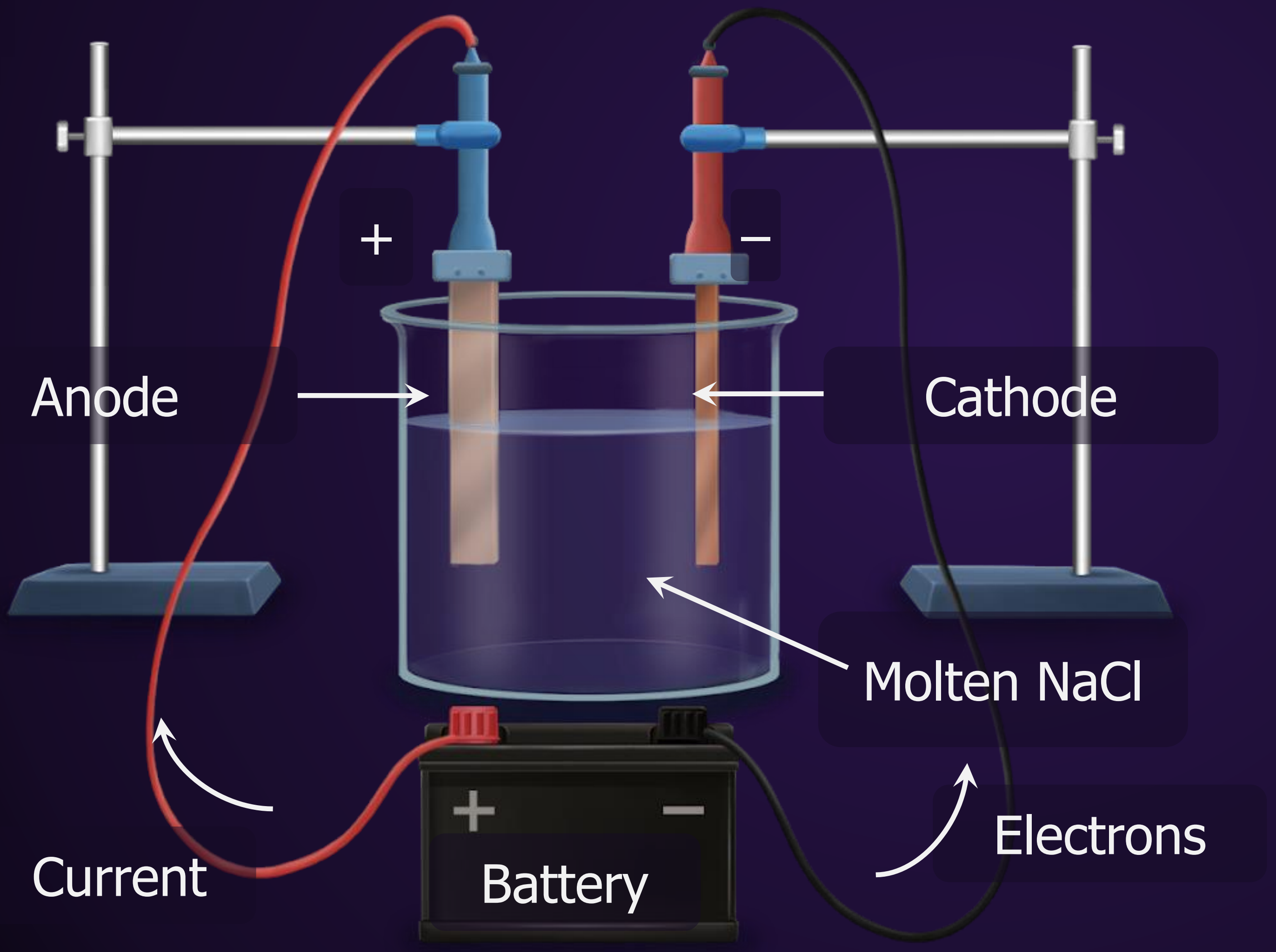
So, the anode acts as a **positive** electrode.

Construction of Electrolytic Cell



Electrolysis of Molten NaCl

Electrolysis of Molten NaCl



Electrolysis of Molten NaCl

Electrode	Half-Reaction
Cathode	$Na^+ (\ell) + e^- \longrightarrow Na (\ell)$
Anode	$2Cl^- (\ell) \longrightarrow Cl_2 (g) + 2e^-$

Overall reaction:

$$2Na^+ (\ell) + 2Cl^- (\ell) \longrightarrow 2Na (\ell) + Cl_2 (g)$$

$$E^0_{cell} < \mathbf{0\ V}$$

Electrolysis of Molten NaCl

Sodium metal and chlorine gas are knowns as **product of electrolysis** of molten NaCl.

Factors Affecting Product of Electrolysis

Product obtained during electrolysis depends on following factors:

- Amount of charge passed into the electrolyte
- Nature of the electrolyte
- Concentration of the electrolyte
- Nature of the electrode

Faraday’s Laws of Electrolysis

Faraday’s Laws of Electrolysis

These laws are about the **amount** of product of electrolysis (or the mass of substance **produced or deposited** on electrodes).

Faraday’s Laws of Electrolysis

Faraday’s first law

Faraday’s First Law

The **mass** deposited/released/produced of any substance during electrolysis

Is proportional to the **amount of charge** passed into the electrolyte

Faraday’s First Law

$$W \propto Q$$

$$W = ZQ$$

W: Mass deposited or liberated
Q: Amount of charge passed
Z: **Electrochemical equivalent** of the substance

Electrochemical Equivalent of the Substance (Z)

If $Q = 1\ C$

$W = Z$

Z

Mass deposited or liberated when **1 C** of charge is passed into the solution

Unit: **kg/C** or **g/C**

Equivalent Mass (E)

It is mass of any substance produced when **1 mole of electrons** are passed through the solution during electrolysis.

Equivalent Mass (E)

$$E = \frac{\text{Molar mass}}{\text{No. of } e^- \text{ involved in oxidation/reduction}}$$

$$= \frac{M}{\textbf{n-factor}}$$

Calculating Equivalent Mass (E)

1. $Ag^{+}\,(aq) + e^{-} \longrightarrow Ag\,(s)$

$$E = \frac{M}{1}$$

2. $Cu^{2+}\,(aq) + 2e^{-} \longrightarrow Cu\,(s)$

$$E = \frac{M}{2}$$

Calculating Equivalent Mass (E)

3

$$Al^{3+}\,(aq) + 3e^- \longrightarrow Al\,(s)$$

$$E = \frac{M}{3}$$

Faraday’s First Law

We know,

1 mole of e^- = **1 F** of Charge

1 F = 96500 C

96500 C charge flow = **E gram** metal deposited or liberated

Faraday’s First Law

1 C charge flow $= \frac{E}{96500}$ **g** metal deposited

So, $Z = \frac{E}{96500}$

Z is the mass deposited or liberated when **1 C** of charge is passed into the solution.

Faraday’s First Law

From Faraday’s first law,

$$W = ZQ$$

Substituting the value of Z,

$$W = \frac{E}{96500} \times Q$$

Faraday's First Law

$$W = \frac{EQ}{96500}$$

$$E = \frac{M}{\text{n-factor}}$$

$$Q = i \times t$$

$$W = \frac{\text{Molar mass}}{\text{n-factor}} \times \frac{i \times t}{96500}$$

Find the number of electrons involved in the electro-deposition of 63.5 g of copper from a solution of copper sulphate.

- a 12.04×10^{23}
- b 13.04×10^{21}
- c 10.04×10^{20}
- d 12.04×10^{22}

Find the total charge required for the oxidation of 2 moles of $Mn_3O_4^{2-}$ to MnO_4 in presence of an alkaline medium.

- a 15 F
- b 20 F
- c 22 F
- d 25 F

Faraday’s Laws of Electrolysis

Faraday’s Second Law

Faraday’s Second Law

If equal charge **(Q)** is passed through two electrolytic cells and cells are connected in series,

↓

The mass deposited at the electrode will be in the ratio of their **electrochemical equivalents** or **equivalents masses.**

Faraday’s Second Law

Considering two electrolytic cells 1 and 2 connected in series

Applying the first law,

$$W_1 = Z_1 \times Q_1$$

$$W_2 = Z_2 \times Q_2$$

For two cells

Faraday’s Second Law

Since charge passed is same for both the cells,

$$Q_1 = Q_2$$

So, $$\frac{W_1}{W_2} = \frac{Z_1}{Z_2}$$

Faraday's Second Law

As, $Z = \frac{E}{96500}$

$Z_1 = \frac{E_1}{96500}$ and $Z_2 = \frac{E_2}{96500}$

$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

Faraday's Second Law

$$\frac{W_1}{W_2} = \frac{Z_1}{Z_2} = \frac{E_1}{E_2}$$

Four moles of electrons were transferred from anode to cathode in an experiment on electrolysis of water. Find the approximate total volume of the two gases (dry and at STP) produced (in litres).

- a 22.4
- b 44.8
- c 67.2
- d 89.4

Electrolyte

- Molten form
- Aqueous form

Molten Electrolyte

Electrolysis of **molten NaF** solution

Electrode	Half-reaction	E^0
Cathode	$Na^+ (\ell) + e^- \rightarrow Na (\ell)$	$E^0 = -2.71$ V
Anode	$2F^- \rightarrow F_2 + 2e^-$	$E^0 = -2.87$ V

Product of electrolysis:

Anode	**F_2**
Cathode	**Na**

Aqueous Electrolyte

When **electrolysis** of an aqueous solution of electrolyte is carried out,

There may be **two or more species** present in the solution which may **compete** for reduction at cathode
or oxidation at anode.

Aqueous Electrolyte

For the species competing for **reduction** at **cathode**,

Higher is the **SRP,** greater will be its ease to undergo **reduction** at cathode.

Aqueous Electrolyte

For the species competing for **oxidation** at **anode**,

Lower is the **SRP** (or higher in SOP), greater will be its ease to undergo **oxidation** at anode.

Aqueous Electrolyte

Electrolysis of **aq. NaF** solution

Possibilities at cathode:

$Na^+ (aq) + e^- \longrightarrow Na (s)$	$E^0 = -2.71$ V
$2H_2O (\ell) + 2e^- \longrightarrow H_2 (g) + 2OH^-_{(aq)}$	$E^0 = -0.83$ V

Product of electrolysis at **cathode**	**H_2**

Aqueous Electrolyte

Electrolysis of **aq. NaF** solution

Possibilities at anode:

$2F^- (aq) \longrightarrow F_2 (g) + 2e^-$ $E^0_{ox} = -2.87\ V$

$2H_2O (\ell) \longrightarrow O_2 + 4H^+ + 4e^-$ $E^0_{ox} = -1.23\ V$

Product of electrolysis at **anode**	**O_2**

Aqueous Electrolyte

Electrolysis of **aq. NaCl** solution

Possibilities at cathode:

$Na^+ (aq) + e^- \longrightarrow Na (s)$	$E^0 = -2.71\ V$
$2H_2O (\ell) + 2e^- \longrightarrow H_2 (g) + 2OH^- (aq)$	$E^0 = -0.83\ V$

Product of electrolysis at **cathode**	H_2

Aqueous Electrolyte

Electrolysis of **aq. NaCl** solution

Possibilities at anode:

$2Cl^{-}\ (aq) \longrightarrow Cl_2\ (g) + 2e^{-}$	$E^0_{ox} = -1.36\ V$
$2H_2O\ (\ell) \longrightarrow O_2\ (g) + 4H^{+}\ (aq) + 4e^{-}$	$E^0_{ox} = -1.23\ V$

Product of electrolysis at **anode**: $\mathbf{Cl_2}$

If the oxidation potential of H_2O is more than that of Cl^-, then why **Cl_2 is liberated**?

According to **thermodynamics**, the oxidation of H_2O to produce O_2 should take place at the **anode**.

However **experimentally,** the rate of oxidation of water is found to be **very slow**.

To **increase its rate**, a greater potential difference is applied known as **overvoltage** or overpotential.

However, because of this, the **oxidation of Cl^- ions** also becomes **feasible** and it takes place at the anode.

Concentration of the electrolyte

- Dilute
- Concentrated

Dilute Electrolyte

Electrolysis of **aq. H_2SO_4** solution

Possibilities at cathode:

$2H^+ (aq) + 2e^- \longrightarrow H_2 (g)$ $E^0 = 0.00$ V

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

Product of electrolysis at **cathode**   **H_2**

Dilute Electrolyte

Electrolysis of **aq. H_2SO_4** solution

Possibilities at anode:

$2SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^-$	$E^0_{ox} = -2.05\ V$
$2H_2O(\ell) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$	$E^0_{ox} = -1.23\ V$

Product of electrolysis at **anode**: **O_2**

Concentrated Electrolyte

Electrolysis of **highly conc. aq H_2SO_4** solution

Possibilities at cathode:

$2H^+ (aq) + 2e^- \longrightarrow H_2 (g)$

$E^0 = 0.00$ V

$2H_2O (\ell) + 2e^- \longrightarrow H_2 (g) + 2OH^- (aq)$

$E^0 = -0.83$ V

Product of electrolysis at **cathode**

H_2

Concentrated Electrolyte

Electrolysis of **highly conc. aq H_2SO_4** solution

Possibilities at anode:

$2SO_4^{2-}\,(aq) \longrightarrow S_2O_8^{2-}\,(aq) + 2e^-$ $E^0_{ox} = -2.05\ V$

$2H_2O\,(\ell) \longrightarrow O_2\,(g) + 4H^+\,(aq) + 4e^-$ $E^0_{ox} = -1.23\ V$

Product of electrolysis at **anode** **$S_2O_8^{2-}$**

“Stay Positive. Work Hard. Make It Happen!”

THANK YOU