24.1 ELECTROLYSIS

Learning outcomes

Candidates should be able to:

1. Predict the identities of substances liberated during electrolysis from the state of electrolyte (molten or aqueous), position in the redox series (electrode potential), and concentration
2. State and apply the relationship $F = Le$ between the Faraday constant, F, the Avogadro constant, L, and the charge on the electron, e
3. calculate:
   (a) The quantity of charge passed during electrolysis, using $Q = It$
   (b) the mass and/or volume of substance liberated during electrolysis
4. Describe the determination of the value of the Avogadro constant by an electrolytic method

Introduction

Electrolysis is the breaking down of a compound into its elements using an electric current

For example, the electrolysis of zinc chloride (ZnCl) into its elements, zinc and chlorine.

$ZnCl_2(s) \rightarrow Zn\ (s) + Cl_2\ (g)$

Electrolytic cell (Volta meter):

- The electrochemical cell in which **electrical energy is used to bring about a chemical reaction** is called an electrolytic cell.
- In this cell, **two metallic electrodes are dipped into the solution of a suitable electrolyte**.
- Then, the **electrodes are connected to an external source of electricity,** such as batteries. (DC is required)
- The electrode that is connected to the positive terminal of the battery is called the anode, and the electrode that is connected to the negative terminal of the battery is called the cathode.
- When **electricity is passed, chemical reactions take place inside the cell.** i.e., cations move towards the cathode and anions move towards the anode.
- As an example, let us consider the electrolysis of molten NaCl.

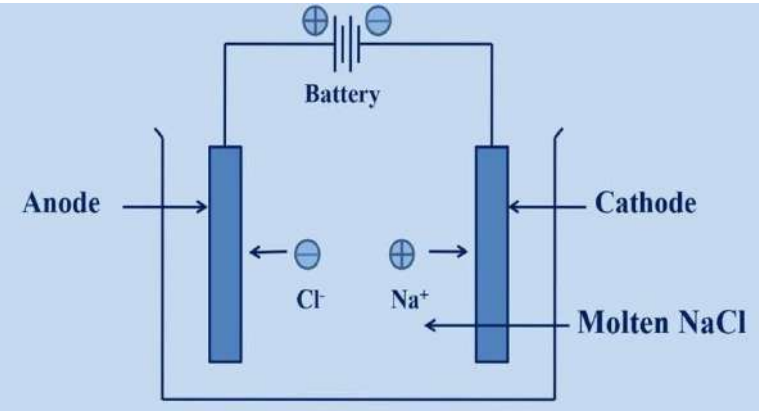

Fig.- Electrolysis of molten NaCl (Schematic)

Reactions involved:

$$NaCl \rightarrow Na^+ + Cl^- \text{ (Molten)}$$

$$\text{At anode: } Cl^- - 1e^- \rightarrow Cl \text{ (oxidation) } Cl + Cl \rightarrow Cl_2$$

$$\text{At cathode: } Na^+ + 1e^- \rightarrow Na \text{ (reduction)}$$

Electrolysis: the decomposition of an ionic compound when molten or in aqueous solution by an electric current.

Electrolyte: a molten ionic compound of an aqueous solution of ions that is decomposed during electrolysis

Electrode: a rod of metal or carbon(graphite) which conducts electricity to or from an electrolyte

Cathode: electrode where reduction occurs

Anode: electrode where oxidation occurs

During electrolysis, reduction occurs at the cathode because ions gain electrons from the cathode, and oxidation occurs at the anode because ions lose electrons to the anode.

Video – the electrolysis of copper (II) chloride using carbon electrodes:
www.youtube.com/watch?v=tCHE_7QeRUc&t=79s
The electrolysis of copper (II) sulfate using carbon electrodes:
www.youtube.com/watch?v=L_BjGKdM2Bk

Electrolysis is a redox reaction.

The role of water in the electrolysis of aqueous solutions of electrolytes

The situation is more complicated when you electrolyse a solution rather than a melt because of the presence of water.

Water itself is a very weak electrolyte because it splits to a very small extent into hydrogen ions and hydroxide ions.

That means that you may have more than one ion arriving at each electrode, and there can be a choice over which gets discharged.

For example, if you electrolyse sodium chloride solution, sodium ions and hydrogen ions (from the water) are both attracted to the cathode, and chloride ions and hydroxide ions (from the water) are both attracted to the anode

The electrochemical series

The table below lists a few metals (and hydrogen) showing their tendency to lose electrons. The more negative the E° value (usually read as "E-nought"), the further to the left the position of equilibrium lies.

Equilibrium	E° (volts)
$Li^+_{(aq)} + e^- \rightleftharpoons Li_{(s)}$	-3.03
$K^+_{(aq)} + e^- \rightleftharpoons K_{(s)}$	-2.92
$Ca^{2+}_{(aq)} + 2e^- \rightleftharpoons Ca_{(s)}$	-2.87
$Na^+_{(aq)} + e^- \rightleftharpoons Na_{(s)}$	-2.71
$Mg^{2+}_{(aq)} + 2e^- \rightleftharpoons Mg_{(s)}$	-2.37
$Al^{3+}_{(aq)} + 3e^- \rightleftharpoons Al_{(s)}$	-1.66
$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$	-0.76
$Fe^{2+}_{(aq)} + 2e^- \rightleftharpoons Fe_{(s)}$	-0.44
$Pb^{2+}_{(aq)} + 2e^- \rightleftharpoons Pb_{(s)}$	-0.13
$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)}$	0

$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$	+0.34
$Ag^{+}_{(aq)} + e^- \rightleftharpoons Ag_{(s)}$	+0.80
$Au^{3+}_{(aq)} + 3e^- \rightleftharpoons Au_{(s)}$	+1.50

That means that the more negative the E° value, the greater the tendency for one of these elements to lose electrons and form its ions.

That also means that something like lithium will have little tendency to pick up electrons to form atoms once it has ionised.

By contrast, something with a positive E° value will be reluctant to lose electrons to form ions, but it will be quite easy to make one of its ions pick up electrons to make the neutral element again.

So, gold won't be very reactive, because it has a very positive E° value. It won't be easy to remove electrons to make gold ions, but it will be easy to convert gold ions back into gold metal again.

The electrochemical series can be thought of as an extended, and slightly modified, reactivity series.

The Two Golden Rules

Electrolysis is simply a competition between ions.

- At the **cathode (–)**, **reduction** occurs (gain of electrons).
- At the **anode (+)**, **oxidation** occurs (loss of electrons).

The products formed depend on **which ions are discharged more easily**.

▽ **What Happens at the Cathode?**

Positive ions (**cations**) move towards the negative electrode.

Rule 1: Metals below hydrogen

Metals **less reactive than hydrogen** (e.g. Cu, Ag) are discharged.

✓ Metal is deposited.

Examples

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

Rule 2: Metals above hydrogen

Highly reactive metals (e.g. Na, K, Mg, Ca) are **not discharged** from aqueous solutions.

Instead, **water is reduced**, producing hydrogen gas.

2H2O+2e−→H2+2OH−2H_2O + 2e^- \rightarrow H_2 + 2OH^-2H2O+2e−→H2+2OH−

✓ Hydrogen gas is evolved.

Borderline metals

Metals such as **Pb^{2+}** and **Zn^{2+}** lie close to hydrogen in the electrochemical series.

Their discharge depends on the **ion concentration**.

- Concentrated solution → metal deposited.
- Dilute solution → hydrogen produced.
- Intermediate concentrations → both may be formed.

△ What Happens at the Anode?

Negative ions (**anions**) move towards the positive electrode.

Rule 1: Halide ions

If **Cl^-, Br^- or I^-** are present, the corresponding halogen is usually produced.

Examples:

2Cl−→Cl2+2e−2Cl^- \rightarrow Cl_2 + 2e^-2Cl−→Cl2+2e−

✓ Chlorine gas

2Br−→Br2+2e−2Br^- \rightarrow Br_2 + 2e^-2Br−→Br2+2e−

✓ Bromine

Rule 2: Other anions

Common anions such as

- SO_4^{2-}
- NO_3^-

are **not discharged**.

Instead, **water is oxidised** to form oxygen.

4OH−→O2+2H2O+4e−4OH^- \rightarrow O_2 + 2H_2O + 4e^-4OH−→O2+2H2O+4e−

(or the equivalent water half-equation)

✓ Oxygen gas is evolved.

⚠ Concentration Matters!

A concentrated sodium chloride solution behaves differently from a dilute one.

Solution	Cathode	Anode
Concentrated NaCl	H_2	Cl_2
Dilute NaCl	H_2	Mainly O_2

As the solution becomes more dilute, oxygen is produced more readily than chlorine.

▧ Worked Examples

Example 1: $CuSO_4$(aq), Graphite Electrodes

Cathode

Cu^{2+} ions are discharged because copper is below hydrogen.

Cu2++2e−→Cu(s)Cu^{2+}+2e^- \rightarrow Cu(s)Cu2++2e−→Cu(s)

✓ Copper coats the cathode.

Anode

Sulfate ions are not discharged.

Water is oxidised.

4OH−→O2+2H2O+4e−4OH^- \rightarrow O_2+2H_2O+4e^-4OH−→O2+2H2O+4e−

✓ Oxygen gas is produced.

Example 2: NaCl(aq), Graphite Electrodes

Cathode

Na^+ is too reactive to be discharged.

Water is reduced.

2H2O+2e−→H2+2OH−2H_2O+2e^- \rightarrow H_2+2OH^-2H2O+2e−→H2+2OH−

✓ Hydrogen gas is produced.

Anode

In concentrated solution,

2Cl−→Cl2+2e−2Cl^- \rightarrow Cl_2+2e^-2Cl−→Cl2+2e−

✓ Chlorine gas is produced.

In dilute solution, oxygen is formed instead.

Quick Memory Trick

Cathode (Reduction)

☑ Metal below hydrogen → **Metal deposited**

☑ Metal above hydrogen → **Hydrogen gas**

Anode (Oxidation)

☑ Halide ions → **Halogen**

☑ Sulfate, nitrate, hydroxide/water → **Oxygen**

Exam Tips

✓ Always identify the **electrode** first (cathode or anode).

✓ Check whether the electrolyte is **molten or aqueous**.

✓ Compare the ions with **hydrogen** in the electrochemical series.

✓ Remember that **concentration mainly affects chlorine production** from chloride solutions and some borderline metal ions.

Calculation applying the relationship F = Le

During electrolysis, current is forced through the cell, and these processes take place:

at the cathode: Zn^{2+} (aq) + 2e → Zn(s)

at the anode: Cu(s) → Cu^{2+} (aq) + 2e

To deposit one mole of zinc and dissolve one mole of copper, two moles of electrons need to be passed through the cell. One mole of electrons carries a charge of −96 500 C. This is the same charge as the charge on one electron, 1.603×10^{-19} C, multiplied by the Avogadro constant, 6.022×10^{23} mol−1. Numerically, the same amount of charge is carried by one mole of protons; this quantity is called the **Faraday constant**, *F*, and has a value of 96 500 C mol^{-1}.

$F = Le$

where *F* = the Faraday constant

L = Avogadro constant

e = the charge on the electron (with a positive sign)

The **coulomb** (symbol C) is the unit of electrical charge. One coulomb is the amount of charge that is passed when one ampere flows for one second. Hence, Q, the amount of charge passed in time t, is:

$$Q = It$$

The amount of charge on one mole of *z*+ ions is *zF*, and so the number of moles deposited is given by:

$$\text{amount} = \frac{\text{charge passed}}{\text{charge per mole of ions}} = \frac{I \times t}{zF} \text{ mol}$$

where z is the charge on the ion, I *is* the current in amperes, and t *is* the time in seconds.

Faraday: the quantity of electric charge (in coulombs) carried by one mole of electrons or one mole of singly charged ions.

1. One Faraday of electricity is equivalent to:

   a. 1602×10^{-12} coulombs b. 96500 coulombs c. 95.5 coulombs d. 22400 coulombs

Calculation of mass and volume

Determination of Avogadro's number by electrolysis
www.youtube.com/watch?v=vp9QYJqFq5s

2. In a cell, oxidation takes place at

   a. anode c. cathode b. electrolyte d. none of these

*** Use this guide alongside the prescribed textbooks for complete coverage & exam preparation.***