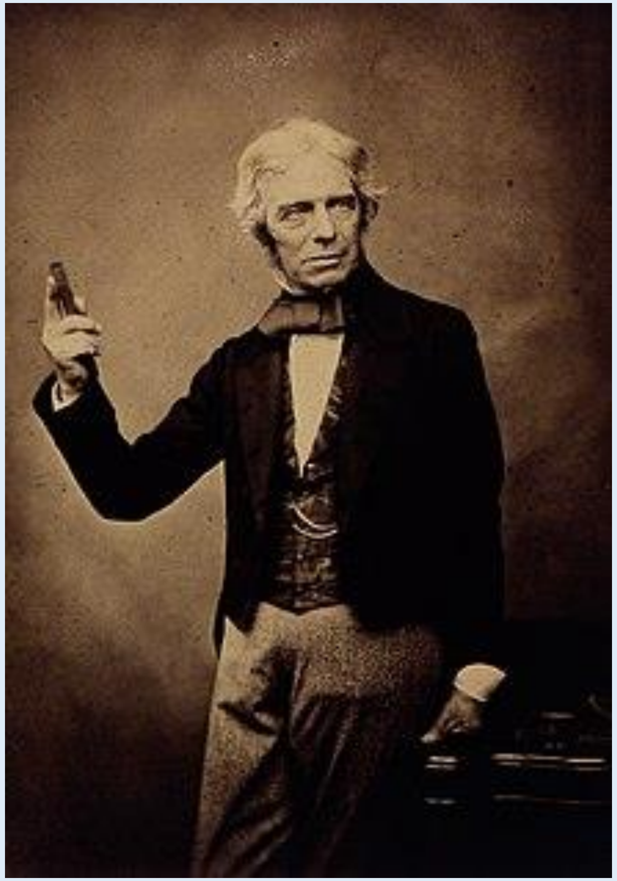
Electrochemical Cells and Electrolytic Cells

Electrochemical	Electrolytic
1. Conversion of chemical energy obtained from a chemical reaction to electrical energy.	1. Utilization of electrical energy to drive a chemical reaction which is non-spontaneous in the absence of electric energy.
2. The anode of a electrochemical cell is negative while the cathode is positive.	2. The anode of a electrolytic cell is positive while the cathode is negative.
3. **In** electrochemical cells, electrons flow from anode to cathode.	3. In electrolytic cells, the electrons flow from the cathode to anode.
4. Salt bridge is required	4. Salt bridge is not required.

Electrolysis

- In chemistry and manufacturing, electrolysis is a process that uses direct electric current to drive a otherwise nonspontaneous chemical reaction.
- The word “electrolysis” was introduced by Michael Faraday



Definition

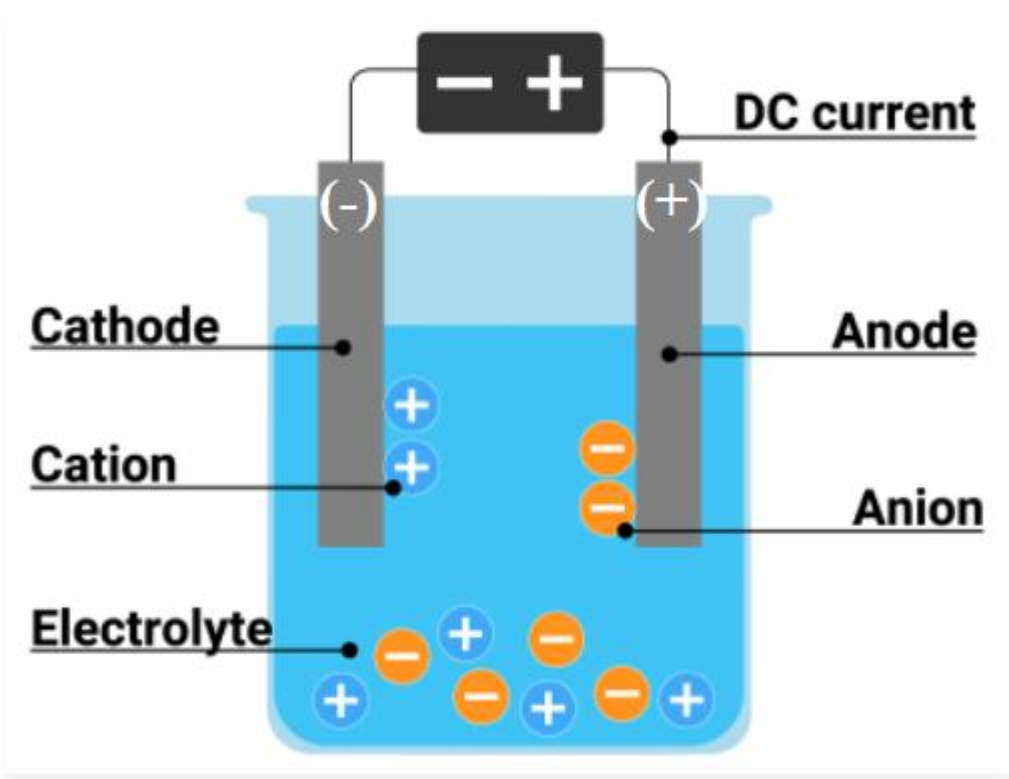
- Electrolysis is defined as a process of decomposing ionic compounds into their elements by passing a direct electric current through the ionic compound in a liquid form. The **cations are reduced at the cathode (negative)** while the **anions are oxidized at the anode**.
- The instrumental setup that is used to conduct the process of electrolysis is called an electrolytic cell.
- The electrolytic cell has four major components.

(i) Electrolyte vessel

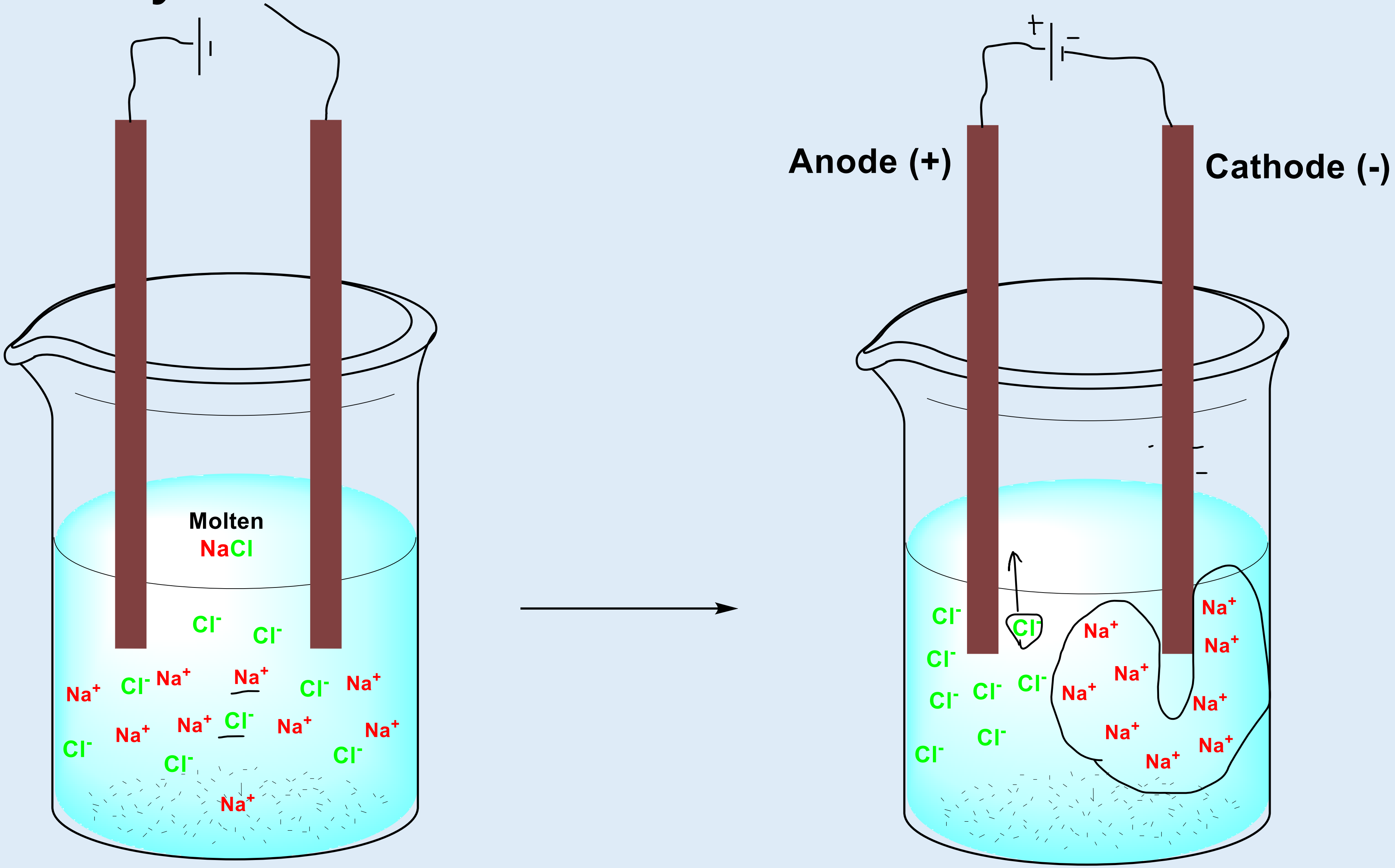
(ii) Electrolyte

(iii) Electrodes

(iv) Direct current source (DC)



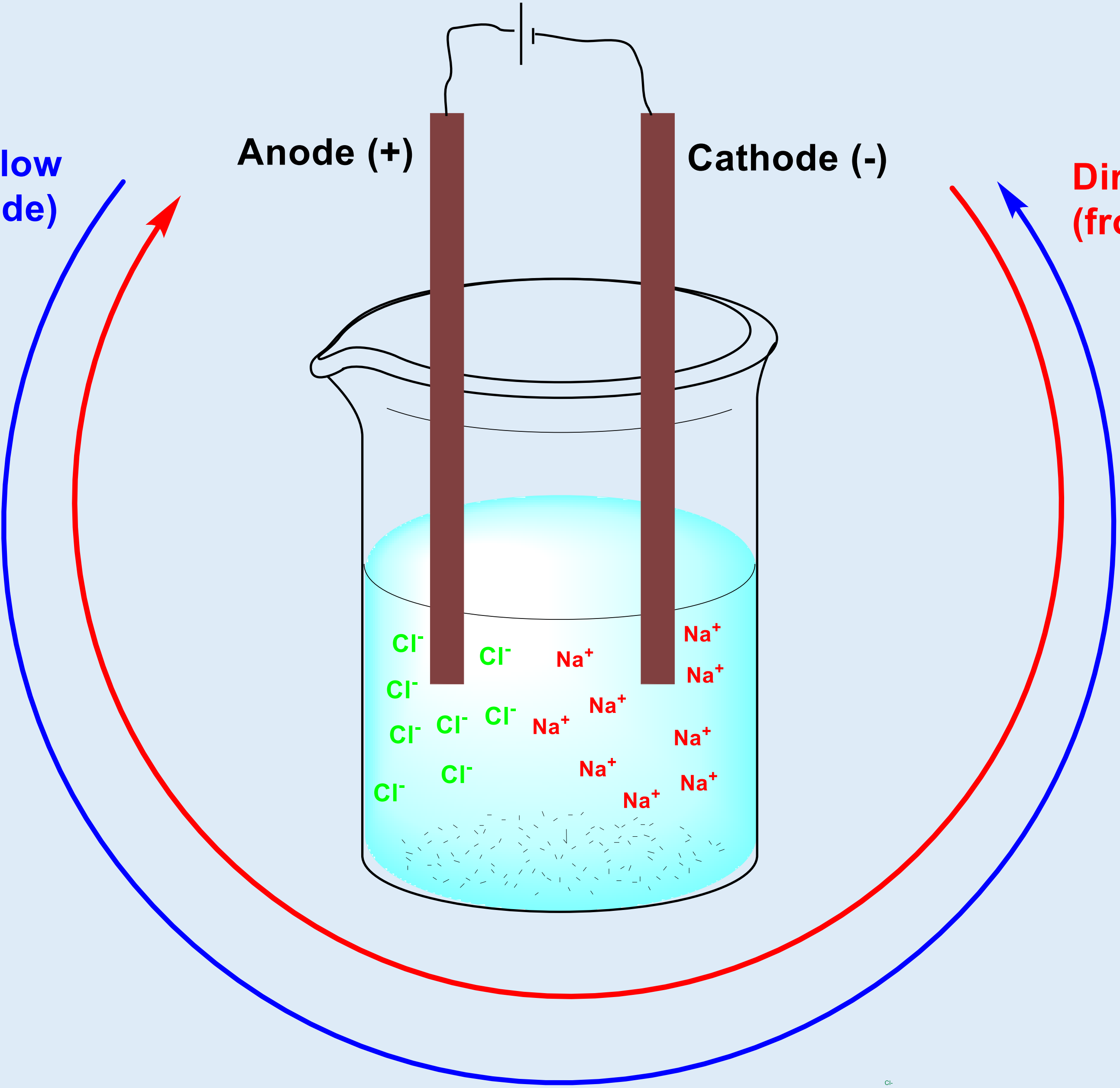
Electrolysis of Molten NaCl


Molten
NaCl
Cl⁻
Cl⁻
Na⁺
Cl⁻
Na⁺
Na⁺
Cl⁻
Na⁺
Cl⁻
Na⁺
Na⁺
Cl⁻
Na⁺
Na⁺
Cl⁻
Cl⁻
Cl⁻
Na⁺
+
−
Anode (+)
Cathode (-)
Cl⁻
Cl⁻
Cl⁻
Cl⁻
Cl⁻
Cl⁻
Cl⁻
Cl⁻
Na⁺
Na⁺
Na⁺
Na⁺
Na⁺
Na⁺
Na⁺
Na⁺
Na⁺
Na⁺

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

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

Direction of current flow
(from anode to cathode)


Anode (+)
Cathode (-)
Cl^-
Cl^-
Na^+
Na^+
Na^+
Cl^-
Na^+
Cl^-
Cl^-
Cl^-
Na^+
Na^+
Cl^-
Na^+
Cl^-
Na^+
Na^+

Direction of electron flow
(from cathode to anode)

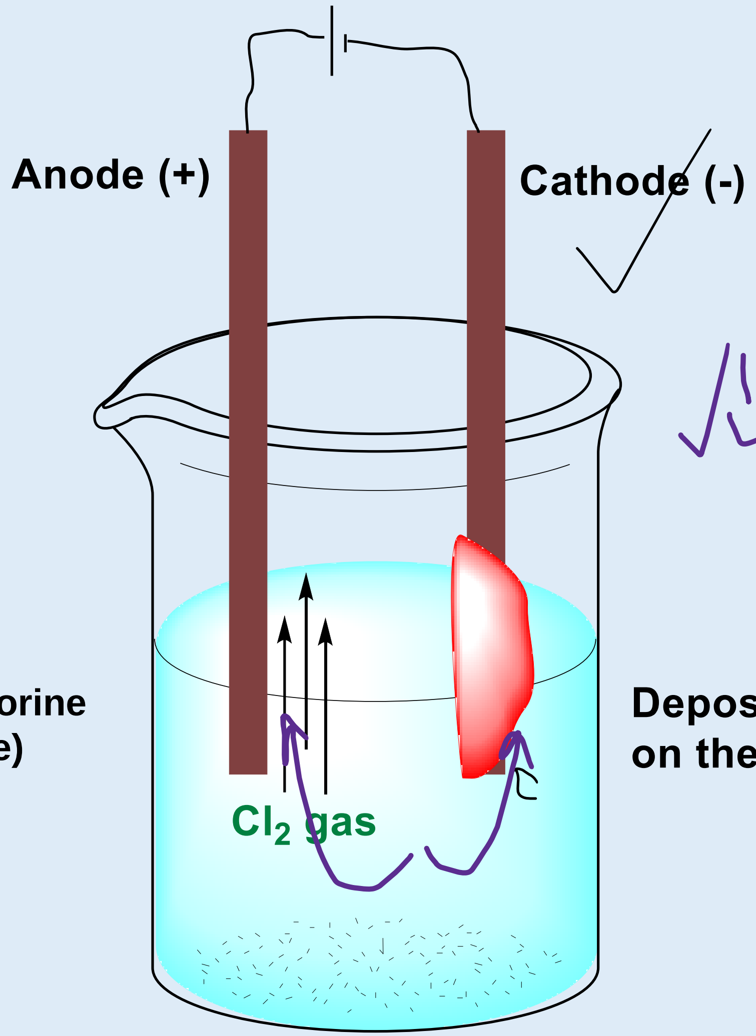
$q = I \times t$

$Na_{(s)} + Cl_{2\,(g)} \rightarrow NaCl$

$\boxed{1000\,C}$

1g

$\frac{100\,A}{400\,A}$ $\frac{10\,s}{20\,s}$



Evolution of Chlorine
(Cl_2 gas at anode)

Deposition of sodium
on the cathode

At cathode (-ve)

$Na^+_{(l)} + e^- \longrightarrow Na_{(s)}$

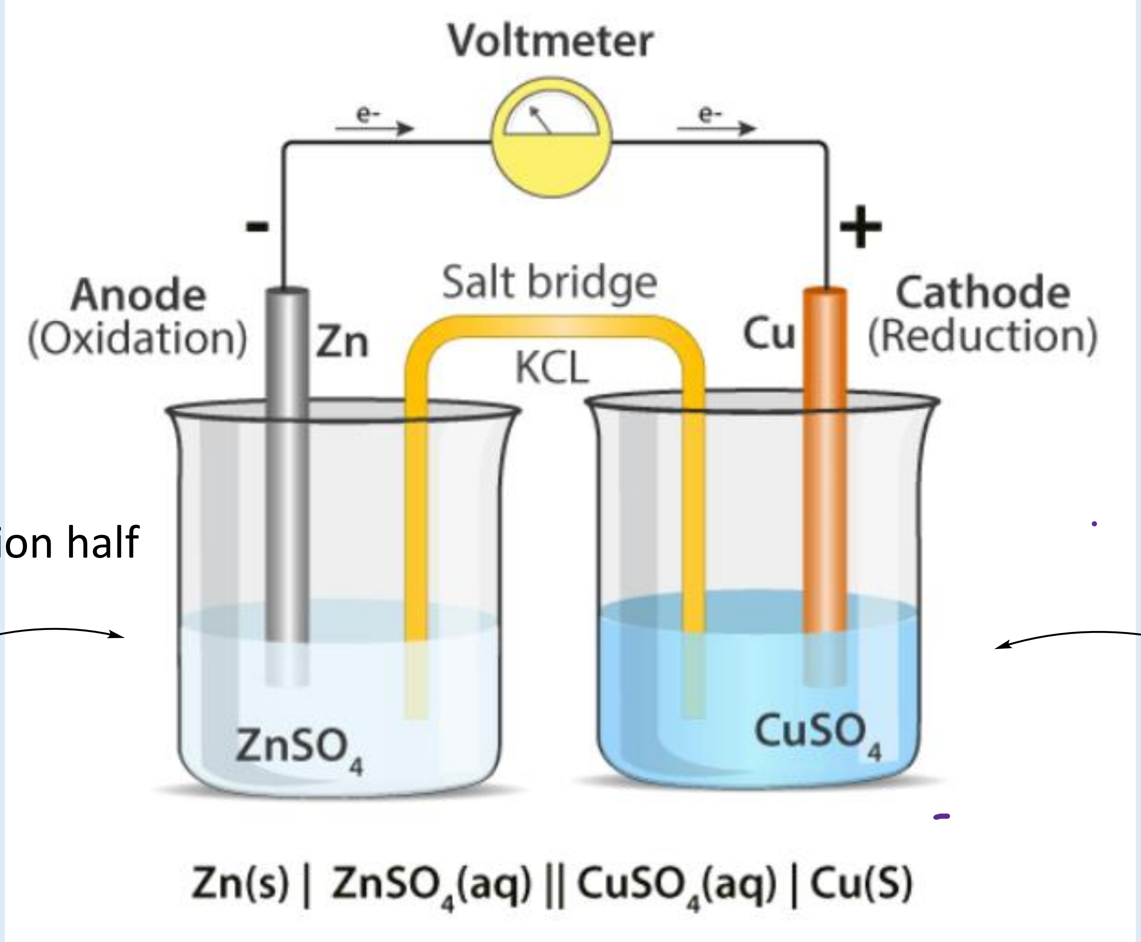
At anode (+ve)

$2Cl^-_{(l)} \longrightarrow Cl_{2\,(g)} + e^-$

-1 0

Daniel Cell

$Zn_{(s)} | Zn^{2+}_{(aq)} || Cu^{2+}_{(aq)} | Cu_{(s)}$


Voltmeter
e-
e-
-
+
Anode
(Oxidation)
Zn
Salt bridge
KCL
Cu
Cathode
(Reduction)
$ZnSO_4$
$CuSO_4$

$Zn(s) | ZnSO_4(aq) || CuSO_4(aq) | Cu(S)$

Anodic compartment / Oxidation half cell

Cathodic compartment/
Reduction half cell

Oxidation is taking place

It is the oxidation half cell

Oxidation half reaction

$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$

Reduction is taking place

It is the reduction half cell

Reduction half reaction

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

Overall Reaction

$Zn\ (s) + Cu^{2+}\ (aq) \longrightarrow \underline{Zn}^{2+}\ (aq) + \underline{Cu}\ (s)$

Standard Reduction Potential (SRP) (eV)

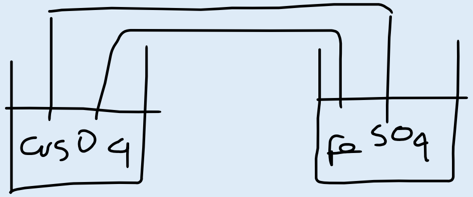
Constant for a particular electrode.

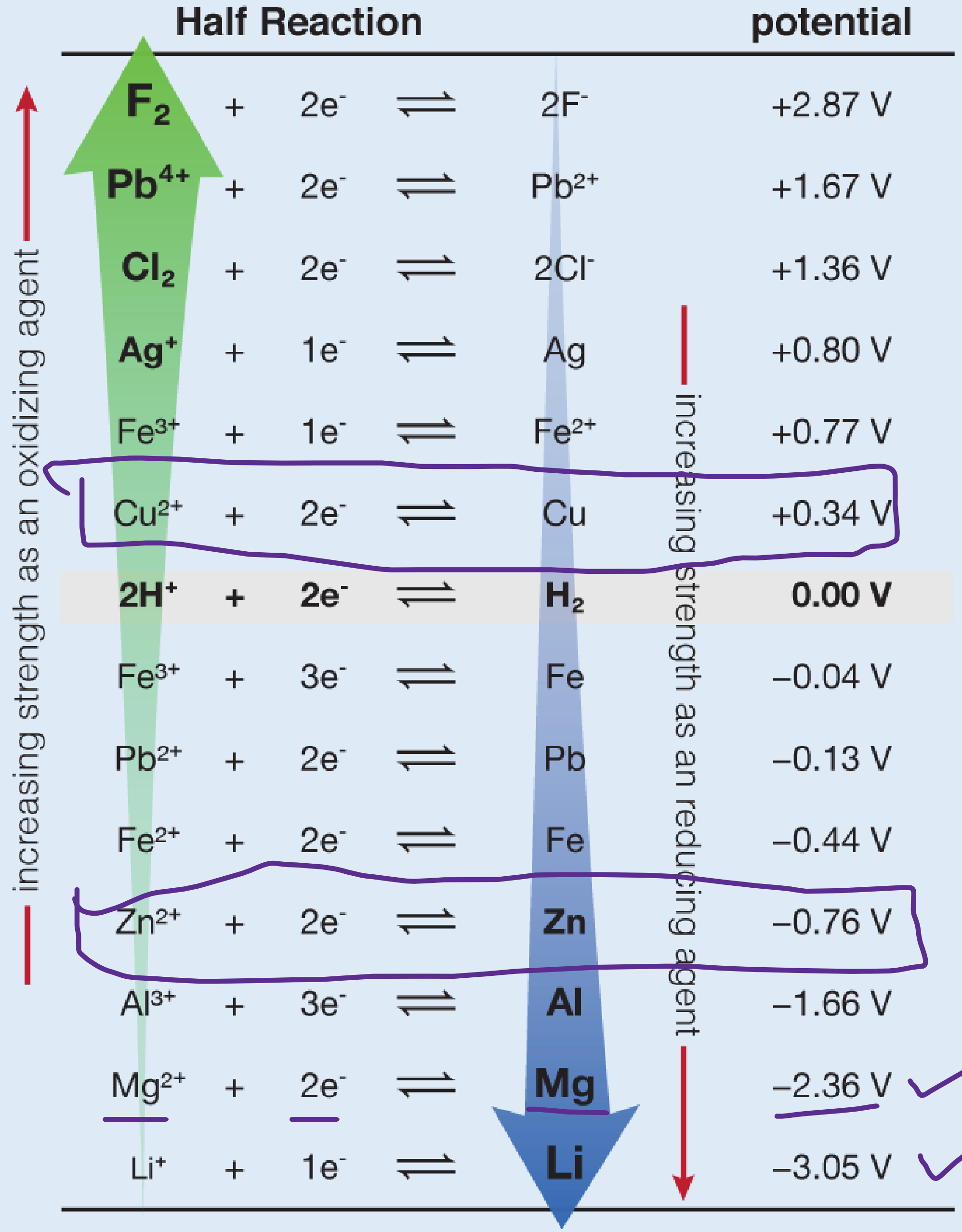
$E^o_{M+/M}$

$E^o_{Mg^{2+}/Mg} = -2.36\ V$

$E^o_{Mg/Mg^{2+}\ (SOP)} = +\ 2.36\ V$

Element with a more negative or smaller standard reduction potential is a better reducing agent.


CuSO4
FeSO4


increasing strength as an oxidizing agent
increasing strength as an reducing agent

Half Reaction					potential
F_2	+	$2e^-$	⇌	$2F^-$	+2.87 V
Pb^{4+}	+	$2e^-$	⇌	Pb^{2+}	+1.67 V
Cl_2	+	$2e^-$	⇌	$2Cl^-$	+1.36 V
Ag^+	+	$1e^-$	⇌	Ag	+0.80 V
Fe^{3+}	+	$1e^-$	⇌	Fe^{2+}	+0.77 V
Cu^{2+}	+	$2e^-$	⇌	Cu	+0.34 V
$2H^+$	**+**	**$2e^-$**	⇌	**H_2**	**0.00 V**
Fe^{3+}	+	$3e^-$	⇌	Fe	−0.04 V
Pb^{2+}	+	$2e^-$	⇌	Pb	−0.13 V
Fe^{2+}	+	$2e^-$	⇌	Fe	−0.44 V
Zn^{2+}	+	$2e^-$	⇌	**Zn**	−0.76 V
Al^{3+}	+	$3e^-$	⇌	**Al**	−1.66 V
Mg^{2+}	+	$2e^-$	⇌	**Mg**	−2.36 V ✓
Li^+	+	$1e^-$	⇌	**Li**	−3.05 V ✓

Faraday’s Laws of Electrolysis

- 1^{st} Law of Electrolysis

It states, during electrolysis, the amount of chemical reaction which occurs at any electrode under the influence of electrical energy is proportional to the quantity of electricity (charge) passed through the electrolyte.

OR

When an electric current is passed through an electrolyte during electrolysis, the amount of substance deposited at an electrode is proportional to the amount of electric charge (current) passed through the electrolyte.

If “**W**” is the mass of a substance deposited at an electrode, then $\boxed{W \propto Q}$, where **Q** = charge passed through the electrolyte.

The SI unit of charge is coulomb (**C**). One coulomb (C) is the amount of charge that flows when 1 **Ampere (A)** of current is passed for 1 second.

$$Q = \text{Current (in Amperes) x Time (in seconds)}$$

$$\Rightarrow Q = I \times t \text{ (Eq. 1)}$$

We have,

$$W \propto Q$$

$$\Rightarrow W = \text{constant} \times Q$$

$$\Rightarrow W = \text{constant} \times I \times t \text{ (from Eq. 1)}$$

$$\Rightarrow \underset{g}{W} = \boxed{Z} \times \underset{1A}{I} \times \underset{1s}{t} \; ✓$$

Z is a proportionality constant called the electrochemical equivalent. It is a characteristic for a particular substance deposited. unit g/C

If **I =** 1 Ampere, t = 1 second, then **W** = **Z.**

The electrochemical equivalent (**Z**) of a substance deposited at an electrode during electrolysis is the mass of the substance deposited on passing 1 Ampere of current for 1 second through the electrolyte.

For a particular element with an equivalent mass **E,** the electrochemical equivalent (**Z**) is related as:

Where **F** is a constant called Faraday's constant and has a value **96500 C mol^{-1}**. (96487 C mol^{-1})

$$\mathbf{Z} = \frac{\mathbf{E}}{\mathbf{F}}$$

g

Equivalent mass: Unit = gram per equivalent (g eq^{-1})

H_2SO_4

For Acids: $E = \frac{\text{molar mass}}{\text{basicity (no.of H+)}}$, e.g. For HCl, E = 36.5/1 = 36.5 g eq^{-1}

For bases: $E = \frac{\text{molar mass}}{\text{acidity (no of OH ions)}}$, e.g., For $Ca(OH)_2$, E = 74/2 = 37 g eq^{-1}

For cations/anions: $E = \frac{\text{atomic mass}}{\text{valency (charge)}}$, e.g., For Ca^{2+}, E = 40/2 = 20 g eq^{-1}