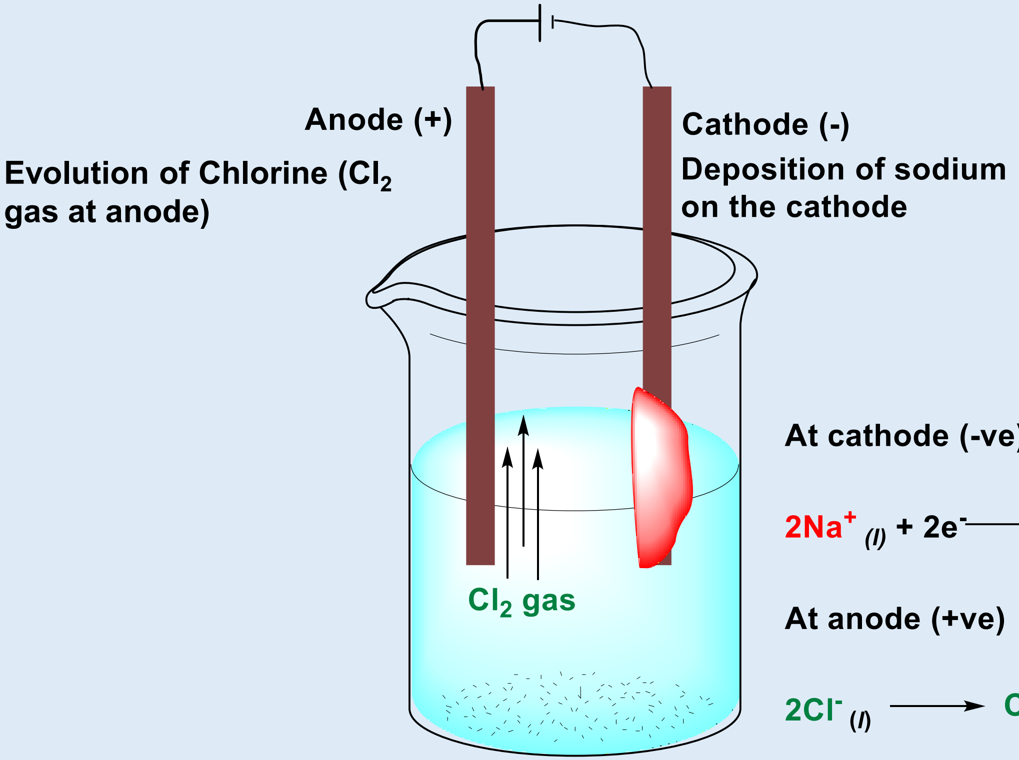

At cathode (-ve)

$2Na^{+}_{(l)} + 2e^{-} \longrightarrow 2Na_{(s)}$; $E^{o}_{Na+/Na} = -2.713$ V

At anode (+ve)

$2Cl^{-}_{(l)} \longrightarrow Cl_{2\,(g)} + 2e^{-}$; $E^{o}_{Cl-/Cl2} = -1.36$ V

Overall Reaction

$2Na^{+}_{(aq)} + 2Cl^{-}_{(aq)} \rightarrow 2Na_{(s)} + Cl_{2\,(g)}$; $E^{o}_{cell} = -4.073$ V

Gibbs' Free Energy; $\Delta G^{o} = -\ n \times F \times E^{o}_{cell}$

n = electrons transferred = 2

F = constant

E^{o}cell = negative => ΔG^{o} = positive??

A minimum of more than +4.073 V of external voltage must be supplied for the above reaction to occur.

Faraday's Constant

- Faraday's Constant (F) is defined as the charge on one mole of electrons
- Charge on one electron = 1.6×10^{-19} C
- No. of electrons in 1 mole = 6.022×10^{23} mol^{-1}

$\Rightarrow$Charge on one mole of electrons = 6.022×10^{23} mol^{-1} $\times 1.6 \times 10^{-19}$ C = 96487 C/mol

Q. Calculate the number of electrons present in one coulomb of charge.

Q1. Molten copper sulfate was electrolysed for 10 minutes with a current of 1.5 Amperes. What is the mass of copper deposited at the cathode? (F = 96487 C mol^{-1})

Ans:

Given, Current passed I = 1.5A, Time (t) = 10 minutes = 10 x 60 = 600 s

Mass of Copper deposited, **W = Z x I x t**

Z for copper = E/F (where E = equivalent mass), F = Faraday's constant

Equivalent mass of copper = Atomic mass/ Valency = 63.546 g mol^{-1}/ 2 = 31.773 g/mol

Z = 31.773 gmol^{-1}/96487 Cmol^{-1} = 3.292 x 10^{-4}g C^{-1}.

$\Rightarrow$ W = 3.292 x 10^{-4}g C^{-1} x 1.5 A x 600 s = 0.2962 g

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OR

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

For the reduction of 1 mole of Cu^{2+}, 2 moles of electrons are required => 2 x 96487 C Charge = 192974 C

Charge supplied in the present case Q = I x t = 1.5 x 600 = 900 C

$\Rightarrow$ 192974 C reduces 1 mole Cu^{2+}

$\Rightarrow$ 900 C will reduce = 900/192974 Cu^{2+} ions = 4.66 x 10^{-3} moles of Cu^{2+} = 4.66 x 10^{-3} x 64 g = 0.2984 g

Q2. How much charge is required for the following transformations?

(i) Reduction of 1 mole Al^{3+} to Al

(ii) Reduction of 1 mole Cu^{2+} to Cu

(iii) Reduction of 1 mole MnO_4^- to Mn^{2+}

A:

(iii) Reduction reaction of MnO_4^-

$$\overset{7+}{Mn}O_4^- + 8\ H^+ + 5\ e^- \rightarrow Mn^{2+} + 4\ H_2O$$

The reduction of 1 mole of MnO_4^- requires 5 moles of electrons.

Charge on 1 mole of electrons = 96487 C => Charge on 5 mol electrons = 482435 C

Q3. How much electricity (in Faradays) will be required for the production of 20 g Ca from molten $CaCl_2$?

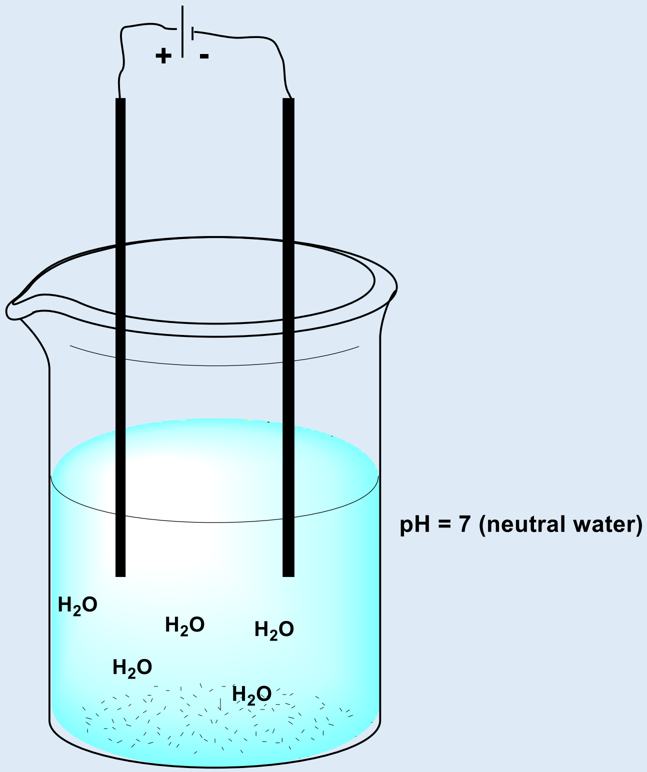
$Ca^{2+}{}_{(aq)} + 2\ e^- \rightarrow Ca_{(s)}$

For the reduction of 1 mole i.e., 40 g Cu^{2+}, 2 mole electrons are required i.e. 2 F charge.

20g Ca = 0.5 mol => 1 F charge will be required.

Q4. **How much electricity (in Faradays) will be required for the production of 20 g Al from molten Al_2O_3**

Electrolysis of water



Self ionization of water

$$\mathbf{H_2O_{(l)} \rightarrow H^+ (aq) + OH^- (aq);\ K_w = 10^{-14}, [H^+] = [OH^-] = 10^{-7} M, [H_2O] = 55.56\ M}$$

During the electrolysis of water, reduction takes place at the cathode

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2\,(g)} + 2OH^-_{(aq)};\ E^o_{H2O/OH^-} = -0.83\ V$$

Also, oxidation takes place at the anode

$$2OH^-_{(l)} \rightarrow O_{2\,(g)} + 2H^+_{(l)} + 4e^-;\ E^o_{OH-/H2O} = -0.4\ V$$

Overall Reaction:

$$2H_2O_{(l)} \rightarrow 2H_{2\,(g)} + O_{2\,(g)};\ E^o_{Cell} = -1.23\ V \Rightarrow GFE > 0$$ (not feasible in the absence of external potential)

A minimum of 1.23V has to be supplied externally. (theoretically)

Faraday’s second law of electrolysis

- Faraday’s second law of electrolysis states that if the same amount of electricity is passed through different electrolytes, the masses of ions deposited at the electrodes are directly proportional to their equivalent masses.