09 December 2020 05:00

Quantitative Aspect of Electrolysis

Faraday's laws of Electrolysis:

First law:

The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt)

$W \propto Q$ $\quad W \rightarrow$ weight of substance deposited, $Q \rightarrow$ charge flown

$W = zQ$

$W = zIt \quad \left[I = \frac{Q}{t}\right] \quad I \rightarrow$ current

$z \rightarrow$ Electrochemical equivalent of a substance

Electrochemical equivalent (z)

$W = zQ$

If $Q = 1C$

$W = z$

z is weight of substance release at electrode by passing 1 C charge.

units: $\frac{g}{C}$, $\frac{g}{As}$

Equivalent weight of a substance (E)

The weight of substance released by passing 1 mole electrons.

charge on 1 mole $e^- = 6.022 \times 10^{23} \times 1.6 \times 10^{-19} C$

$\simeq 96500C = 1F$ (F → Faraday)

Weight deposited by passing 96500 C charge = E

" " " " 1 C " = $\frac{E}{96500}$

$z = \frac{E}{96500}$

$W = zIt$

$$\boxed{W = \frac{EIt}{96500}}$$

$E = \frac{M}{n \text{ factor}}$ $\quad M \rightarrow$ Molar mass

n factor = electrons exchanged by 1 mol of substance

= change in oxidation number of element
× number of atoms of the element in 1 molecule

eg: $\overset{+7}{Mn}O_4^- + 5e^- \rightarrow \overset{2+}{Mn}$ (n factor MnO_4^- = 5)

$\overset{+3}{C_2}O_4^{2-} \rightarrow 2\overset{+4}{C}O_2 + 2e^-$ (n factor $C_2O_4^{2-}$ = 1 × 2 = 2)

i) $Al^{3+} + 3e^- \rightarrow Al$

$\frac{1}{3}Al^{3+} + e^- \rightarrow \frac{1}{3}Al$

$\frac{27}{3} = 9$ gm $E = 9\text{ gm} = \frac{M}{n\text{ factor}}$

ii) $Mg^{2+} + 2e^- \rightarrow Mg$ (n factor = 2)

$\frac{1}{2}Mg^{2+} + e^- \rightarrow \frac{1}{2}Mg$.

(12 gm) $E = \frac{M}{n\text{ factor}} = \frac{24}{2} = 12$.

Second law

The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weight.

$W \propto E$

eg.

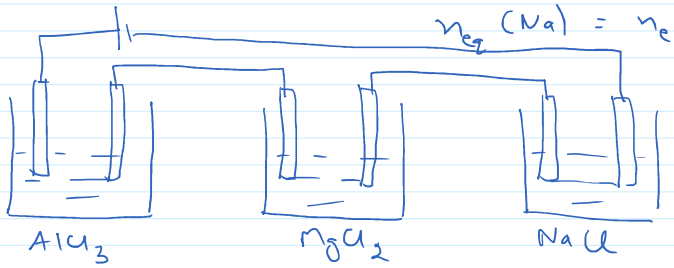
($Na^+ + e^- \rightarrow Na$ $2Cl^- \rightarrow Cl_2 + 2e^-$)

$W_{Na} \propto E_{Na}$ $W_{Cl_2} \propto E_{Cl_2}$

($2Na^+ + 2Cl^- \rightarrow 2Na + Cl_2$) $\frac{W_{Na}}{W_{Cl_2}} = \frac{E_{Na}}{E_{Cl_2}}$

$\frac{W_{Na}}{E_{Na}} = \frac{W_{Cl_2}}{E_{Cl_2}}$

$n_{eq}(Na) = n_{eq}(Cl_2)$



$$n_{eq}(Al) = n_{Mg} = n_{Na} = n_{Cu}$$

Number of equivalents of each substance in a chemical reaction are same

When cells are connected in series, then number of equivalents deposited of each substance are same.

$$W = \frac{E\,I\,t}{96500}$$

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