

CHEM 9.5.4 SODIUM HYDROXIDE

The industrial production of sodium hydroxide requires the use of electrolysis

4.1 Explain the **difference between galvanic cells and electrolytic cells** in terms of **energy requirements**

- Electrolytic cells – **electrolysis – non-spontaneous, requires electrical current – cathode –'ve, E⁰ negative**
- Galvanic cells – **spontaneous, creates electrical current – cathode is +'ve, E⁰ positive**
- **Anode – oxidation, Cathode – reduction** applies to both and electrons always flow from **anode to cathode**
 - **Only the sign of the electrodes are swapped**

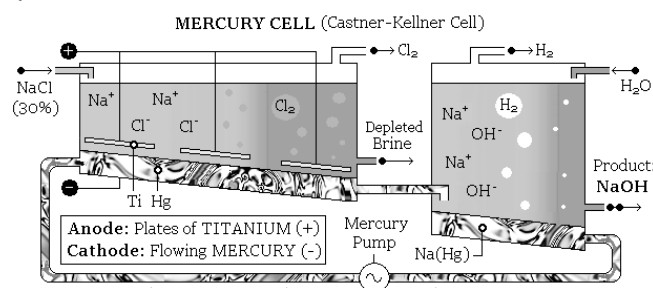
4.2 Outline the **steps in the industrial production of sodium hydroxide** from **sodium chloride solution** and describe the reaction in terms of **net ionic and full formulae equations**

- Three types of **electrolytic cells** used – **mercury, diaphragm, membrane**, generally same steps occur
- **Impurities removed** from saturated brine (sodium chloride and water)
 - Ca removed by NaCO₃, Mg removed by NaOH, Fe removed by NaCO₃/NaOH, SO₄ removed by CaCl₂
 - Precipitates removed as a **sludge**
- **Electricity** passed through brine and **products separated** (Cl₂, NaOH, H₂ and wastes)

4.3 Distinguish between the **three electrolysis methods** used to extract sodium hydroxide: **mercury process, diaphragm process and membrane process**, by describing each process and analysing the **technical and environmental difficulties** involved in each process

MERCURY PROCESS (MERCURY CELL) – TITANIUM AND MERCURY (AMALGAM ONE)

- **Process and Structure:**
 - Two tanks connected with **mercury (cathode)**, where Na⁺ reduced (gains electrons)
 - 1. Purified brine pumped into **first tank – Cl⁻ oxidised on titanium plates (anode)** (loses electrons)
 - 2. **Cl₂ gas bubbles** collected, Na forms **amalgam with mercury (Na/Hg)**
 - 3. Second tank contains purified **water** – reacts with sodium
 - 4. **H₂ gas bubbles** collected, NaOH removed, mercury pumped back to first tank
- **Chemistry:**
 - At the anode: $\text{Na}^+_{(\text{aq})} + \text{e}^- \rightarrow \text{Na}/\text{Hg}$
 - At the cathode: $2\text{Cl}^-_{(\text{aq})} \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$ (titanium anode)
 - In the second tank: $2\text{Na}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{NaOH}(\text{aq}) + \text{H}_2(\text{g})$
 - **Overall:** $2\text{NaCl}(\text{aq}) + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH}(\text{aq}) + \text{H}_2(\text{g}) + \text{Cl}_2(\text{g})$
- **Technical Difficulties:**
 - **Anode** is made of inert **titanium plates** as Cl₂ is corrosive and strong oxidant
 - **Mercury** used as it **forms amalgams with metals, liquid:** easily pumped around
 - **Large amounts of currents** used to allow electrolysis – 3 to 4 V
 - Produces **very pure NaOH** and avoids using **asbestos** (see Diaphragm)
- **Environmental Difficulties:**
 - **Mercury** may be lost and discharged into environment – **heavy metal and neurotoxin**



DIAPHRAGM PROCESS (DIAPHRAGM CELL) – CARBON AND STEEL MESH (ASBESTOS ONE)

- **Process and Structure:**
 - **Asbestos diaphragm** separates anode and cathode compartments
 - **Carbon (anode), steel mesh (cathode)**
 - Water reduces in cathode to OH⁻ ions
 - Na⁺ ions **attracted to cathode**, migrate across asbestos diaphragm
 - **Cl₂ gas, H₂ gas** removed and **NaOH and NaCl solution purified by crystallising NaCl**
- **Chemistry:**
 - At the anode: $2\text{Cl}^-_{(\text{aq})} \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$
 - At the cathode: $2\text{H}_2\text{O}_{(\text{l})} + 2\text{e}^- \rightarrow 2\text{OH}^-_{(\text{aq})} + \text{H}_2(\text{g})$
 - **Overall:** $2\text{NaCl}_{(\text{aq})} + 2\text{H}_2\text{O}_{(\text{l})} \rightarrow 2\text{NaOH}_{(\text{aq})} + \text{Cl}_2(\text{g}) + \text{H}_2(\text{g})$
- **Technical Difficulties:**
 - Chlorine gas – anode made of **carbon**
 - **Cl₂ gas and H₂ gas** separated to prevent reaction to form **HCl gas** (corrosive)
 - Many cells used to increase current – 3.5 to 5 V
 - Asbestos does not always stop Cl⁻ and OH⁻ ions – NaCl and ClO⁻ (strong oxidant) created
- **Environmental Difficulties:**
 - Asbestos fibres **dangerous, inhalation causes lung diseases**
 - Depleted brine may contain NaOH – cannot be released into environment

MEMBRANE PROCESS (MEMBRANE CELL) – TITANIUM AND STEEL MESH (PTFE ONE)

- Diaphragm cell, but with **ion exchange polymer membrane** made of **polytetrafluoroethylene (PTFE)**
 - Membrane **only allows movement of water and Na⁺ ions**
- **Chemistry:**
 - At the anode: $\text{Cl}^-_{(\text{aq})} \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$
 - At the cathode: $2\text{H}_2\text{O}_{(\text{l})} + 2\text{e}^- \rightarrow 2\text{OH}^-_{(\text{aq})} + \text{H}_2(\text{g})$
 - Overall: $\text{NaCl}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightarrow \text{NaOH}_{(\text{aq})} + \text{Cl}_2(\text{g}) + \text{H}_2(\text{g})$
- **Technical Difficulties:**
 - **No toxic materials** used – polymer is **inert**
 - Polymer also **has selective permeability**
 - Anode made of titanium due to resistance to Cl₂, 3.5 to 5 V, large amount of current
 - **Environmental Difficulties:** very few, other than **leakages of Cl₂, NaOH or depleted brine**

4.P2 Analyse information from secondary sources to **predict and explain the different products** of the electrolysis of **aqueous and molten sodium chloride**

- Some substances **oxidise or reduce more easily** than others – see standard potentials
- Molten **NaCl** – only **Na⁺ and Cl⁻ ions** present for oxidation/reduction, therefore:
 - At the **anode**: $2\text{Cl}_{(l)}^- \rightarrow \text{Cl}_{2(g)} + 2e^-$
 - At the **cathode**: $\text{Na}_{(l)}^+ + e^- \rightarrow \text{Na}_{(s)}$
 - **Overall**: $2\text{NaCl}_{(l)} \rightarrow 2\text{Na}_{(l)}^+ + \text{Cl}_{2(g)}$
- **Aqueous NaCl** – Na⁺ and Cl⁻, but also H₂O is present and can oxidise/reduce:
 - At the **anode**:
 - $2\text{Cl}_{(aq)}^- \rightarrow \text{Cl}_{2(g)} + 2e^-$ ($E^0 = -1.36\text{V}$)
 - $2\text{H}_2\text{O}_{(l)} \rightarrow 2\text{H}_{(aq)}^+ + \text{O}_{2(g)} + 2e^-$ ($E^0 = -1.23\text{V}$) – easier to oxidise than Cl⁻ ions
 - However, with **concentrated amount of NaCl**, Cl⁻ ions preferentially oxidised
 - At the **cathode**:
 - $\text{Na}_{(aq)}^+ + e^- \rightarrow \text{Na}_{(s)}$ ($E^0 = -2.71\text{V}$)
 - $2\text{H}_2\text{O}_{(l)} + 2e^- \rightarrow 2\text{OH}_{(aq)}^- + \text{H}_{2(g)}$ ($E^0 = -0.83\text{V}$) – easier to reduce than H₂O
 - **Overall for dilute amount of NaCl (< 0.1 mol/L)**
 - $6\text{H}_2\text{O}_{(l)} + 4\text{H}_{(aq)}^+ + 4\text{OH}_{(aq)}^- + 2\text{H}_{2(g)} + \text{O}_{2(g)}$ (but $4\text{H}_{(aq)}^+ + 4\text{OH}_{(aq)}^-$ is $4\text{H}_2\text{O}$)
 - $2\text{H}_2\text{O}_{(l)} \rightarrow 2\text{H}_{2(g)} + \text{O}_{2(g)}$ – so it is just electrolysis of water