

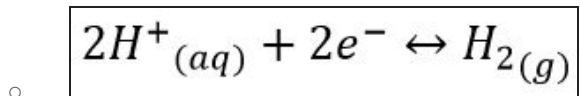
19.1 Electrochemical cells

Voltaic Cells

- **Electromotive Force (EMF):** The energy supplied by a source divided by the electric charge transported through the source
- In voltaic cell, a **cell potential** is generated, resulting in movement of electrons from anode to cathode via external circuit.
- **Cell potential:** the potential difference between the cathode and the anode when the cell is operating
- Under standard conditions, cell potential is called **Standard Cell potential**
 - $E^\circ_{\text{cell}} = E^\circ_{\text{cat}} - E^\circ_{\text{an}}$
- In order to calculate E°_{cell} for a **spontaneous** cell, the cathode is taken as the more positive value from the two electrodes
- The more positive one is also the **strongest oxidizing agent**

Standard Hydrogen Electrode (SHE)

- Consists of an inert platinum electrode in contact with 1 mol dm^{-3} hydrogen ions and hydrogen gas at 100 kPa and 298 K. This is an example of a gas electrode
- Standard electrode potential of a single half-cell cannot be measured on its own. Has to be relative to another cell
- Standard electrode potentials are measured relative to SHE
- SHE has E°_{cell} of 0V
- The reduction half equation corresponding to the SHE cell is



Cell potential and Gibbs free energy

- Spontaneous:
 - E°_{cell} is positive, ΔG is negative
- Non-Spontaneous
 - E°_{cell} is negative, ΔG is positive

- When ΔG is 0, E_{cell} is 0
- Both are related by following equation:

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

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- Where:
 - n = amount, in mol, of electrons
 - F = Faraday's constant = 96500 C mol^{-1}

Electrolytic Cells

- Convert electrical to chemical energy
 - In SL, we looked at electrolysis of molten salt, now we will look at types of electrolysis
 - The higher the reduction potential, higher the tendency to react
1. Electrolysis aqueous NaCl
 - Concentrated
 - You have to take into account water as well
 - At cathode, water is reduced to create **hydrogen gas**
 - At anode, Cl^- is oxidized to create **Cl_2 gas**
 - Diluted
 - At cathode, hydrogen ions are reduced to create **hydrogen gas**
 - At anode, water is oxidized to produce **oxygen gas**
 - **This is equivalent to electrolysis of water**
 2. Electrolysis of CuSO_4
 - Inert graphite (carbon) electrodes
 - Electrodes don't take part in reactions
 - At cathode, copper ions are reduced to create copper deposits
 - At anode, water is oxidized to produce **oxygen gas**
 - Active copper electrodes
 - Electrodes take part in reaction
 - At cathode, copper ions are reduced to create copper deposits
 - At anode, sludge of impurities is found
 - Process known as **electrorefining** in which the impurities in copper are separated from copper itself

- Also the basis of **electroplating** in which a thin layer of metal is deposited onto cathode of another

3. Electrolysis of water

- Water is poor conductor of electricity
- Electrolysis of water is done in **dilute** solutions of sulfuric acid or sodium hydroxide using **inert** Pt electrodes
- At cathode, hydrogen ions are reduced to create **hydrogen gas**
- At anode, water is oxidized to produce **oxygen gas**

Factors affecting amount of product formed

1. **Current**

- Higher the current, greater yield
- $Q = It$

2. **Duration of electrolysis**

- Longer the time, greater yield

3. **Charge on the ion**

- Na^+ required 1 mol of electrons however Pb^{2+} requires 2 mols of electrons