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**
    - $E\square_{cell} = E\square_{cat} - E\square_{an}$
- In order to calculate $E\square_{cell}$ 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 $E\square_{cell}$ of 0V
- The reduction half equation corresponding to the SHE cell is
    - $$2H^+{}_{(aq)} + 2e^- \leftrightarrow H_{2(g)}$$

Cell potential and Gibbs free energy

- Spontaneous:
    - $E\square_{cell}$ is positive, ΔG is negative
- Non-Spontaneous
    - $E\square_{cell}$ is negative, ΔG is positive

- When ΔG is 0, E☐$_{cell}$ is 0
- Both are related by following equation:
    - $$\Delta G^\circ = -nFE^\circ_{cell}$$
    - 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 CuSO4
    - 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