Edexcel Chemistry A-Level

Topic 14: Redox II

Detailed Notes

Redox

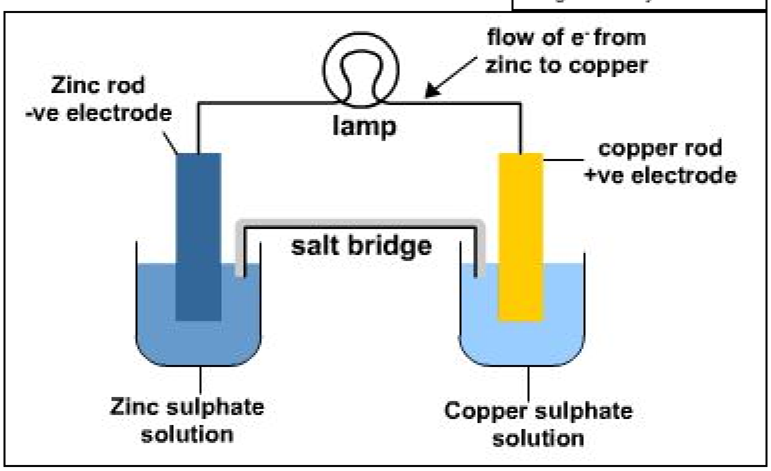
Oxidation is loss of electrons and **reduction is gain** of electrons. Oxidation results in oxidation number becoming more positive and with reduction, it becomes more negative.

Electrochemical Cells

Electrochemical cells use **redox reactions** as the **electron transfer** between products creates a flow of electrons. This flow of charged particles is an **electrical current** which flows between **electrodes** in the cell. A **potential difference** is produced between the two electrodes which can be measured.

Most electrochemical cells consist of **two solutions with metal electrodes** and a **salt bridge**. A salt bridge is a tube of **unreactive ions** that can move between the solutions to carry the flow of charge but will not interfere with the reaction.

Image courtesy of S-cool



Each solution is a **half-cell** which make up the full chemical cell. These half-cells have a **cell potential** which indicates how it will react, either as an oxidation or reduction reaction.

Cell Potentials (E°)

If measured under **standard conditions**, cell potentials are measured compared to the **Standard Hydrogen Electrode (SHE)** to give a numerical value for the half-cell potential.

Positive potentials mean the substances are more easily **reduced** and will **gain electrons**. **Negative** potentials mean the substances are more easily **oxidised** and will **lose electrons** to become more stable.

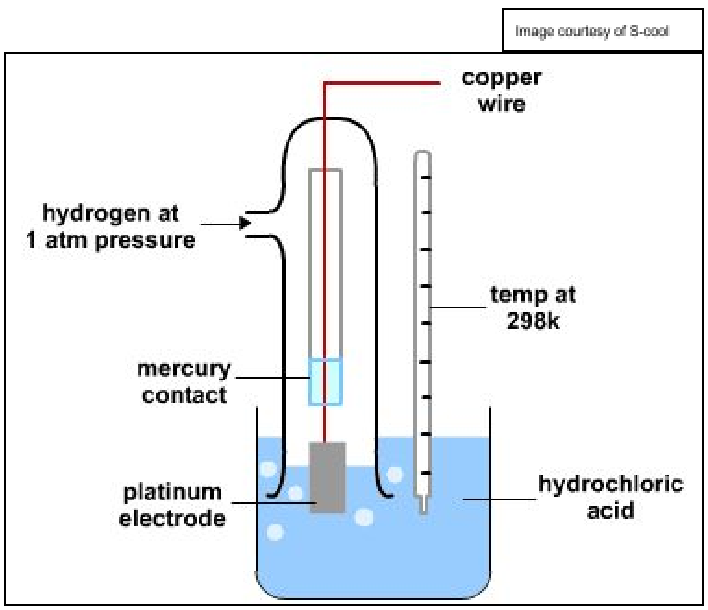
Standard Hydrogen Electrode (SHE)

The standard hydrogen electrode is the **measuring standard** for half-cell potentials. It has a cell potential of **0.00V**, measured under **standard conditions**. These conditions are:

- Solutions of **1.0 moldm^{-3}** concentration
- A temperature of **298K**
- **100 kPa** pressure

The cell consists of **hydrochloric acid, hydrogen gas** and uses **platinum electrodes**. These are very useful as they are **metallic**, so will conduct electricity, but are **inert**, so will not interfere with the reaction.

Example:



Conventional Cell Representation

Cells are represented in a simplified way so that they don't have to be drawn out each time. This representation has **specific rules** to help show the reactions that occur:

- The half-cell with the **most negative** potential goes on the **left**.
- The **most oxidised** species from each half-cell goes **next to the salt bridge**.
- A salt bridge is shown using a **double line**.
- Always include **state symbols**.

Example:

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$$

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

$$\boxed{Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel Cu^{2+}_{(aq)} \mid Cu_{(s)}}$$

Calculating Cell Emf

Standard cell potential values are used to calculate the **overall cell emf**. This is always done as **potential of the right of the cell minus the potential of the left** of the cell when looking at the cell representation.

$$\boxed{Emf_{(cell)} = E^o_{(right)} - E^o_{(left)}}$$

It can also be remembered as the **most positive potential minus the most negative potential**.

If the overall cell potential is a **positive** value, the reaction taking place is **spontaneous and favourable**. The more positive the potential, the more favourable the reaction.

Cell Reactions (Anticlockwise rule)

In a similar way to redox reactions, half-cell reactions can be **combined** to give the overall cell reaction. The **'anti-clockwise rule'** is a good method for ensuring the reaction is formed correctly.

1. Write the **most negative** emf out of the pair on **top**.
2. Draw **anticlockwise arrows** around the reactions.
3. **Balance** the electrons on both sides of the reaction.
4. Write out the cell reaction.

Example:

$$Ni^{2+}_{(aq)} + 2e^- \longrightarrow Ni_{(s)} \qquad E^o = -0.25V$$
$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)} \qquad E^o = +0.34V$$

$$Ni_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Cu_{(s)} + Ni^{2+}_{(aq)}$$

Oxidising and Reducing Agents

Standard electrode potentials can be ordered into a series.

Electrode potentials that are very **positive** are better **oxidising agents** and will oxidise those species more negative than it.

Species that are very **negative** are better **reducing agents** and will reduce those less negative than it.

Example:

Image courtesy of Quora

Half Reaction				Standard Potential (V)
F_2	+ $2e^-$	$\rightleftharpoons$	$2F^-$	+2.87
Pb^{4+}	+ $2e^-$	$\rightleftharpoons$	Pb^{2+}	+1.67
Cl_2	+ $2e^-$	$\rightleftharpoons$	$2Cl^-$	+1.36
O_2 + $4H^+$	+ 4e-	$\rightleftharpoons$	$2H_2O$	+1.23
Ag^+	+ $1e^-$	$\rightleftharpoons$	Ag	+0.80
Fe^{3+}	+ $1e^-$	$\rightleftharpoons$	Fe^{2+}	+0.77
Cu^{2+}	+ $2e^-$	$\rightleftharpoons$	Cu	+0.34
$2H^+$	+ $2e^-$	$\rightleftharpoons$	H_2	0.00
Pb^{2+}	+ $2e^-$	$\rightleftharpoons$	Pb	-0.13
Fe^{2+}	+ $2e^-$	$\rightleftharpoons$	Fe	-0.44
Zn^{2+}	+ $2e^-$	$\rightleftharpoons$	Zn	-0.76
Al^{3+}	+ $3e^-$	$\rightleftharpoons$	Al	-1.66
Mg^{2+}	+ $2e^-$	$\rightleftharpoons$	Mg	-2.36
Li^+	+ $1e^-$	$\rightleftharpoons$	Li	-3.05

stronger oxidizing agent

stronger reducing agent

Effects of Concentration and Pressure

Increasing the concentration of the solutions used in the electrochemical cell makes the cell emf more **positive** as fewer electrons are produced in the reaction.
Increasing the pressure of the cell will make the cell emf more **negative** as more electrons are produced.

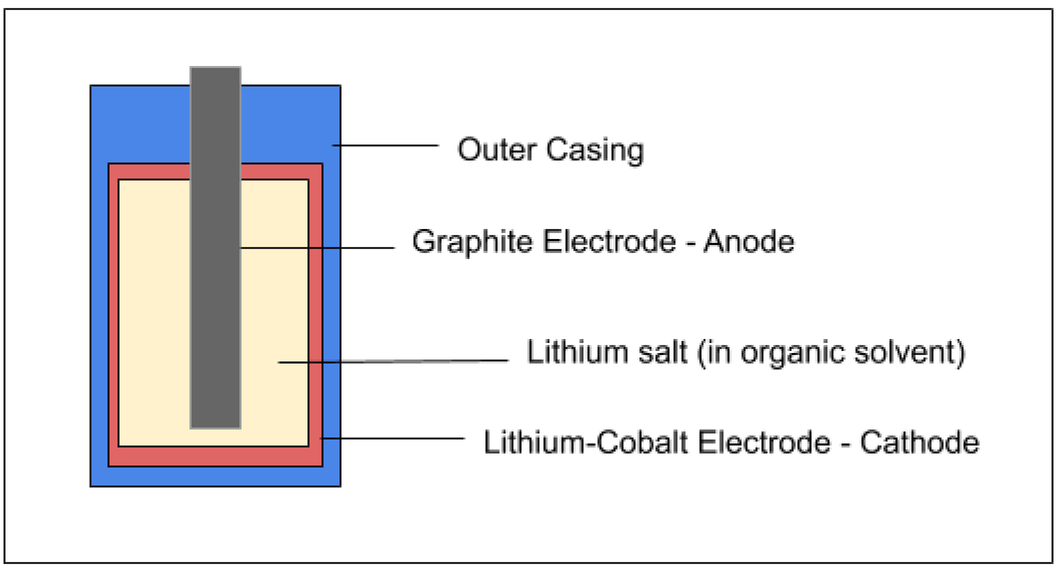
Commercial Cells

Electrochemical cells can be a useful **source of energy for commercial use**. They can be produced to be **non-rechargeable, rechargeable or fuel cells**.

Rechargeable Cells

The reaction that takes place within a rechargeable cell is a **reversible reaction** meaning the reactants can reform. Therefore the cell can be ‘reformed’ meaning it is a rechargeable cell.

Lithium ion cells are a commonly used as rechargeable batteries in phones, laptops and cars. They consist of a **lithium cobalt oxide electrode** and a **graphite (carbon) electrode**. An electrolyte of a **lithium salt** in an organic solvent is used to carry the flow of charge.



The half-cell equations for the reactions can be **combined** to give the full cell equation:
Example: discharging of a lithium-ion cell

Anode $Li \longleftrightarrow Li^+ + e^-$

Cathode $e^- + Li^+ + CoO_2 \longleftrightarrow Li[CoO_2]$

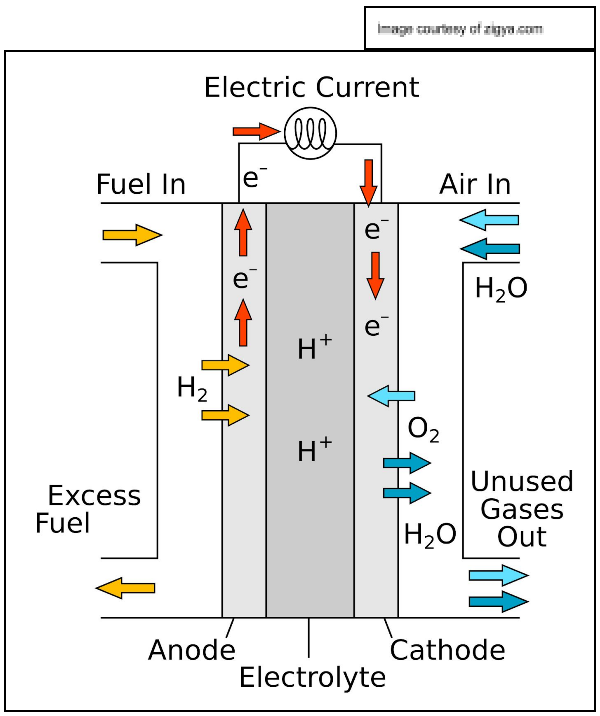
$Li[CoO_2] \longrightarrow Li + CoO_2$

In order to be recharged, a **current has to be applied** over the cell which forces electrons to move in the **opposite direction**. This causes the reaction to reverse, recharging the cell.

Non-rechargeable cells are not able to do this as the reactions used are **impossible to reverse**.

Fuel Cells

This type of electrochemical cell is used to generate an electrical current without needing to be recharged. The most common type of fuel cell is the **hydrogen fuel cell**, which uses a **continuous supply** of hydrogen and oxygen from the air to generate a **continuous current**.



The reaction that takes place produces **water** as the only waste product, meaning the hydrogen fuel cell is seen as being much more **environmentally friendly**.

$$\text{Anode} \qquad H_2 \longleftrightarrow 2H^+ + 2e^-$$

$$\text{Cathode} \qquad \tfrac{1}{2}O_2 + 2H^+ + 2e^- \longleftrightarrow H_2O$$

$$\text{Overall} \qquad H_2 + \tfrac{1}{2}O_2 \longleftrightarrow H_2O$$

The downsides to hydrogen fuel cells include the **high flammability of hydrogen** and that they are **expensive to produce** meaning they are not yet used too commonly.