WJEC Chemistry A-level

3.1: Redox and Standard Electrode Potential

Detailed Notes

Welsh Specification

Oxidation and Reduction (Redox)

Oxidation involves the **loss** of electrons. Reduction involves the **gain** of electrons. This can be remembered using the acronym **OILRIG** (oxidation is loss, reduction is gain).

When oxidation and reduction occur **simultaneously** in a reaction, the reaction is known as a **redox reaction.** The species being **oxidised** loses electrons which are then **donated** and **gained** by the other species which is being **reduced**.

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 then be measured.

Oxidation Number

Oxidation number gives the **oxidation state** of an element or ionic substance. Allocation of oxidation number to a species follows a number of rules:

- Oxidation number of an **element is zero**.
- Oxidation numbers in a **neutral** compound add up to **zero**.
- Oxidation numbers in a charged compound add up to **total the charge**.
- Hydrogen has an oxidation number of **+1** (except in metal hydrides where it is -1).
- Oxygen has an oxidation number of **-2** (except in peroxides and F_2O where it is -1).
- All **halogens** have an oxidation number of **-1**.
- **Group I** metals have an oxidation number of **+1**.

These rules can be used to work out the oxidation number of species or elements in a reaction.
Example:

This compound's oxidation state must total zero, therefore using the rules above, the oxidation number of sulfur can be found:

$$2 - 8 + x = 0$$
$$-6 + x = 0$$
$$X = 6$$

$2 \times (+1) = 2$

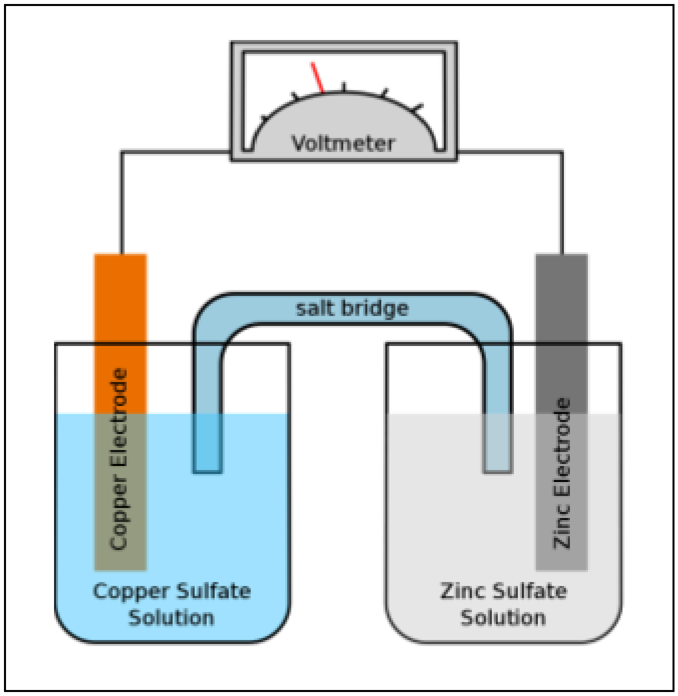
$$\boxed{Na_2}S\boxed{O_4}$$

$2 \times (-2) = -8$

Electrochemical Cells

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. **KNO_3** or **KCl** is commonly used as the solution in the salt bridge.

Example:



(https://commons.wikimedia.org/wiki/File:Galvanic_Cell.svg)
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Each solution is a **half-cell** which together makes 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.

Half Equations

Half equations are used to show the **separate oxidation and reduction** reactions that occur in a redox reaction. They must be **balanced** in terms of the species present and the charges of the species on both sides of the equation.
In order to help write the equations, there is a useful method:

1. Balance **all species** excluding oxygen and hydrogen.
2. Balance **oxygen** using H_2O.
3. Balance **hydrogen** using H^+ ions.
4. Balance **charges** using e^- (electrons).

Following this method ensures the half equations are correctly balanced.

Example: Consider the reduction of $Cr_2O_7^{2-}$ to Cr^{3+}:

	$Cr_2O_7^{2-} \rightarrow Cr^{3+}$
Balance chromiums:	$Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$
Balance oxygens:	$Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$
Balance hydrogens:	$Cr_2O_7^{2-} + 14H^{+} \rightarrow 2Cr^{3+} + 7H_2O$
Balance charges:	$\mathbf{Cr_2O_7^{2-} + 14H^{+} + 6e^{-} \rightarrow 2Cr^{3+} + 7H_2O}$

Half equations can be **combined** in order to determine the overall redox reaction. In order to do this, the number of electrons must be the same for both half equations. This can be done by **scaling up** the number of moles.

Half equations can also be represented for electrochemical cells as **half cells**. These show the separate reactions taking place and can be **combined** to give the overall, **standard cell representation**.

Standard 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:

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

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

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

Cell Potentials

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.

More positive potentials mean the substances are more **easily reduced** and will **gain electrons**. **More negative** potentials mean the substances are more **easily oxidised** and will **lose electrons**.

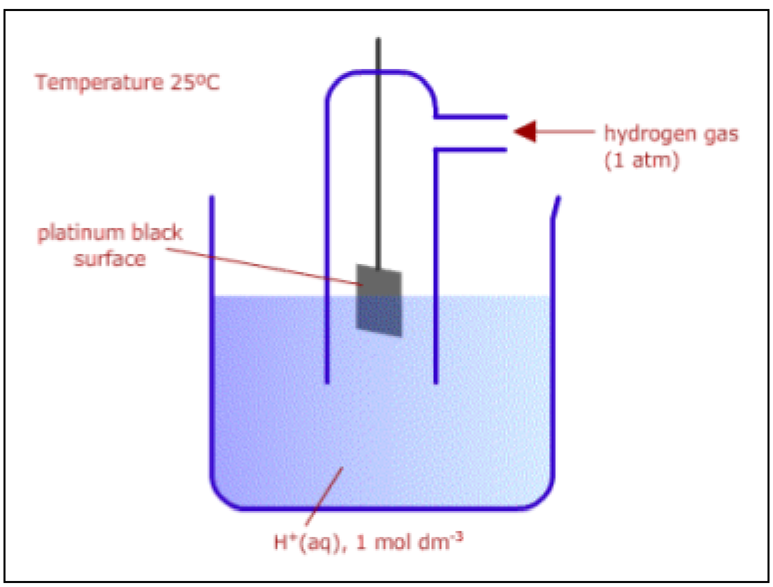
Standard Hydrogen Electrode (SHE)

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

- Solutions of **1.0 mol dm^{-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 also **inert** so will not interfere with the reaction.

Example:



(Modified from http://alevelchem.com/aqa_a_level_chemistry/unit3.5/s353/02.htm)
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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 or **reduced species'** potential **minus oxidised species'** potential.

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

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

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

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

Commercial Uses of Chemical Cells

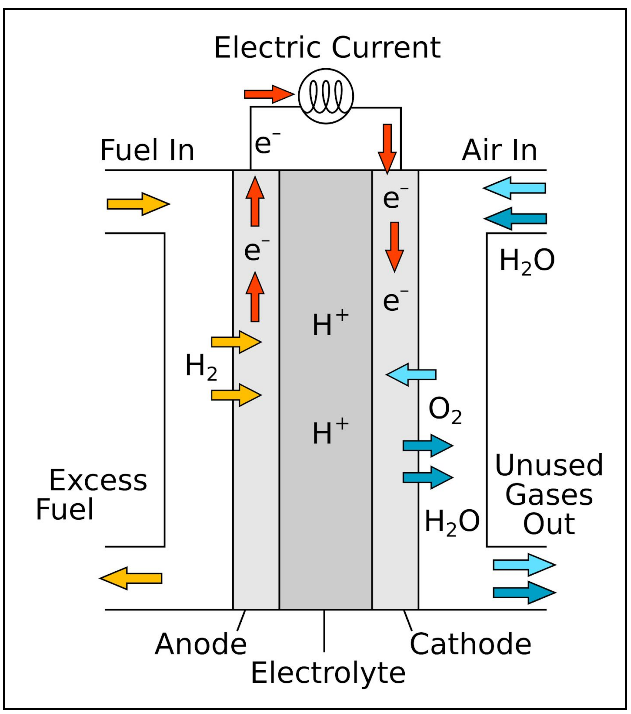
Electrochemical cells can be a useful source of **energy** for **commercial use**. They can be produced to be non-rechargeable, rechargeable or fuel cells.

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 relatively **environmentally friendly**. However, **energy is required** to produce a **supply of hydrogen** and **oxygen**. For example, they can be obtained from the **electrolysis** of water which requires electricity, indicating that hydrogen fuel cells are not completely carbon neutral. Another drawback of hydrogen fuel cells is that hydrogen is **highly flammable** so it requires careful **storage** and **transportation**.

Example:



(https://3dprint.com/29454/3d-printed-fuel-cells/)
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