

Edexcel IAL Chemistry A-level

Topic 16: Redox Equilibria

Detailed notes

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Redox

Oxidation is the loss of electrons and **reduction is the gain** of electrons. Oxidation results in the oxidation number becoming more positive, whereas reduction results in the oxidation number becoming more negative.

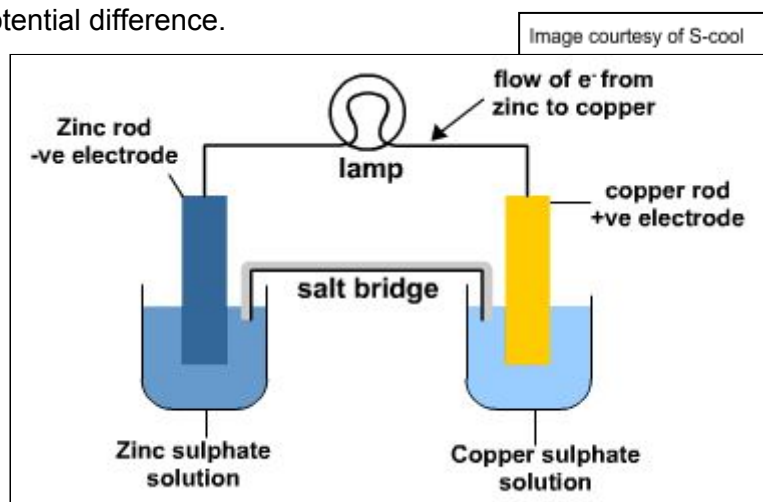
Blocks of the periodic table, such as the s-block and d-block, indicate the orbital of the **outer electron**. During reactions, s-block, d-block and some p-block species tend to undergo **oxidation** whereas p-block elements (further to the right of the periodic table) tend to undergo **reduction**.

Electrochemical Cells

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

Most electrochemical cells consist of **two solutions holding 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, whilst not interfering with the reaction.

Example: Electrochemical cell setup - the position of the lamp is where the voltmeter can be placed to measure the potential difference.



Each electrochemical cell contains two **half-cells** which make up the full chemical cell. These half-cells each have a **cell potential** which indicates how it will react, either in an oxidation or reduction reaction.

Cell Potentials (E^{\ominus})

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. SHE is an electrode used for **reference** on all half-cell potentials since it has a standard electrode potential of **zero**.



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.

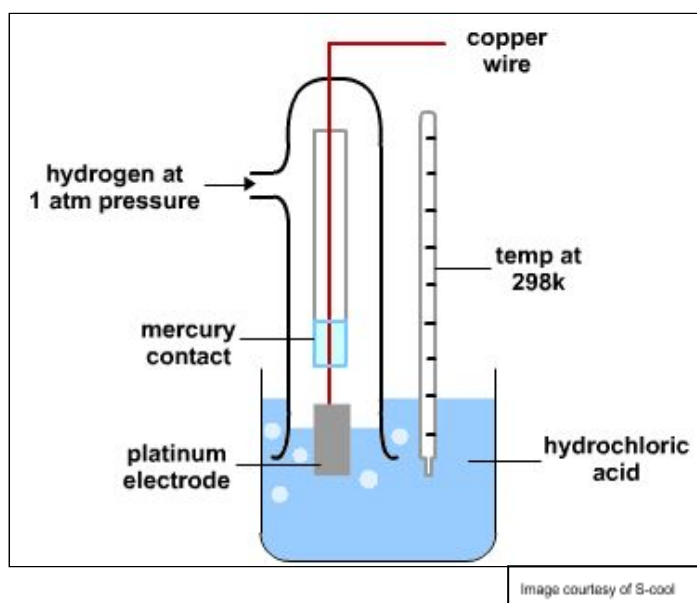
Standard Hydrogen Electrode (SHE)

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 mol dm⁻³** concentration
- A temperature of **298K**
- **100 kPa** pressure

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

Example:



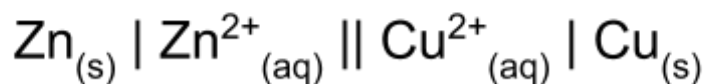
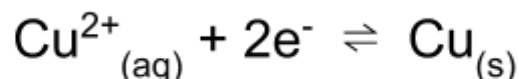
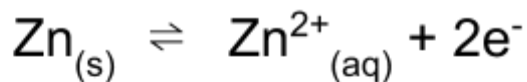
Conventional Cell Representation

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**.
- **State symbols** are always included.



Example: Compared to copper, zinc has the most negative potential so is placed on the left and undergoes oxidation.



Calculating Cell Emf

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

$$\text{Emf}_{(\text{cell})} = E^{\circ}_{(\text{right})} - E^{\circ}_{(\text{left})}$$

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.

The cell emf can be calculated for electrochemical cells containing **different metals or non-metals** in contact with their ions, or alternatively, for electrochemical cells involving two half cells containing **the same element but in different oxidation states**.

For example, a Fe^{2+} half cell and a Fe^{3+} half cell could be combined to make up an electrochemical cell.

Effects of Concentration and Pressure

The conditions are important when measuring the standard cell potential because changing the conditions will change the emf value obtained.

- **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.

E°_{cell} and Entropy

The standard emf of a cell is **directly proportional** to both $\ln(K)$, where K is the equilibrium constant of the reaction, and the **total entropy change**, (ΔS_{total}). This means that a positive E°_{cell} value will have an overall positive entropy change.

Limitations

There are **limitations** to both calculating a standard cell potential using the SHE and using the calculated value to determine reaction **feasibility**.

Although the cell emf value will tell you if a reaction is thermodynamically feasible or not, it does not take into account the **kinetics** of the reaction. Even if a reaction is feasible, it may occur at such a **slow rate** that, in practice, it does not actually occur.

The standard cell potential relies on conditions being **standard** throughout the experiment, when in reality, the system may **deviate** from standard conditions.

Oxidising and Reducing Agents

Standard electrode potentials can also be referred to as **standard reduction potentials** and can be ordered into a series known as the **electrochemical series**.

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

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

Image courtesy of Quora

Half Reaction	Standard Potential (V)
$\text{F}_2 + 2\text{e}^- \rightleftharpoons 2\text{F}^-$	+2.87
$\text{Pb}^{4+} + 2\text{e}^- \rightleftharpoons \text{Pb}^{2+}$	+1.67
$\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$	+1.36
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.23
$\text{Ag}^+ + 1\text{e}^- \rightleftharpoons \text{Ag}$	+0.80
$\text{Fe}^{3+} + 1\text{e}^- \rightleftharpoons \text{Fe}^{2+}$	+0.77
$\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}$	+0.34
$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$	0.00
$\text{Pb}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pb}$	-0.13
$\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe}$	-0.44
$\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}$	-0.76
$\text{Al}^{3+} + 3\text{e}^- \rightleftharpoons \text{Al}$	-1.66
$\text{Mg}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mg}$	-2.36
$\text{Li}^+ + 1\text{e}^- \rightleftharpoons \text{Li}$	-3.05

↑ stronger oxidizing agent ↓ stronger reducing agent



Disproportionation

In a **disproportionation reaction**, a species is both oxidised **and** reduced. This is indicated by both an increase and decrease in the oxidation number for that species.

Electrode potentials can be used to assess whether a species will undergo disproportionation. If the overall E^\ominus_{cell} value is **positive**, then the disproportionation reaction is **feasible**.

Example:

Will Cu^+ ions undergo disproportionation into Cu^{2+} ions and copper?

Reaction	E^\ominus_{cell}
$\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}$	+0.34
$\text{Cu}^{2+} + \text{e}^- \rightleftharpoons \text{Cu}^+$	+0.15
$\text{Cu}^+ + \text{e}^- \rightleftharpoons \text{Cu}$	+0.52

The disproportionation of Cu^+ ions involves the second and third halfreactions.

$$E^\ominus_{\text{cell}} = +0.52 - (+0.15) = +0.37\text{V}$$

This value is positive, therefore the reaction is thermodynamically feasible.

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**.

Fuel Cells

Fuel cells are a type of electrochemical cell used to generate an electrical current without needing to be recharged. In fuel cells, a fuel undergoes **combustion** in **oxygen** and the energy released is used to **generate a voltage**.

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**. Other common fuels include **hydrogen-rich compounds** like methane.



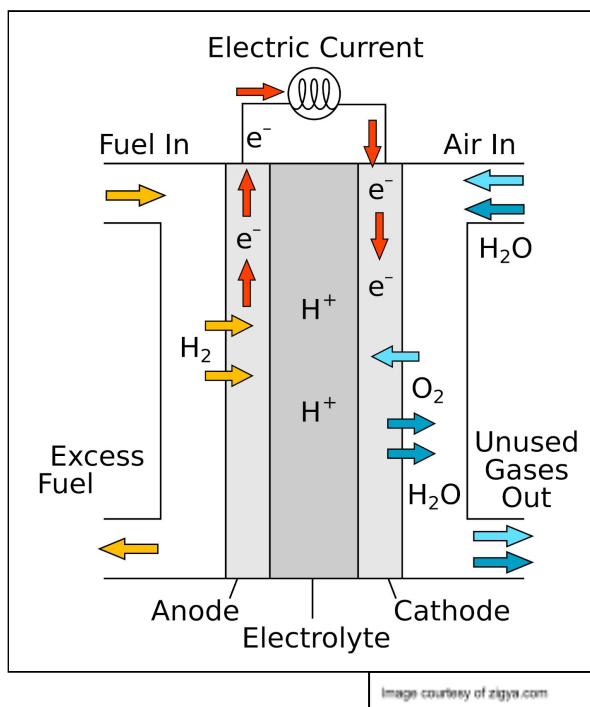
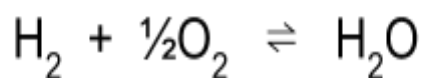


Image courtesy of zigya.com

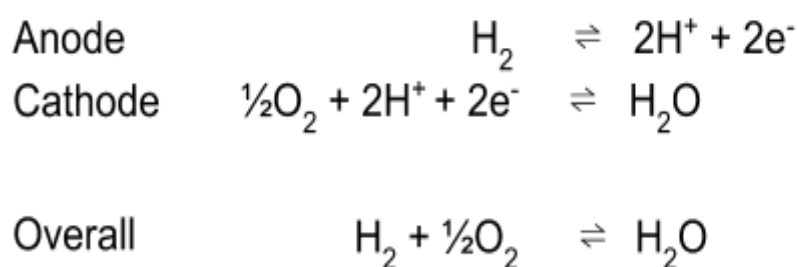
The reaction that takes place in a hydrogen fuel cell produces **water** as the only waste product, so the hydrogen fuel cell is seen as being relatively **environmentally friendly**.

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

The hydrogen fuel cell can be carried out with either an **acidic** or an **alkaline electrolyte**. The overall equation in both systems is the same:

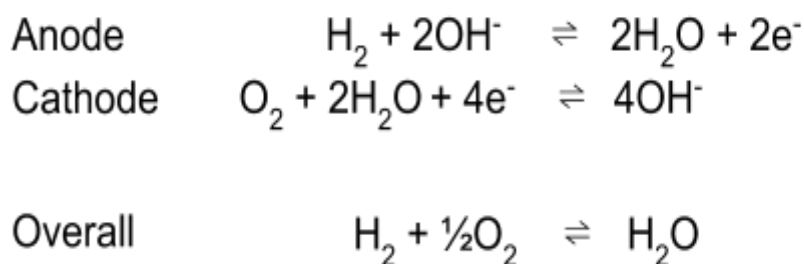


In an acidic electrolyte, such as H_2SO_4 , there are **H^+ ions in solution**. The half equations are as follows:



In an alkaline electrolyte, there are **OH^- ions in solution**. The half equations are as follows:





Redox Titration Calculations

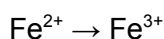
Method for balancing half equations:

1. Balance all atoms except for oxygen and hydrogen.
2. Add **H₂O** to balance **oxygens** (if needed).
3. Add **H⁺ ions** to balance **hydrogens** (if needed).
4. Add **e⁻** to balance **charges**.

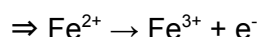
Example:

Write the full half equations for $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ and $\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+}$ and then combine the half equations.

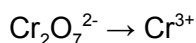
Step 1: Write the full half equation for iron.



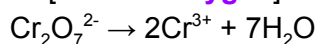
[The only thing that isn't balanced are the **charges**.]



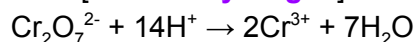
Step 2: Write the full half equation for chromium.



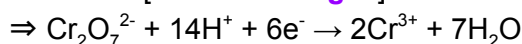
[Balance **oxygen**]



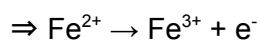
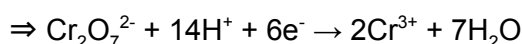
[Balance **hydrogen**]



[Balance **charges**]

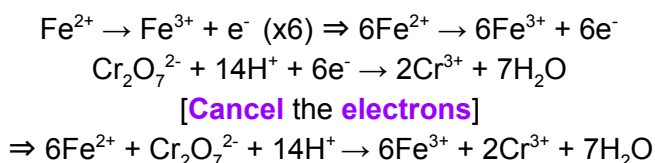


Step 3: Combine the two half equations.



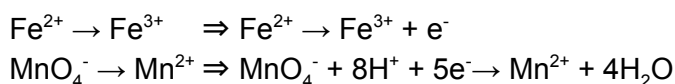
[Balance **electrons**]



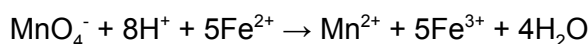


Reaction between Iron ions and Potassium Manganate

In the redox titration between iron ions and manganate ions, the **iron ions are oxidised** while the **manganate ions are reduced**. Their half equations can be found using the method described above.



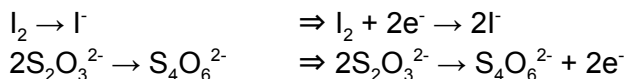
These can be combined to give the overall equation:



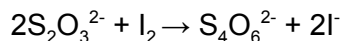
The endpoint of the titration is indicated when the solution in the conical flask has a permanent **pale pink colour**.

Reaction between Iodine and Sodium Thiosulphate

In the redox titration between iodine and thiosulphate ions, the **thiosulphate ions are oxidised** while the **iodine is reduced**. Their half equations can be found using the method described above.



These can be combined to give the overall equation:



Errors and Uncertainty

When using apparatus in experiments, no measuring instrument is 100% accurate - there is always **some degree of uncertainty in the value recorded**. The percentage uncertainty of a measurement can be calculated if the uncertainty of the instrument is known.

$$\text{Percentage uncertainty} = \frac{\text{instrument uncertainty}}{\text{measurement}} \times 100$$



Example:

Calculate the percentage uncertainty when a 25 cm³ volume was recorded using a pipette which has a 0.5 cm³ uncertainty.

$$\begin{aligned}\text{Percentage uncertainty} &= \frac{0.5}{25} \times 100 \\ &= 0.02 \times 100 \\ &= 2\%\end{aligned}$$

The error in apparatus measurements has implications for **validity**. This relates to how close the answer is to the true answer.

The best way of reducing uncertainties in a titration is to **increase the titre volume needed** for the reaction. This can be done by increasing the volume and concentration of the substance in the conical flask or by decreasing the concentration of the substance in the burette.

