OCR (B) Chemistry A-level

Storyline 9: Developing Metals

Detailed Notes

Redox Titrations

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.

A **redox reaction** is a reaction in which reduction and oxidation both occur. Redox reactions can be split into half-equations which show the electron gain and loss of the species undergoing reduction and oxidation respectively.

Likewise, half equations can be combined to form full redox equations. They must first be balanced.

Method for balancing half equations:

1. Balance all atoms except for oxygen and hydrogen.
2. Add **H_2O** 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 $Fe^{2+} \rightarrow Fe^{3+}$ and $Cr_2O_7^{2-} \rightarrow Cr^{3+}$ and then combine the half equations.

Step 1: Write the full half equation for iron.

$Fe^{2+} \rightarrow Fe^{3+}$

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

$\Rightarrow Fe^{2+} \rightarrow Fe^{3+} + e^-$

Step 2: Write the full half equation for chromium.

$Cr_2O_7^{2-} \rightarrow Cr^{3+}$

[Balance **oxygen**]

$Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$

[Balance **hydrogen**]

$Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$

[Balance **charges**]

$\Rightarrow Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Step 3: Combine the two half equations.

$\Rightarrow Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$\Rightarrow Fe^{2+} \rightarrow Fe^{3+} + e^-$

[Balance **electrons**]

$Fe^{2+} \rightarrow Fe^{3+} + e^-$ (x6) $\Rightarrow 6Fe^{2+} \rightarrow 6Fe^{3+} + 6e^-$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

[**Cancel** the **electrons**]

$$\Rightarrow 6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

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.

$$Fe^{2+} \rightarrow Fe^{3+} \quad \Rightarrow \quad Fe^{2+} \rightarrow Fe^{3+} + e^-$$
$$MnO_4^- \rightarrow Mn^{2+} \;\Rightarrow\; MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

These can be combined to give the overall equation:

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

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

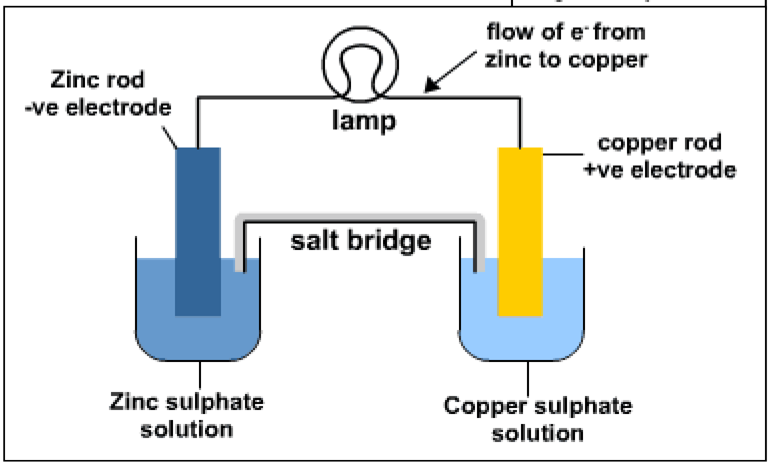
Electrochemical Cells

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, two 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. The salt bridge is crucial as it creates a closed loop for the circuit.

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

Image courtesy of S-cool



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°)

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, so, by definition 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**. The half equation for the standard hydrogen electrode is as shown:

$$2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)$$

Platinum electrodes are chosen as they are **metallic**, so will conduct electricity, but **inert**, so will not interfere with the reaction.

Example:

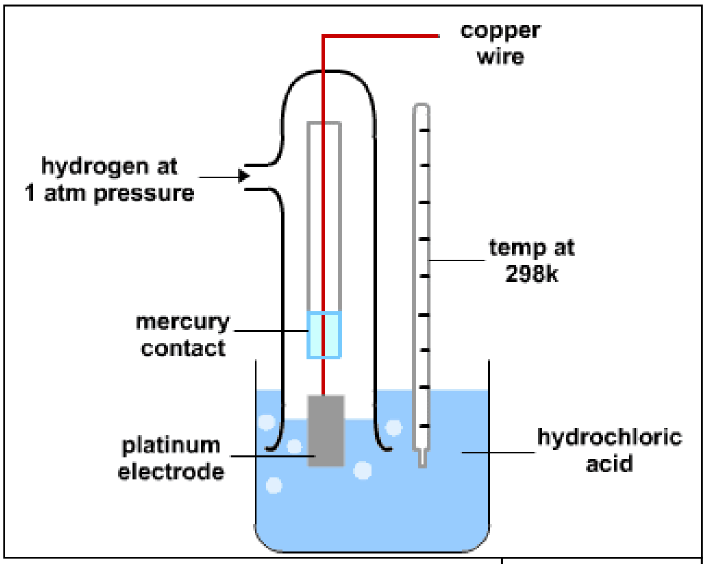


Image courtesy of S-cool

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.

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

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

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

Calculating E_{Cell}

Standard cell potential values are used to calculate the **overall cell potential**. 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.

$$\boxed{E_{(cell)} = E^{o}_{(right)} - E^{o}_{(left)}}$$

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.

The cell potential 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.

$E^\ominus_{cell}$ and Entropy

The standard cell potential 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 $E^\ominus_{cell}$ 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 potential 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.

Rusting

Rusting is a type of corrosion of the surface of a metal which occurs when it is exposed to oxygen and water. Rusting is a **redox reaction** where the metal is oxidised and oxygen is reduced.

Metal + Water + Oxygen → Hydrated Metal Oxide

Rusting can be **prevented** by applying a coating to the surface of a metal, this coating acts as a barrier to the oxygen in air and water. Examples of the coatings include electroplating, greasing or painting.

Transition Metals

The transition metals are elements in the **d-block** of the periodic table that form one or more **stable ions** with a **partially filled d-orbital**. Transition metals lose electrons to form positive ions, with the s-orbital electrons being removed first.

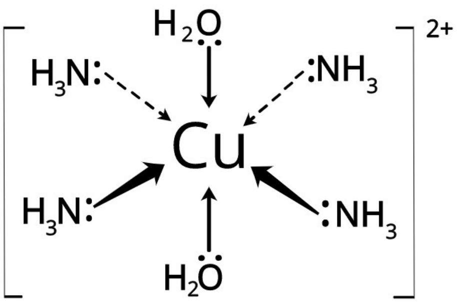
Coordination Number

The **coordination number** of a transition metal complex is the total number of **coordinate bonds** formed with the central metal ion. Silver complexes have a coordination number of 2 and platinum complexes commonly have a coordination number of 4. The coordination number determines the **shape** of the complex ion.

Shapes of Complex Ions

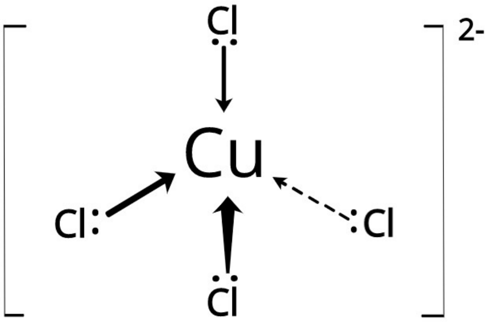
Octahedral Complexes

Transition metal complexes with H_2O and NH_3 ligands commonly form **octahedral** complexes with a **bond angle of 90°**. Octahedral complexes are formed when there is six-fold coordination.



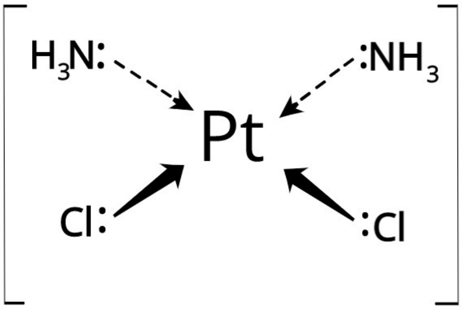
Tetrahedral Complexes

When complexes form with **larger ligands** such as Cl^-, they form **tetrahedral** complexes with a **bond angle of 109.5°** and 4 ligands coordinated. Tetrahedral complexes can show optical isomerism.



Square Planar Complexes

Platinum and nickel complexes form in a **square planar** shape. This consists of four coordinate bonds with a **bond angle of 90°**.



Properties of Transition Metals

All transition metals have **similar physical properties** including similar atomic radius, high densities and high melting points. In addition, they all have **special chemical properties**:

- Form complexes
- Form coloured ions in solution
- Variable oxidation states
- Good catalysts

Variable Oxidation States

Transition metals have variable oxidation states because the 4s and 3d orbitals are very close in energy levels. This not only makes it possible for electrons to be lost from both orbitals relatively easily, but also means that the remaining electrons can form **stable configurations.**

Copper and **chromium** are exceptions to the rule that the 4s subshell is filled before the 3d subshell.

- Chromium has 24 electrons. According to the rule above, its electron configuration should be [Ar] $4s^2\ 3d^4$. However, it is more stable if one of the electrons from the 4s orbital is placed into the 3d orbital, **so that each 3d orbital contains one unpaired electron**. Therefore, the actual electron configuration of chromium is [Ar] $4s^1\ 3d^5$.
- Similarly with copper, instead of the electron configuration [Ar] $4s^2\ 3d^9$, it is more stable if the 3d subshell is **completely filled**. Therefore, one of the 4s electrons is moved to a 3d orbital to give the electron configuration [Ar] $4s^1\ 3d^{10}$.

Catalysts

A catalyst is a substance that **speeds up the rate of a reaction without being used up** in the reaction. It provides an alternative reaction pathway with a **lower activation energy**. Catalysts don't affect the position of equilibrium but allow it to be **reached faster.** Transition metals make good catalysts due to their variable oxidation states.

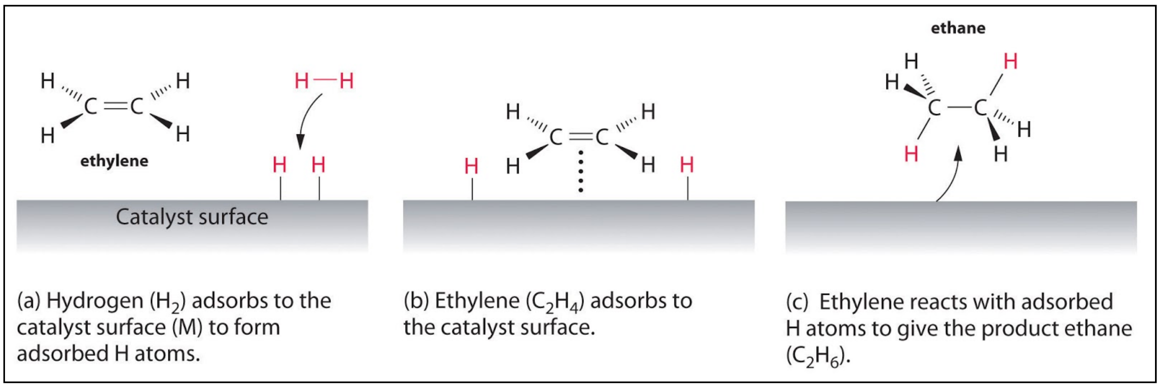
There are two main types of catalyst: **heterogeneous and homogeneous**.

Heterogeneous

Heterogeneous catalysts are in a **different phase or state** to the species in the reaction.

A solid catalyst works by **adsorbing** molecules onto an **active site** on the surface of the catalyst. These active sites **increase the proximity** of molecules and **weaken the covalent bonds** in the molecules so that reactions occur more easily. This increases the rate of reaction.

Example:



(a) Hydrogen (H_2) adsorbs to the catalyst surface (M) to form adsorbed H atoms.

(b) Ethylene (C_2H_4) adsorbs to the catalyst surface.

(c) Ethylene reacts with adsorbed H atoms to give the product ethane (C_2H_6).

Adsorption occurs inside **catalytic converters** where carbon and nitrogen monoxide adsorb onto the surface of the catalyst. This weakens their bonds and allows reactions to occur. As a result, CO_2 and N_2 are **desorbed** from the catalyst surface.

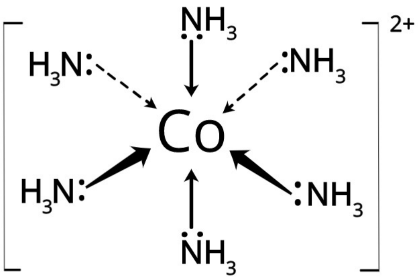
Homogeneous Catalysts

Homogeneous catalysts are in the **same phase** as the species in the reaction, these catalysts rely on the ability to have varying oxidation states to catalyse a reaction.

Ligands and Complex Ions

Transition metals form **complexes**, consisting of a **central metal ion** surrounded by **ligands**.

Example:



Complexes can also be represented by formulas using square brackets.

Example:

$[Co(NH_3)_6]^{2+}$

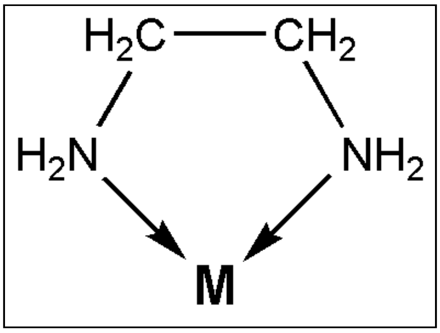
Ligands

A ligand is a molecule or ion with a **lone electron pair** that is able to form a **dative (coordinate) bond** to the central metal ion by donation of this electron pair. Common ligands include:

- Cl^-
- H_2O
- NH_3

Monodentate ligands each form **one** coordinate bond. Examples: H_2O, Cl^-, NH_3.

Bidentate ligands each form **two** coordinate bonds. Example: $NH_2CH_2CH_2NH_2$.



Hexadentate ligands each form six coordinate bonds. Example: $EDTA^{4-}$.

'Polydentate' and **'multidentate' ligands** are general terms for any ligands that form **more than one** coordinate bond.

Coloured Ions

Transition metal ions can be identified by their **colour**, which changes depending on the **coordination number** of the complex, the type of **ligand** bonded to the ion and the **oxidation state**. Aqueous solutions of transition metal ions tend to be coloured.

Colour arises because of how substances **absorb and reflect** light. When white light shines on a substance, some of the wavelengths of light are absorbed, but the remaining wavelengths are **reflected and transmitted** to the human eye.

Example:

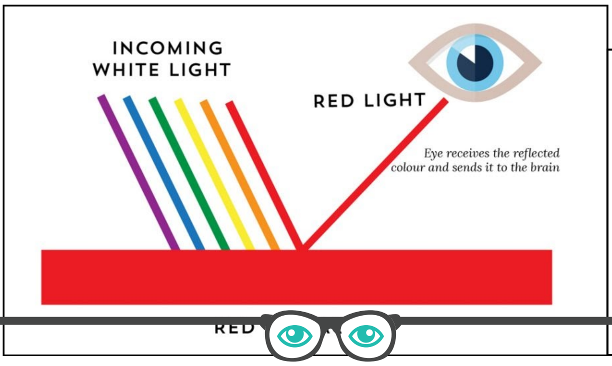


Image courtesy of Emma Brooks Design

In transition metal complexes, ligands cause the d-orbital to split, meaning some electrons exist in a slightly higher energy level (in an **'excited state'**).

The change in energy (**ΔE**) between these states corresponds to a specific **wavelength and frequency** of light. If this wavelength of light is within the visible region of the electromagnetic spectrum then a coloured compound will be seen.

Colourless Ions

Some metal ions and complexes are colourless. Colour arises when some wavelengths of light are absorbed while others are reflected. This involves the **excitation of electrons.** Ions and complexes where there are **no available electrons to excite** cannot absorb light and are therefore **colourless**.

For example, zinc is in the d-block of the periodic table and has completely filled d-orbitals. Therefore, there are **no unfilled or partially filled d orbitals** into which an electron can be promoted. Therefore, zinc is colourless.

Ligand Substitution

Ligands in a transition metal complex can be **exchanged** for other ligands.

Copper and cobalt aqua ions can undergo substitution with chloride ions.
The Cl^- ligand is much **larger** than the NH_3 and H_2O ligands meaning substitution with this ligand results in a **change in coordination number** for that complex.

$$\underset{\text{Blue solution}}{[Cu(H_2O)_6]^{2+}} + 4Cl^- \longrightarrow \underset{\text{Yellow solution}}{[CuCl_4]^{2-}} + 6H_2O$$

Complexes with just Cl- ligands always have a coordination number of **four**, producing a **tetrahedral** shaped complex.

Reactions of Transition Metal Ions with Sodium Hydroxide and Ammonia

Metal ions become **hydrated** in water when **H_2O ligands** form around the central metal ion. The reactions shown below have to be known for this A-level specification: **iron(II), iron(III) and copper(II)**. These metal aqua ions react with sodium hydroxide and ammonia to form **coloured precipitates**.

Solutions of metal aqua ions react as **acids** with aqueous sodium hydroxide. Some react further with **excess sodium hydroxide.**

Reactions with NaOH:

Transition Metal Ion	Metal-aqua ion	With OH^-	With excess OH^-
Fe^{2+}	Green solution $[Fe(H_2O)_6]^{2+}$	Green precipitate $Fe(OH)_2(H_2O)_4$	No change

Fe^{3+}	Yellow solution $[Fe(H_2O)_6]^{3+}$	Brown precipitate $Fe(OH)_3(H_2O)_3$	No change
Cu^{2+}	Blue solution $[Cu(H_2O)_6]^{2+}$	Blue precipitate $Cu(OH)_2(H_2O)_4$	No change

It is easiest to remember the formulas of the precipitates by remembering that the number of OH- substituted is the same as the value of the charge on the initial ion.

Example equations:

$$[Fe(H_2O)_6]^{2+} + 2OH^- \longrightarrow [Fe(H_2O)_4(OH)_2] + 2H_2O$$

$$[Cu(H_2O)_6]^{2+} + 2OH^- \longrightarrow [Cu(H_2O)_4(OH)_2] + 2H_2O$$

$$[Fe(H_2O)_6]^{3+} + 3OH^- \longrightarrow [Fe(H_2O)_3(OH)_3] + 3H_2O$$

Solutions of metal aqua ions react as **acids** with aqueous ammonia. Some react further with **excess ammonia**. Initially, ammonia acts as a **base** to remove one H^+ ion per ammonia molecule used. With excess ammonia, some metal ions undergo **ligand substitution** with NH_3.

Reactions with NH_3:

Transition Metal Ion	Metal-aqua ion	With NH_3	With excess NH_3
Fe^{2+}	Green solution $[Fe(H_2O)_6]^{2+}$	Green precipitate $Fe(OH)_2(H_2O)_4$	No change
Fe^{3+}	Yellow solution $[Fe(H_2O)_6]^{3+}$	Brown precipitate $Fe(OH)_3(H_2O)_3$	No change
Cu^{2+}	Blue solution $[Cu(H_2O)_6]^{2+}$	Blue precipitate $Cu(OH)_2(H_2O)_4$	Dark blue solution $[Cu(NH_3)_4(H_2O)_2]^{2+}$

It is easiest to remember the formulas of the precipitates by remembering that the number of OH- substituted is the same as the value of the charge on the initial ion.

Example equations:

$$[Fe(H_2O)_6]^{2+} + 2NH_3 \longrightarrow [Fe(H_2O)_4(OH)_2] + 2NH_4^+$$

$$[Cu(H_2O)_6]^{2+} + 2NH_3 \longrightarrow [Cu(H_2O)_4(OH)_2] + 2NH_4^+$$

$$[Fe(H_2O)_6]^{3+} + 3NH_3 \longrightarrow [Fe(H_2O)_3(OH)_3] + 3NH_4^+$$

$$[Cu(H_2O)_4(OH)_2] + 4NH_3 \longrightarrow [Cu(H_2O)_2(NH_3)_4]^{2+} + 2H_2O + 2OH^-$$

Colorimetry

Colorimetry is a technique used to determine the **concentration** of a **coloured solution**. Solutions are coloured due to the wavelengths of light they absorb, a colorimeter measures the absorbance of light by the coloured solution. The wavelength which is used for colorimetric analysis needs to have maximum absorption for the coloured solution, this will be the colour **opposite** in the colour wheel to the colour of the solution. The intensity of the colour of a solution is **correlated** to the concentration of the solution. The less concentrated the solution is, the less intense the colour will be.