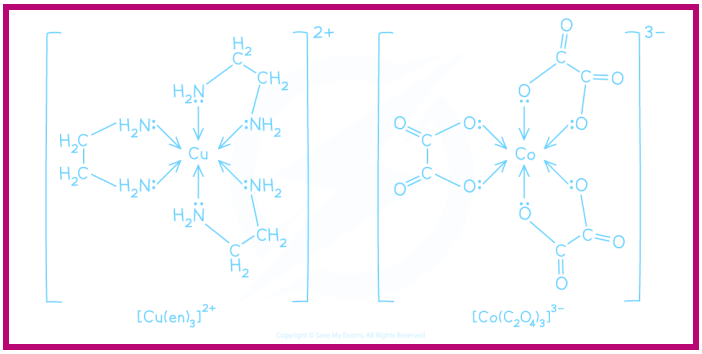


Unit 5: Transition Metals and Organic Nitrogen Chemistry

Topic 16: Redox Equilibria

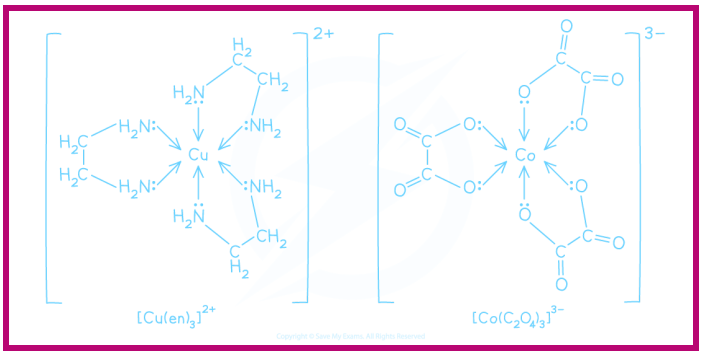
Oxidation and reduction:

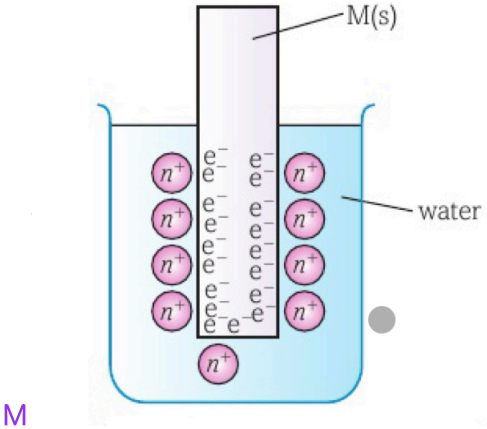
- Oxidation: is the loss of electrons, an element in a species is oxidised when its oxidation number increases.
- Reduction is the gain of electron, an element in a species is reduced when its oxidation number decreases

Redox reactions involve oxidation and reduction occurring together.

Metals and solutions

- M (s) —> M^{n+} (aq) + *n*e-
- When metals are placed in water some of their atoms will lose electrons and enter the water as positive (+) ions.
- The lost electrons will remain on the surface of the water as positive (+) ions will be attracted to the negative charge on the metal's surface.
-
- Some cations will regain their electrons from the surface and form part of the metal again.
- Eventually a dynamic equilibrium is established (rate of the forward = rate of backwards)
- Mn+ (aq) + *n*e- = M (s)





Absolute potential difference

- Both magnesium and copper will undergo this reaction but the equilibrium position will be further to the left for magnesium.
- This is because magnesium is higher than copper in the reactivity series.
- Magnesium has a higher tendency to release electrons and go into solution as cations.

$$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$$

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

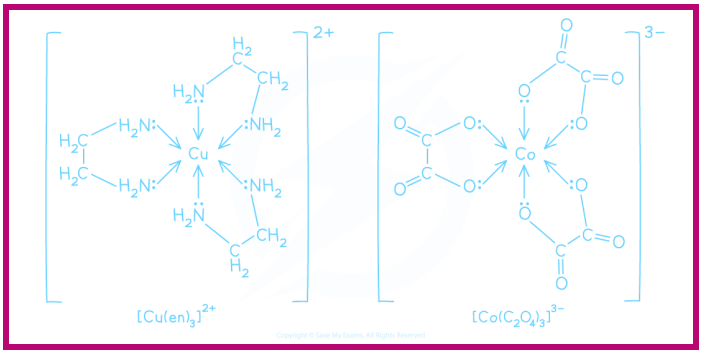
- Electrode potentials (voltmeter) use numbers to display the position of equilibrium between the different metals as potential difference in volts(v).

Limitations

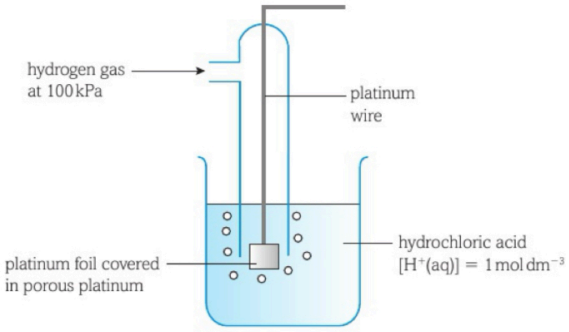
- It is not possible to measure the absolute potential difference because the solution would need to be connected to another metal, which would have its own potential difference.
- Although the difference between a reference electrode and the metal electrode can be measured

Reference electrode (standard hydrogen electrode)

- Hydrogen gas at 100 kPa
- HCl at 1 mol dm3



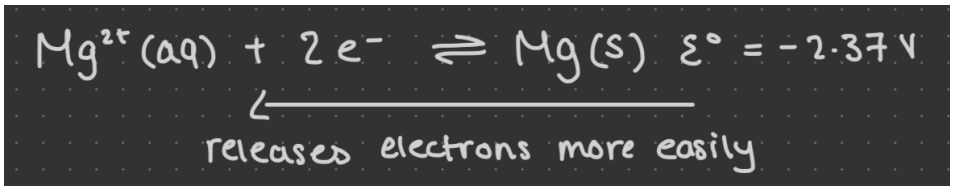
- Temp at 298 K
- The porous platinum has a large surface area which allows the equilibrium to be established quickly.

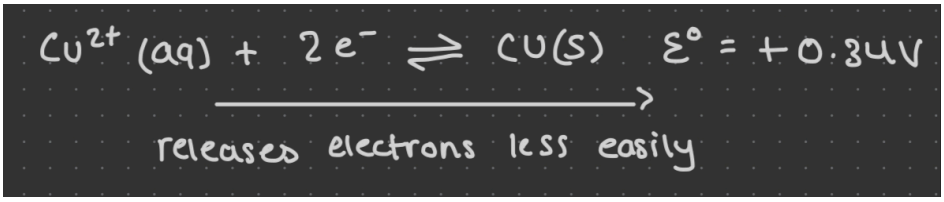


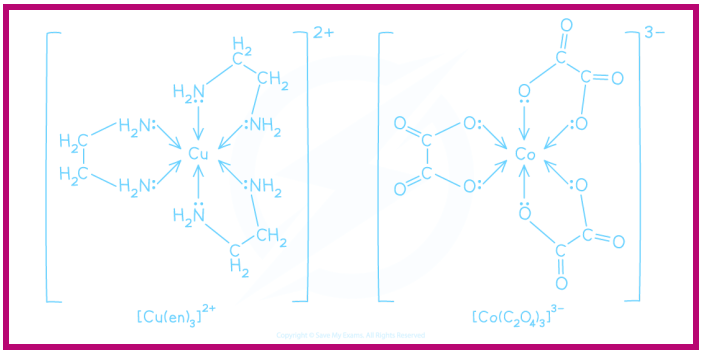
When asked for what type of solution to use in your electrochemical cell to get Ag+ - use AgNO3

Measuring standard electrode potential

- The high resistance voltmeter is also required to stop the current from flowing in the circuit, from the platinum to the metal being measured as this will affect the potential difference.
- The difference in potential measured is the standard electrode potential, E°.
- The E° has a positive (+) or negative (-) which displayed the position of equilibrium with respect to the standard hydrogen electrode







Summary of the E° value:

- E° values provide a method of comparing the positions of equilibria when metal atoms lose electrons to form ions in solution.
- The more negative the E° value, the further the equilibrium lies to the left, so the more readily the metal loses electrons to form ions.
- The more positive E° value, the further the equilibrium lies to the right, so the metal electrons are less ready to be lost to form ions.

Electromotive force (EMF)

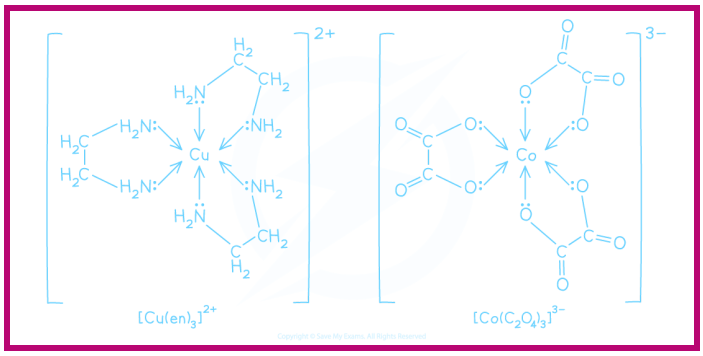
- The standard electrode potential of a half-cell if the emf of a cell containing the half cell connected to the standard hydrogen electrode.
- In the standard conditions of 298 k, 100 kPa and a solution of 1 mol dm-3 concentrations apply.

Reducing agents

- the species on the right-hand side of the half cell reactions are the reducing agents (it oxidises itself as it loses electrons)
- The more negative (-) the E° value the more powerful it is as a reducing agent (Li (s))
    - Equilibrium sits very far to the left.
    - Gives up electrons very easily.
- The less negative (-) the the E° value the weaker the reducing agent is. (F^- (aq))
    - Equilibrium sits very far to the right.

Oxidising agents

- The species on the left-hand side of the half-cell are the oxidising agent as they can gain electrons.
- The more powerful the oxidising agent (reduces itself) the more positive (+) the E° value is.
- The less powerful the oxidising agent would have a more (-) E°.



least powerful oxidising agent

OXIDISED FORM	REDUCED FORM	$E^{\ominus}$ / V
$Li^+(aq)$	Li(s)	−3.03
$K^+(aq)$	K(s)	−2.92
$Ca^{2+}(aq)$	Ca(s)	−2.87
$Na^+(aq)$	Na(s)	−2.71
$Al^{3+}(aq)$	Al(s)	−1.66
$Zn^{2+}(aq)$	Zn(s)	−0.76
$Cr^{3+}(aq)$	Cr(s)	−0.74
$Fe^{2+}(aq)$	Fe(s)	−0.44
$H^+(aq)$	$\frac{1}{2}H_2(g)$	0.00
$Cu^{2+}(aq)$	Cu(s)	+0.34
$\frac{1}{2}I_2(aq)$	$I^-(aq)$	+0.54
$Ag^+(aq)$	Ag(s)	+0.80
$\frac{1}{2}Br_2(aq)$	$Br^-(aq)$	+1.09
$\frac{1}{2}Cl_2(aq)$	$Cl^-(aq)$	+1.36
$\frac{1}{2}F_2(aq)$	$F^-(aq)$	+2.87

most powerful oxidising agent

most powerful reducing agent

least powerful reducing agent

Oxidation and Reduction summary:

- The more negative the E° value, the more the equilibrium shifts to the left.
- The more readily the species on the right loses e^-.
- This means it is a more powerful reducing agent.

- The more positive the E° value is the more the equilibrium shifts to the right.
- The more readily the species on the left loses e^-.
- This means it is a more overruled oxidising agent.

PPQ. Suggest why platinum is used as an electrode and why it is coated in platinum black (porous).

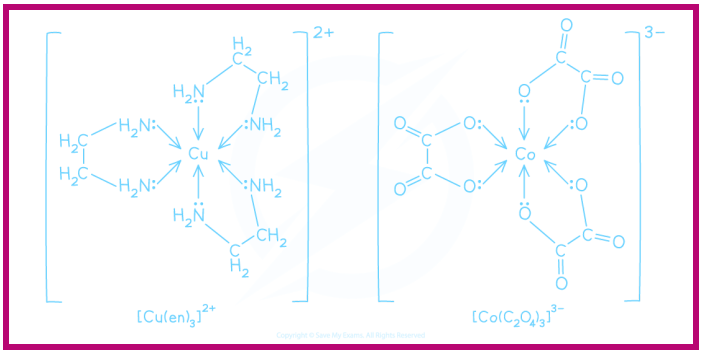
- Platinum is chemically inert.
- It acts as a catalyst.
- It increases the surface area of the electrode

PPQ. Explain why a reference electrode is needed.

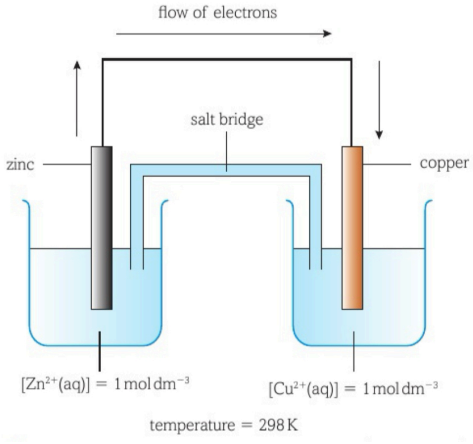
- Because it is not possible to measure the absolute potential difference between a metal and a solution.

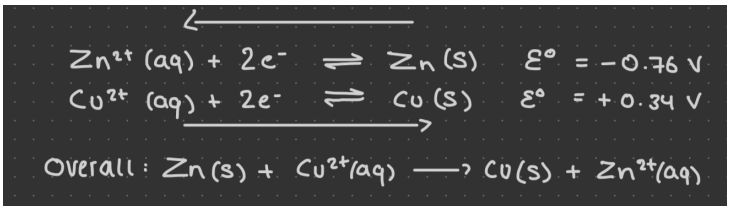
Electrochemical cells: it is a device for producing an electric current from the chemical reactions and It is formed from two half-cells.

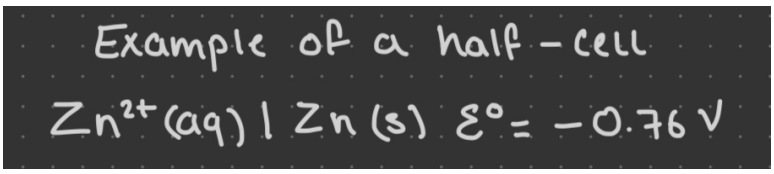
- Ions flow in the salt bridge, not electrons.



- Electrons flow through the external circuit.
- Electrons will always flow from the metal with more negative E° to the more positive one.

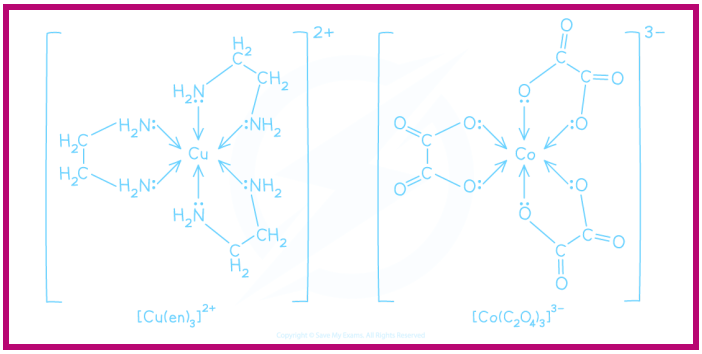


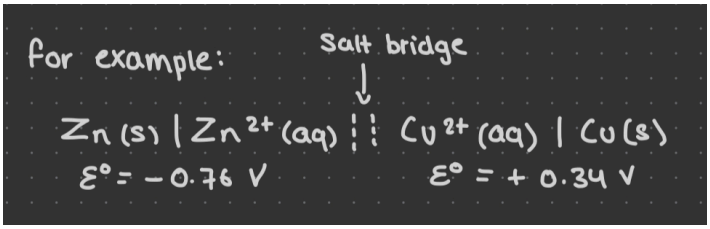




Writing full electrochemical cells

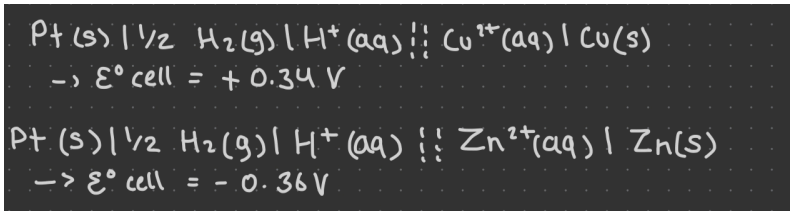
- The positive E° values are shown on the outside. All the reduced forms of the species are written on the outside on either side.
- The positive electrode is shown on the right-hand side. (imagine flow of electron from left to right —>)
- The salt bridge is represented by dashed lines.
- A single line represents the phase boundary.





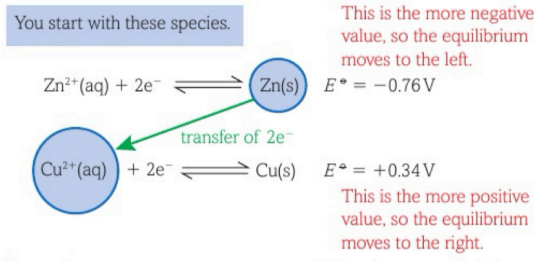
- To calculate the $E°_{cell}$ = right electrode - left electrode
- So, $E°_{cell}$= 0.34 - (-0.76) = 1.10 V

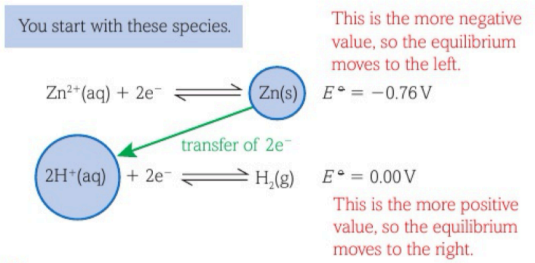
- The standard hydrogen electrode is always on the left.



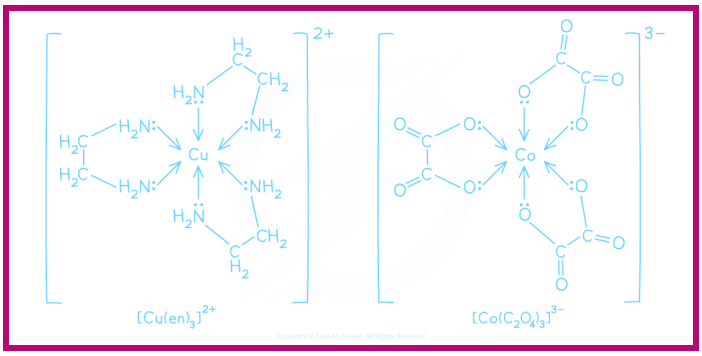
Thermodynamic feasibility:

- The E° value for equilibrium 1 is more negative than for equilibrium 2.
- So the position of equilibrium shifts to the left, releasing electrons.
- Whereas equilibrium 2 will shift to the right accepting electrons.
- This makes the reaction thermodynamically feasible.





- You can also use calculating the E° to determine the feasibility.
  - When the E° value is positive the reaction is thermodynamically feasible.
  - When the E° value is negative the reaction is not thermodynamically feasible.



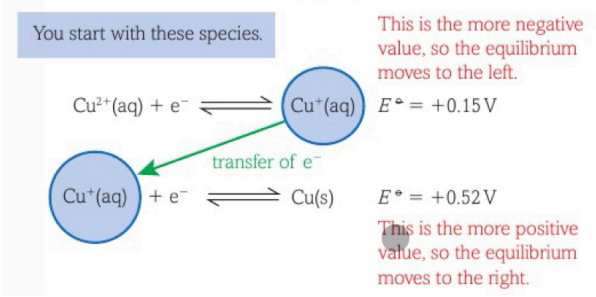
- Total entropy is proportional to E °cell.
-

Thermodynamic feasibility summary

- The feasibility of a reaction can be predicted using the standard electrode potentials.
- Even if the values can predict feasibility - the reaction may not occur.
    - Kinetically stable reactants require large activation energy.
- The reaction can become feasible if you change the standard conditions.
    - Changing the conditions may alter the electrode potential Due to the change in position of the equilibrium of the half-cell.

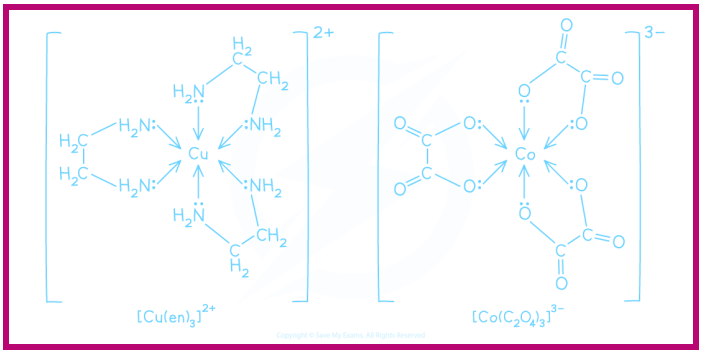
Disproportion reactions

- A reaction in which the same element in a species is both oxidised and reduced in the same reaction at the same time.
- Example: $Cu^{2+}(aq)$ + $Cu^{+}(aq)$ → $Cu^{2+}(aq)$ + Cu(s)
- In terms of standard electrode potential:
    - $Cu^{2+}(aq) + e^{-} = Cu^{+}(aq)$ E° = +0.15 V equilibrium 1
    - $Cu^{+}(aq) + e^{-} = Cu(s)$ E° = +0.52 V equilibrium 2



Relationship between Total Entropy and $E°_{cell.}$

- Cell potential is related to both entropy and the equilibrium constant.
- A larger cell potential means a bigger change in total entropy.
- Therefore The cell potential is directly proportional to the total entropy change.
    - $E^{\theta} \propto \Delta S_{total}$
    - $E^{\theta} \propto \ln K$



Redox in Action

Fuel cells

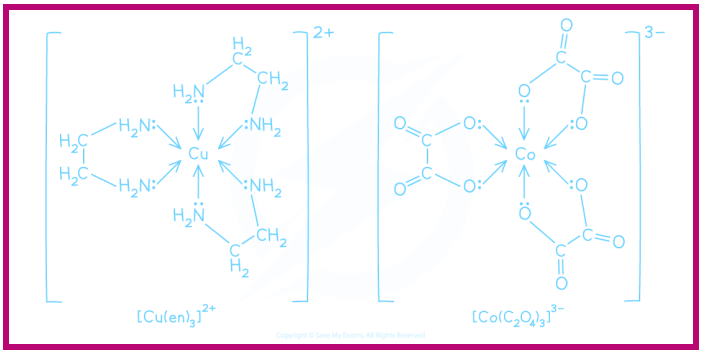
- A fuel cell produces a voltage from the chemical reaction of a fuel with oxygen.
- Most common fuel cells are the hydrogen-oxygen fuel cell.
    - The metal electrodes are coated in platinum which which acts as a catalyst for the reactions
- Acidic electrolyte:
    - Positive electrode: ½ O_2 (g) + $2H^+$ + $2e^-$ —> H_2O (l)
    - Negative electrode: H_2 (g) —-> $2H^+$ (aq) + e^-
    - Overall: H_2 (g) + ½ O_2 (g) —> H_2O (l)
- Alkaline electrolyte
    - Positive electrode: ½ O_2 (g) + H_2O (l) + $2e^-$ -> $2OH^-$ (aq)
    - Negative electrode: H_2 (g) + 2OH —> H_2O (l) + $2e^-$
    - Overall: H_2 (g) + ½ O_2 (g) —> H_2O (l)

Fuel Cells

Advantages	**Disadvantage**
Alternative to direct use of fossil fuels	Hydrogen is easily ignited
Does not produce carbon dioxide or carbon monoxide or nitrogen oxide	compressing the hydrogen for transport is hazardous
lighter and more efficient than fossil fuels	many metals absorb hydrogen
main product is water which can be recycled	Hydrogen is produced from methane which is a finite source.

Redox titrations

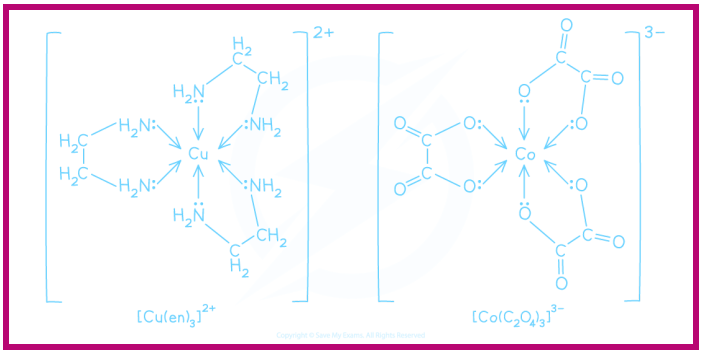
- A titration of a reducing agent by an oxidising agent or titration of an oxidising agent by a reducing agent
- With potassium manganate (VII), $KMnO_4$
    - Potassium manganate(VII) is a powerful oxidising agent.



- It is used for the quantitative estimation of many reducing agents.
- In acidic conditions:
  - $MnO^-_4(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
- In alkaline conditions:
  - Potassium manganate (VII) yields manganese (IV) oxide as a brown ppt and this interferes with the end point colour. This is why it is only used in solutions that are sufficiently acidic.(As it disproportionates in alkali conditions)

- Redox titration of potassium manganate (VII) with iron (II) ions
  - In this reaction the iron (II) ions are oxidised and the manganate (VII) ions are reduced.
  - The ionic half equations:
    - $MnO^-_4(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
    - $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$
  - Overall reaction:
    - $MnO^-_4(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$
- Colours of each ions:
  - $Fe^{2+}(aq)$ - pale green
  - $Fe^{3+}(aq)$ - yellow
  - $Mn^{2+}(aq)$ - pale pink

- Redox titration with iodine and sodium thiosulfate
  - Thiosulfate ions reduce iodine to iodide ions.
  - The ionic half equations:
    - $2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2e^-$
    - $I_2(aq) + 2e^- \rightarrow 2I^-(aq)$
  - Overall equation:
    - $2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$
  - Indicator:
    - A starch solution with free iodine, it appears a deep blue-black colour.
    - The blue-black colour disappears as soon as enough sodium thiosulfate has been added with all the iodine



Topic 17: Transition metals and their chemistry

"Transition metals are elements with an incomplete d-subshell that can form at least one stable ion with an incomplete d-subshell"

- exceptions to this rule is scandium, which only forms Sc^{3+} and zinc that forms Zn^{2+}

Characteristics of transition metals

- are hard solids
- have high melting and boiling temperatures
- can act as catalysts
- form coloured ions and compounds
- form ions with different oxidation numbers
- form ions with incompletely filled d-orbitals.

Electron configuration
Exceptions to the normal electron config are chromium and copper

- Cr is [Ar] $3d^5\ 4s^1$ **not** [Ar] $3d^4\ 4s^2$
- Cu is [Ar] $3d^{10}\ 4s^1$ **not** [Ar] $3d^9\ 4s^2$

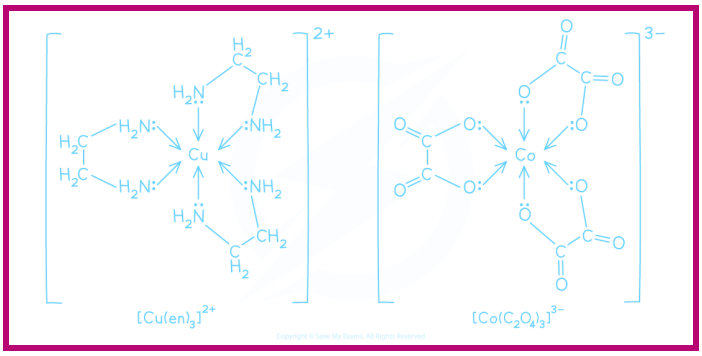
This is because these are energetically more stable than the other.
When transition elements forms ions they lose electrons from the **4s** subshell first

ELEMENT	Z	ELECTRONIC CONFIGURATION	ELECTRONS-IN-BOXES DIAGRAM FOR 3d AND 4s ELECTRONS
scandium	21	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$	↑ ↑↓
titanium	22	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$	↑ ↑ ↑↓
vanadium	23	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$	↑ ↑ ↑ ↑↓
chromium	24	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$	↑ ↑ ↑ ↑ ↑ ↑
maganese	25	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$	↑ ↑ ↑ ↑ ↑ ↑↓
iron	26	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$	↑↓ ↑ ↑ ↑ ↑ ↑↓
cobalt	27	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$	↑↓ ↑↓ ↑ ↑ ↑ ↑↓
nickel	28	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$	↑↓ ↑↓ ↑↓ ↑ ↑ ↑↓
copper	29	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑
zinc	30	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓

unlike other metals, transition elements can form more than one positive ion

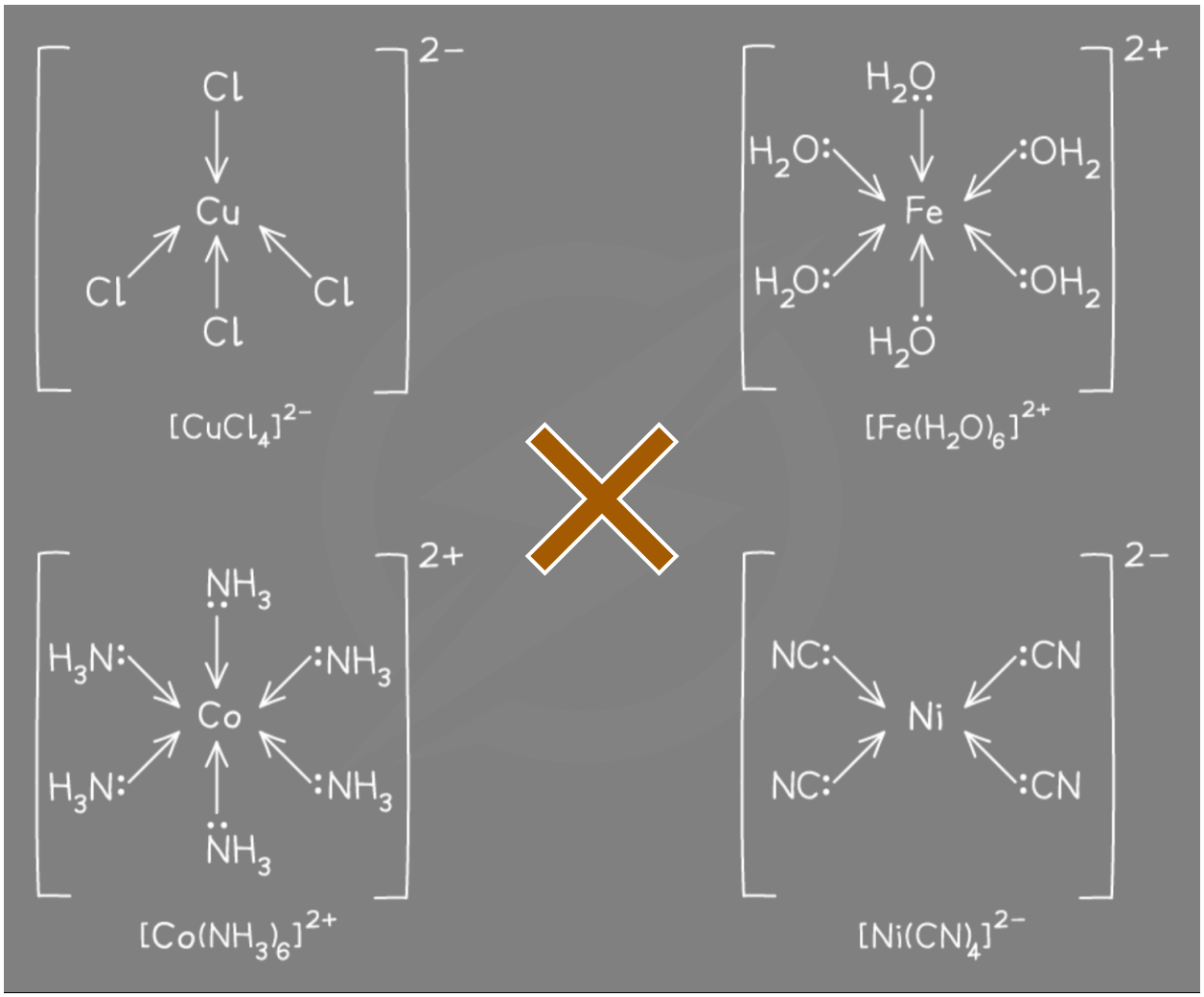
- They are said to have **variable oxidation states**

Ligands

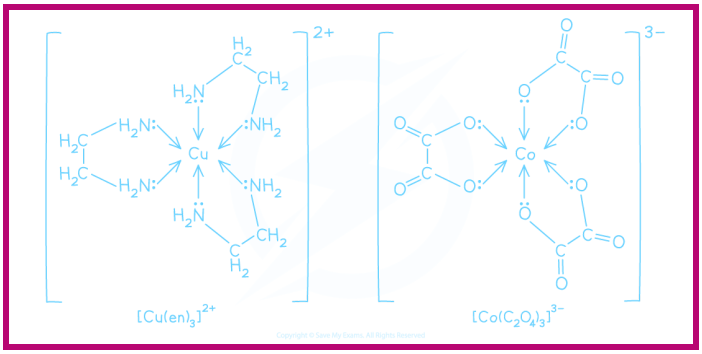


A ligand is a molecule or ion that forms a dative covalent / co-ordinate bond with a transition metal by donating a pair of electrons to the bond.

- This means they have a negative charge or a lone pair of electrons capable of being donated.



- The bonds are shown with arrowheads, indicating that they are **dative (coordinate) bonds**.
- One lone pair of the electron on each oxygen is being used to form the bond.



Co-ordination number is number of dative covalent / co-ordinate bonds to the central metal atom or ion

Metal complexes usually have a coordination number of 6 when smaller ligands, and 4 when larger ligands, like Cl-.

Common ligands

Name	Formula
Water	H_2O
Ammonia	NH_3
Chloride	Cl^-
Cyanide	CN^-
Hydroxide	OH^-

Naming ligands

[cation (ligand) number of ligands] overall charge

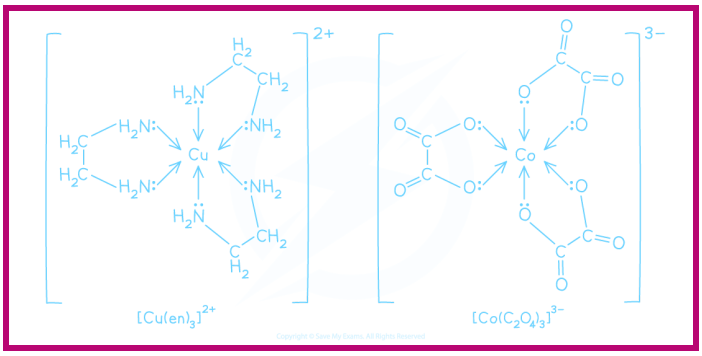
eg:

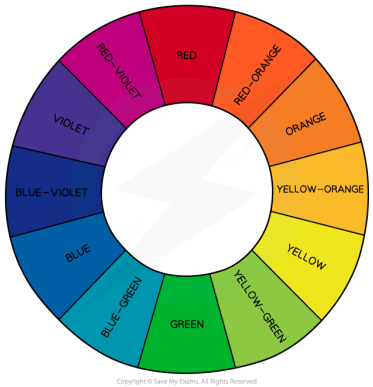
- tetrachlorocuprate(II)
- hexaaquairon(II)
- hexaamminecobalt(II)
- tetracyanonickelate(II)

Colour in aqueous ions

Transition metals appear coloured due to the fact that they absorb energy corresponding to certain parts of the visible electromagnetic spectrum.

When white light is passed through a solution containing a transition metal complex, some wavelengths of light are absorbed by the complex. The light emerging will therefore contain proportionately more of the complementary colour.



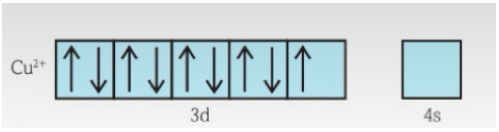


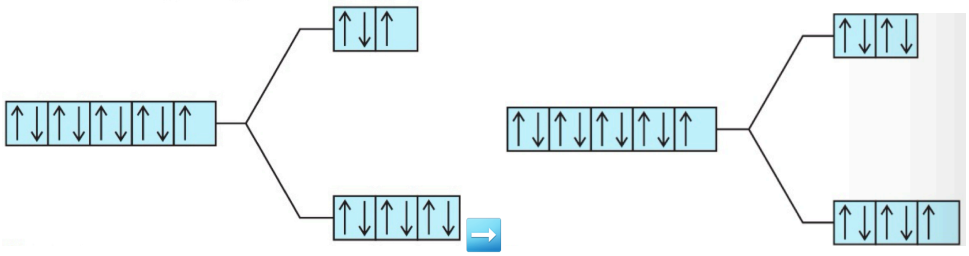
Colour depends on electrons in 3D energy level

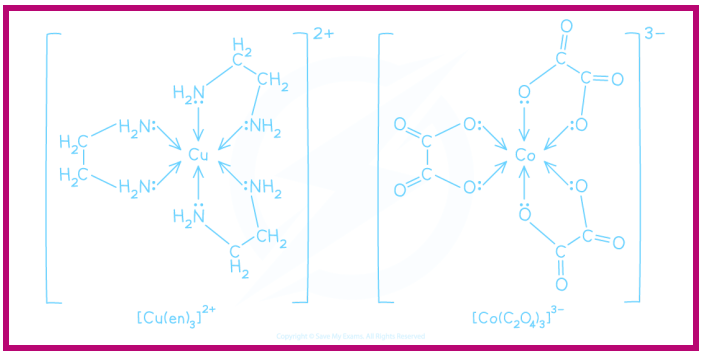
Transition metals have a partially filled 3d energy level.
when ligands attach to the central metal ion, the energy level (3d) splits into two separate levels with slightly different energy.

- The difference in energy depends on the electronic configuration of that metal ion and depending on that number, it splits in half.
- If one of the electrons in the lower energy level absorbs energy from the visible spectrum it can move to the higher energy level
- This process is known as **promotion / excitation**

Below is coppers electronic config and how the d-d transition occurs.
One of the electrons is promoted and goes UP.







Influences on d-orbital energy splitting

These factors affect the splitting and in turn, affect the colour shown.

The size and type of ligands

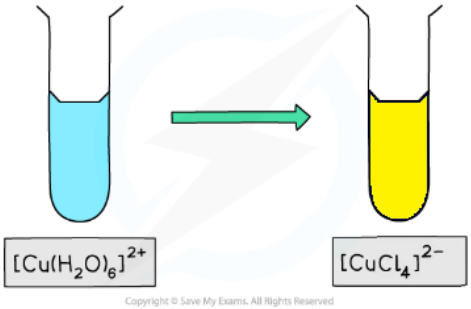
- Nature of the ligand influences the strength of the interaction between ligand-central metal ion.
- Greater the charge density; the more strongly the ligand interacts with the metal ion. This causes GREATER splitting of the d-orbital.
- This means that complexes with the **same transition metal** but **different ligands** can have different colours.

The oxidation state of the metal

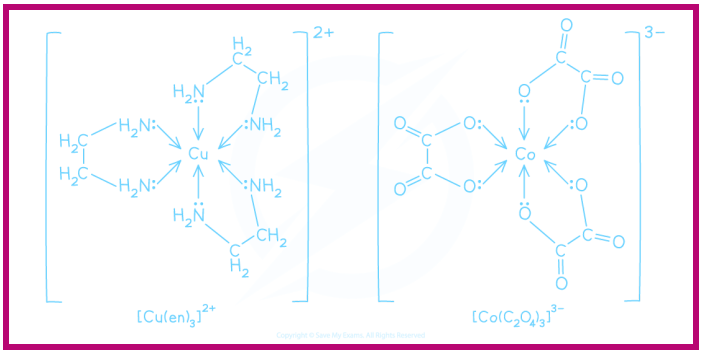
- When the same metal has a higher oxidation number, that will ALSO create a stronger interaction with the ligand.

Coordination number

- The relative orientation of the ligand as well as the d-orbital splitting affects the colour shown.
- changing coordination number usually entails changing ligands as well, so a combo of these definitely changed the colour.
    - For example, the $[Cu(H_2O)_6]^{2+}$ complex has a **light blue** colour
    - Whereas the $[CuCl_4]^{2-}$ has a **yellow** colour due to the change in the ligand and the change in the coordination number from 6 to 4



Monodentate ligands



These can form only **one** dative bond to the central metal ion, this is due to them having a single lone pair of electrons to form a dative bond with. (Examples are the table made above)

Bidentate ligands

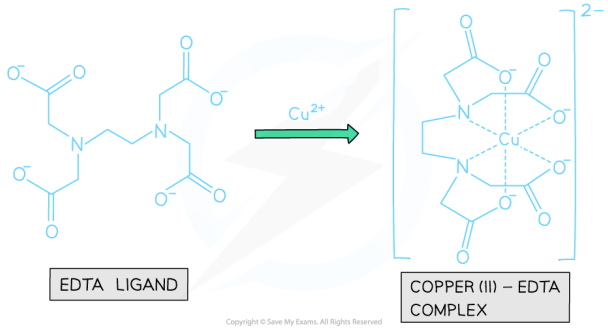
These can each form **two** dative bonds to the central metal ion, due to the ligand containing two atoms with lone pairs of electrons.

- 1,2-diaminoethane ($H_2NCH_2CH_2NH_2$) which is also written as **'en'**
- Ethanedioate ion ($C_2O_4^{2-}$) which is sometimes written as **'ox'**

Multidentate ligands

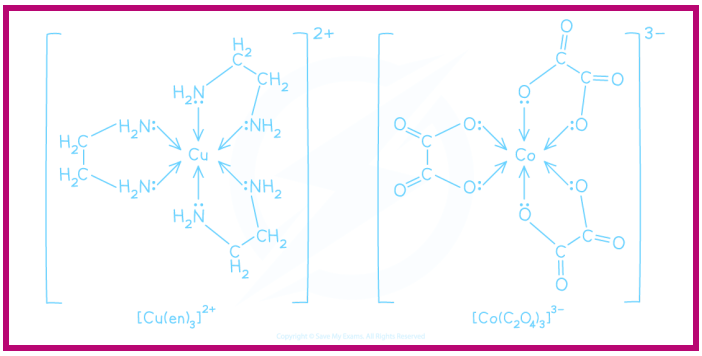
Some ligands that contain more then two atoms with lone pairs of electrons can form **more than two dative bonds**.

- An example is $EDTA^{4-}$ which is a hexadentate as it forms 6 dative bonds to the central ion.

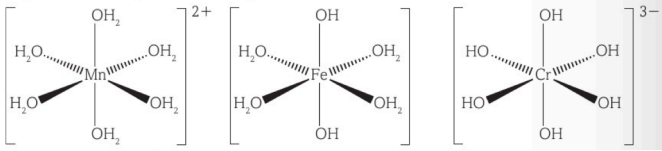


Octahedral complexes

The most common ligand is in this shape like with water, ammonia and hydroxide ion. Sometimes called **six-fold coordination**, these ions might have different numbers of lone pairs, but only use 1 to form dative bonds with the central metal ion.



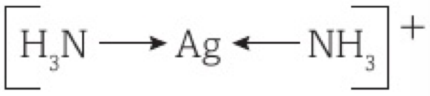
ABBREVIATED FORMULA	NAME	COLOUR
$[Mn(H_2O)_6]^{2+}$	hexaaquamanganese(II)	very pale pink (usually described as colourless)
$[Fe(H_2O)_4(OH)_2]$	tetraaquadihydroxoiron(II)	pale green
$[Cr(OH)_6]^{3-}$	hexahydroxochromate(III)	green



Tetrahedral and linear complexes

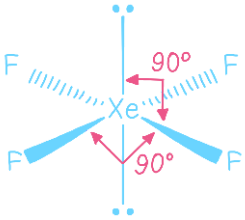
A lot less common.
only one we study is $[CuCl_4]^{2-}$

- Reason for it being tetra-hedral is because chlorine is a much larger ligand than others, and can only make 4 bonds with the electron pair repulsion theory still applying to it.

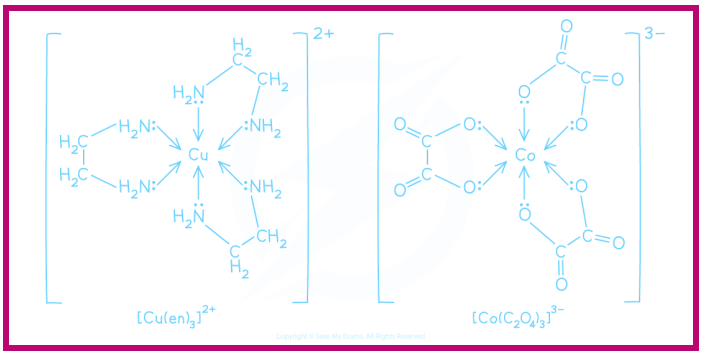
Only linear one is in tollen's reagent. 

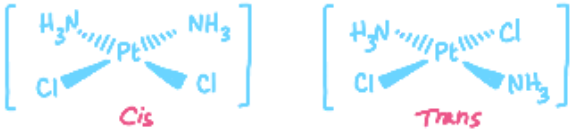
Square planar molecules

An example is xenon tetrafluoride, XeF4.
An atom of xenon has **eight electrons** in its outermost energy level, and each fluorine atom uses **one** of its electrons to form a covalent bond.
These are arranged in six pairs, forming an octahedral arrangement.
Two of these pairs are **lone pairs**, which **repel** each other and are therefore located opposite each other.



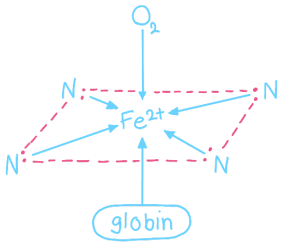
Cis-PLATIN
is used in cancer treatment. It's a square planar. Trans-Platin is actually toxic.





hemoglobin

This is a protein in RBC that plays a vital role in transporting oxygen through the bloodstream.



Carbon monoxide has a lone pair of electrons on its carbon atom that enables it to act as a ligand. Strength of the **dative bond** between oxygen and hemoglobin isn't very strong, so when in presence of CO, the one with stronger dative bond, it binds very hard and does not easily break.

Put very simply, this reaction is reversible:

haemoglobin + oxygen <—>oxyhaemoglobin

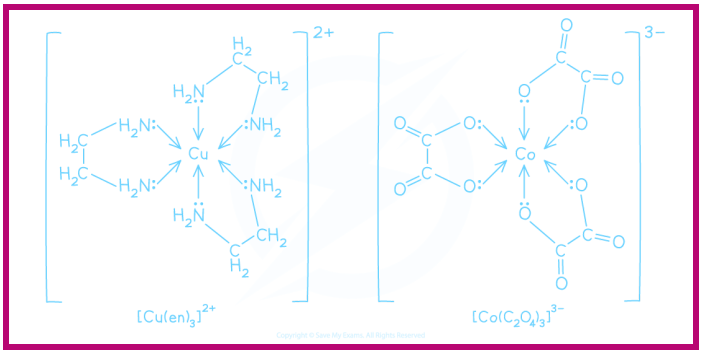
but this reaction is not easily reversible

haemoglobin + carbon monoxide → carboxyhaemoglobin

The chemistry of Vanadium

This is a transition metal that forms ions with several oxidation numbers.

OXIDATION NUMBER	FORMULA	NAME	COLOUR OF AQUEOUS SOLUTION
+2	V^{2+}	vanadium(II)	purple
+3	V^{3+}	vanadium(III)	green
+4	VO^{2+}	oxovanadium(IV)	blue
+5	VO_2^+	dioxovanadium(V)	yellow



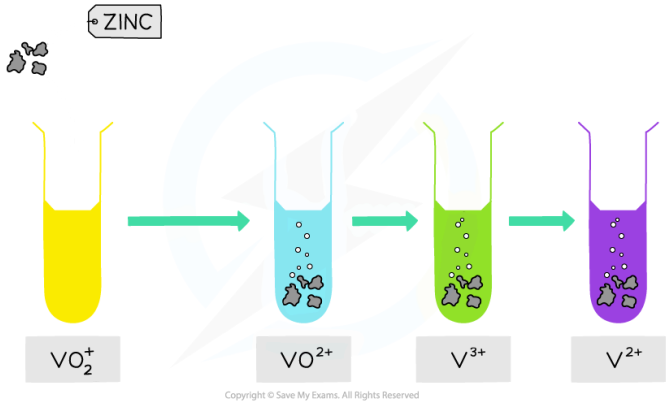
Focus of these metals is mostly on redox reactions. There is a distinct colour for each of the main oxidation states.

Feasibility of these redox reactions are in terms of the E° value.

Reducing from +5 to +2

The +5 store is usually ammonium vanadate(V) NH_4VO_3. An acidic solution of this contains VO_3^+.

when **zinc** is added to this, it gets reduced from yellow –> blue –> green –> purple as the oxidation numbers go from +5 to +2. No ppt, it's an aq solution.



In all of these reactions, the more positive (+) standard electrode potential becomes the reduction reaction and more negative (-) standard electrode potential becomes the oxidation reaction and needs to be reversed.

REDUCTION FROM +5 TO +4

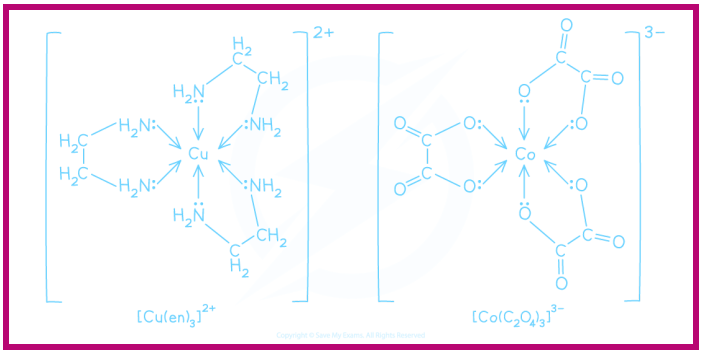
Half equations:

$$Zn^{2+}(aq) + 2e^- \leftrightarrow Zn(s) \quad E^\theta = -0.76\ V$$

$$VO_2^+(aq) + 2H^+(aq) + e^- \leftrightarrow VO^{2+}(aq) + H_2O(l) \quad E^\theta = +1.00\ V$$

Full equation:

$$2VO_2^+(aq) + 4H^+(aq) + Zn(s) \leftrightarrow 2VO^{2+}(aq) + Zn^{2+}(aq) + 2H_2O(l)$$



Since the E° value for half-equation 2 is more negative than the E° value for half-equation 5, Zn is electron releasing with respect to VO. Therefore, the reaction is thermodynamically feasible.

REDUCTION FROM +4 TO +3

Half equations:

$$Zn^{2+}\,(aq) + 2e^- \leftrightarrow Zn\,(s) \quad E^\theta = -0.76\ V$$
$$VO^{2+}\,(aq) + 2H^+\,(aq) + e^- \leftrightarrow V^{3+}\,(aq) + H_2O\,(l) \quad E^\theta = +0.34\ V$$

Full equation:

$$2VO^{2+}\,(aq) + 4H^+\,(aq) + Zn\,(s) \leftrightarrow 2V^{3+}\,(aq) + Zn^{2+}\,(aq) + 2H_2O\,(l)$$

Since the E° value for half-equation 2 is more negative than the E° value for half-equation 4, Zn is electron releasing with respect to VO^{+2}. Therefore, the reaction is thermodynamically feasible.

REDUCTION FROM +3 TO +2

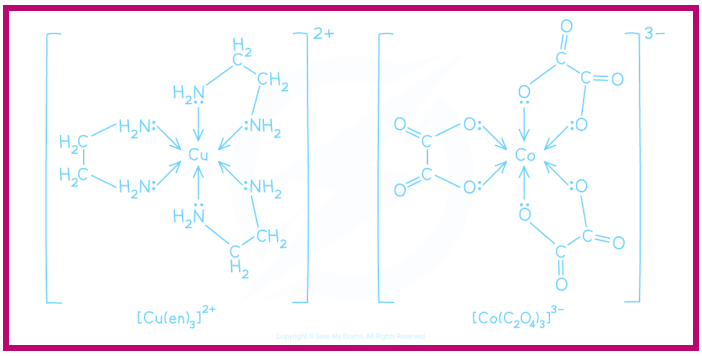
Half equations:

$$Zn^{2+}\,(aq) + 2e^- \leftrightarrow Zn\,(s) \quad E^\theta = -0.76\ V$$
$$V^{3+}\,(aq) + e^- \leftrightarrow V^{2+}\,(aq) \quad E^\theta = -0.26\ V$$

Full equation:

$$2V^{3+}\,(aq) + Zn\,(s) \leftrightarrow 2V^{2+}\,(aq) + Zn^{2+}\,(aq)$$

Since the E° value for half-equation 2 is more negative than the E° value for half-equation 3, Zn is electron releasing with respect to V^{+3}. Therefore, the reaction is thermodynamically feasible.



REDUCTION FROM +2 TO 0

Half equations:

$$Zn^{2+}(aq) + 2e^{-} <\!\!-\!\!> Zn(s) \quad E^{\theta} = -0.76\ V$$

$$V^{2+}(aq) + 2e^{-} <\!\!-\!\!> V(s) \quad E^{\theta} = -1.18\ V$$

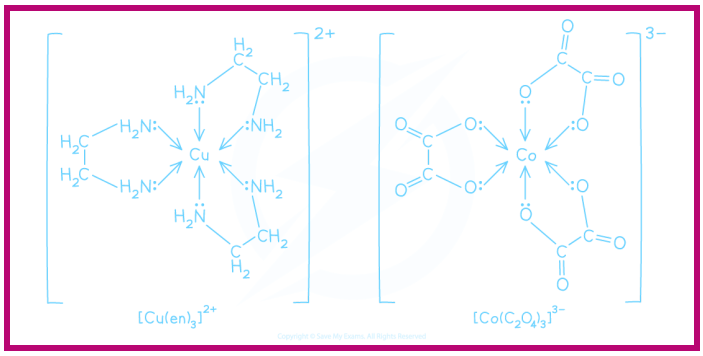
Full equation:

$$V(s) + Zn^{2+}(aq) <\!\!-\!\!> V^{2+}(aq) + Zn(s)$$

Since the E° value for half-equation 2 is less negative than the E° value for half-equation 1, Zn is not electron releasing with respect to V^{+2}. Therefore, the reaction is not thermodynamically feasible.

	Redox equation	$E^{\ominus}$ value
1.	$V^{2+}(aq) + 2e^{-} \rightleftharpoons V(s)$	−1.18 V
2.	$Zn^{2+}(aq) + 2e^{-} \rightleftharpoons Zn(s)$	−0.76 V
3.	$V^{3+}(aq) + e^{-} \rightleftharpoons V^{2+}(aq)$	−0.26 V
4.	$VO^{2+}(aq) + 2H^{+}(aq) + e^{-} \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34 V
5.	$VO_2^{+}(aq) + 2H^{+}(aq) + e^{-} \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	+1.00 V

The chemistry of Chromium



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

orange +6 → green +3

$2Cr^{3+} + Zn \rightarrow 2Cr^{2+} + Zn^{2+}$

green +3 → Blue +2

In all of these reactions, the more positive (+) standard electrode potential becomes the reduction reaction and more negative (-) standard electrode potential becomes the oxidation reaction and needs to be reversed.

Oxidation of Cr from +3 to +6 by H_2O_2

Half-equations:

$$CrO_4^{2-}(aq) + 4H_2O(l) + 3e^- \text{ <—> } Cr(OH)_3(aq) + 5OH^-(aq) \quad E^\theta = -0.13\ V$$

$$4.\ H_2O_2(aq) + 2e^- \text{ <—>} 2OH^-(aq) \quad E^\theta = +1.24\ V$$

Full equation:

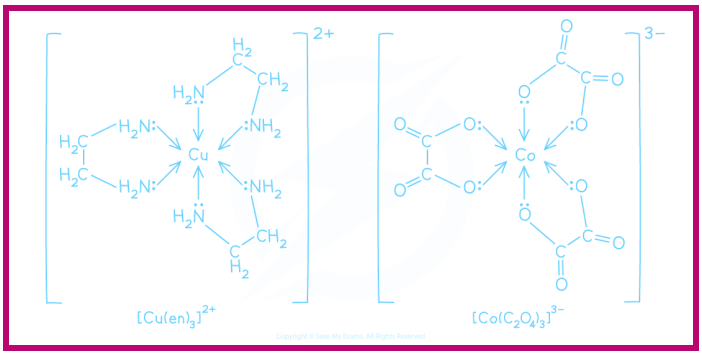
$$2Cr(OH)_3(aq) + 4OH^-(aq) + H_2O_2(aq) \text{ <—> } CrO_4^{2-}(aq) + 8H_2O(l)$$

reaction carried out in alkaline conditions due to the presence of OH^- ions.
Since the E° value for half-equation 3 is more negative than the E° value for half-equation 4, Cr(OH) is electron releasing with respect to H_2O_2 Therefore, the reaction is thermodynamically feasible.

Reduction of Cr from +6 to +3 by Zn

Half-equations:

$$Zn^{2+}(aq) + 2e^- \text{ <—> } Zn(s) \quad E^\theta = -0.76\ V$$



$$Cr_2O_7^{2-}\ (aq) + 14H^+\ (aq) + 6e^- <\!\!-\!\!> 2Cr^{3+}\ (aq) + 7H_2O\ (l) \quad E^\theta = +1.33\ V$$

Full equation:

$$Cr_2O_7^{2-}\ (aq) + 14H^+\ (aq) + 3Zn\ (s) <\!\!-\!\!> 2Cr^{3+}\ (aq) + 7H_2O\ (l) + 3Zn^{2+}\ (aq)$$

reaction carried out under acidic conditions due to the presence of H^+ ions.
Since the E° value for half-equation 1 is more negative than the E° value for half-equation 5, Zn is electron releasing with respect to $Cr_2O_7^{2-}$ Therefore, the reaction is thermodynamically feasible.

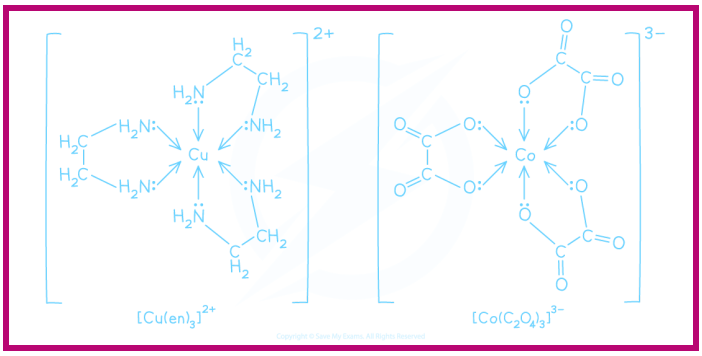
Reduction of Cr from +3 to +2 by Zn
Half-equations:

$$Zn^{2+}\ (aq) + 2e^- <\!\!-\!\!> Zn\ (s) \quad E^\theta = -0.76\ V$$
$$Cr^{3+}\ (aq) + e^- <\!\!-\!\!> Cr^{2+}\ (aq) \quad E^\theta = -0.41\ V$$

Full equation:

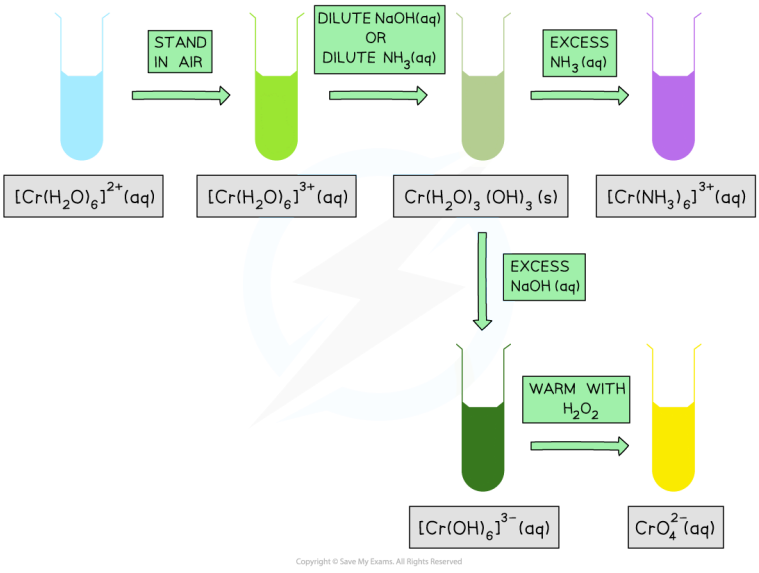
$$2Cr^{3+}\ (aq) + Zn\ (s) <\!\!-\!\!> 2Cr^{2+}\ (aq) + Zn^{2+}\ (aq)$$

reaction also carried out under acidic conditions due to the presence of H^+ ions.
Since the E° value for half-equation 1 is more negative than the E° value for half-equation 2, Zn is electron releasing with respect to Cr^{3+} Therefore, the reaction is thermodynamically feasible.



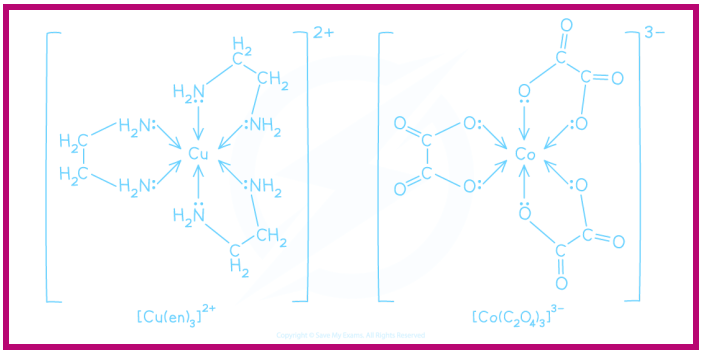
	Redox equation	$E^{\ominus}$ value
1.	$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76 V
2.	$Cr^{3+}(aq) + e^- \rightleftharpoons Cr^{2+}(aq)$	−0.41 V
3.	$CrO_4^{2-}(aq) + 4H_2O(l) + 3e^- \rightleftharpoons Cr(OH)_3(aq) + 5OH^-(aq)$	−0.13 V
4.	$H_2O_2(aq) + 2e^- \rightleftharpoons 2OH^-(aq)$	+1.24 V
5.	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33 V

Colour change of chromium



Dichromate(VI) & Chromate(VI) equilibrium

The chromate CrO_4^{2-} and dichromate $Cr_2O_7^{2-}$ ions can be converted from one to the other by the following equilibrium reaction



$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

Chromate(IV) ions are stable in alkaline solution, but in acidic conditions the dichromate(VI) ion is more stable

- Addition of acid will push the equilibrium to the dichromate, colour change of yellow —> orange
- Addition of alkali will remove the H^+ ions and push the equilibrium to the chromate, colour change of orange —> yellow

Ligand Exchange

when one ligand in a complex is substituted by another. This forms a new complex that is more **stable** then the original one.
original ligand can be **partially** or **entirely** substituted by others.

eg: when conc. HCl is added slowly and continuously to copper(II) sulfate, colour changed from blue to green then yellow

$$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}(aq) + 6H_2O(l)$$

This ligand exchange includes a change in coordination number due to size of chloride ions.
There has been a change in ligand number but not in oxidation number of the metal ion.

Deprotonation

This involved the deprotonation of the ligands with addition of aq NaOH or aq NH_3.

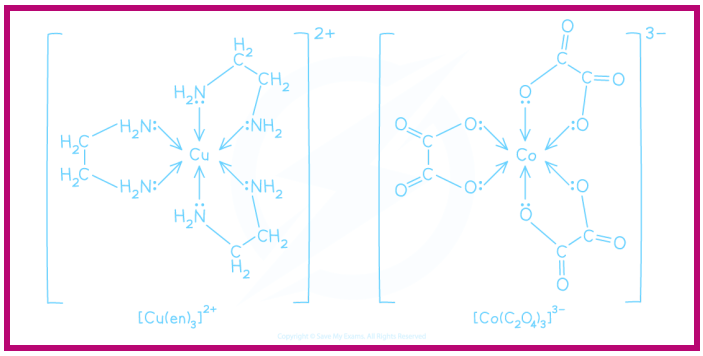
Eg: deprotonation of copper(II)sulfate by OH^-

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

deprotonation of copper(II)sulfate by NH_3

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

Different reactions of Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} with (aq) NaOH and (aq) NH_3 and with excess and colour changes!



Deprotonation:

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

Pink solution — Blue ppt

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

Ligand exchange:

$[Co(H_2O)_4(OH)_2] + 6NH_4^+ \longrightarrow [Co(NH_3)_6]^{3+} + 4H_2O + 2OH^-$

Blue ppt — yellow solution

Deprotonation:

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

Pale Blue Solution — Blue ppt

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

Ligand exchange:

$[Cu(H_2O)_4(OH)_2] + 4NH_4^+ \longrightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 2H_2O + 2OH^-$

Blue ppt — Deep Blue solution

Deprotonation:

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

Yellow/Brown Solution — Brown ppt

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

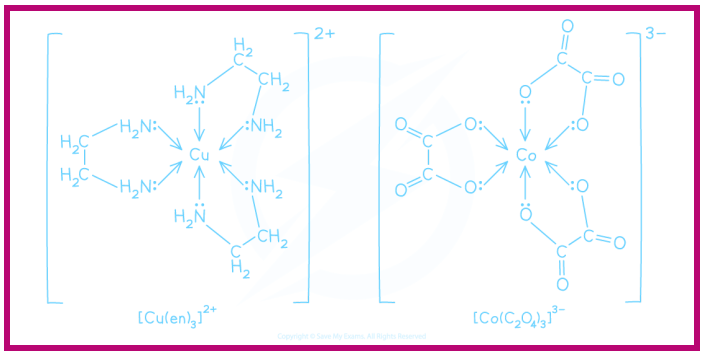
Deprotonation:

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

Pale green Solution — green ppt

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

* if left standing in air, iron oxidises from +2 to +3 and turns brown.



Deprotonation:

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

green solution — green ppt

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

Ligand exchange:

excess NaOH:

$[Cr(H_2O)_3(OH)_3] + OH^- \longrightarrow [Cr(H_2O)_2(OH)_4]^- + H_2O$

* No colour change

$[Cr(H_2O)_2(OH)_4]^- + 2OH^- \longrightarrow [Cr(OH)_6]^{3-} + 2H_2O$

excess aq NH_3:

$[Cr(H_2O)_3(OH)_3] + 6NH_3 \longrightarrow [Cr(NH_3)_6]^{3+} + 3H_2O + 3OH^-$

green ppt — Purple Solution

Deprotonation:

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

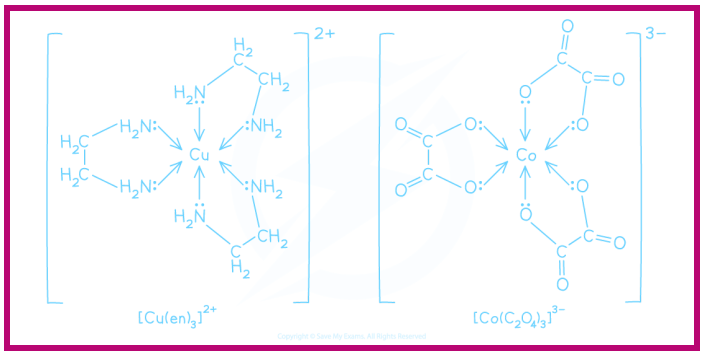
green solution — green ppt

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

Ligand exchange:

$[Ni(H_2O)_4(OH)_2] + 6NH_4^+ \longrightarrow [Ni(NH_3)_6]^{2+} + 4H_2O + 2OH^-$

green ppt — Deep blue Solution



Deprotonation:

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

Pale Pink Solution — Pale Brown ppt

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

* Pale brown ppt does not dissolve in aq excess NaOH or NH_3

Deprotonation:

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

Colourless — white ppt

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

Ligand exchange:

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

white ppt — Colourless

$[Zn(H_2O)_4(OH)_2] + 6NH_3 \longrightarrow [Zn(NH_3)_6]^{2+} + 2H_2O + 2OH^-$

Change in coordination numbers of Cu^{2+} and Co^{2+}

$[Co(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6H_2O$

6 H_2O ligands ⟶ 4 Cl^- ligands

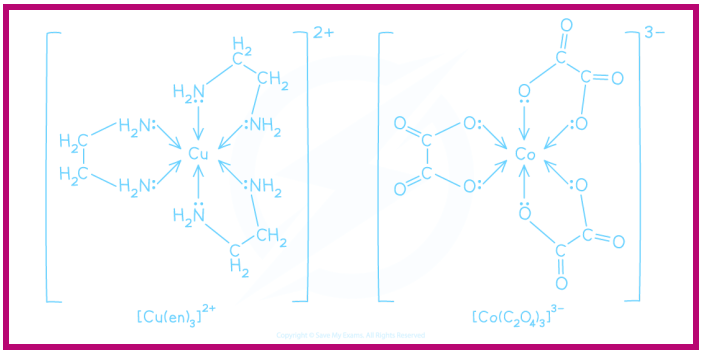
Pink solution ⟶ Blue solution

$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$

6 H_2O ligands ⟶ 4 Cl^- ligands

Blue ⟶ green ⟶ yellow

Amphoteric hydroxides



In the hydrated transition metal ions that are deprotonated by adding a base like aq NaOH to form a ppt of the metal hydroxide, the metal is acting as a **acid** since it is acting with a **base.** In reactions with acid (H^+) the metal hydroxide acts as a **base** as it is reacting with an **acid**.

This is an example of **amphoteric** behaviour.

Reactions with limited OH^- and limited NH_3

- Deprotonation reaction where the two hydroxide ions remove hydrogen ions from two of the water ligands, converting themselves into water molecules.

Reactions with excess OH^-

- The metal hydroxide acts as a **acid** as it is reacting with a **base**

Reactions with excess NH_3

- This is ligand substitution as four ammonia molecules replace the two water and hydroxide ions.
- NH_3 is acting as a lewis base, donating an electron pair

Increase of stability

Stability increases as we go from a monodentate to a bidentate or multidentate as the ΔS_{system} increases, this leads to a more stable complex ion, making it more feasible.

Heterogeneous catalyst

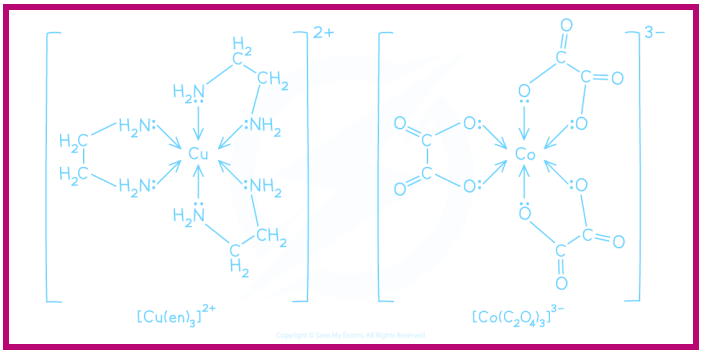
This is a catalyst that is in a different physical phase as the reactants.
They're usually **solids** whereas the reactants are **gaseous** or in **solution**.

Surface absorption theory (HARD):

1. **Adsorption**, in which one or more reactants becomes attached to the surface of the catalyst
2. **Reaction**, following the weakening of the bonds in the adsorbed reactants
3. **Desorption**, in which the reaction product becomes detached from the surface of the catalyst

Factors affecting HARD:

- Strength of adsorption



- stronger the adsorption, the more effective the catalytic activity.
- reactants adorb in higher conc with higher adsorption.
- Ni and Pt are the best in this

- Surface area
  - Increased surface area of a solid catalyst improves its effectiveness.

Advantages:

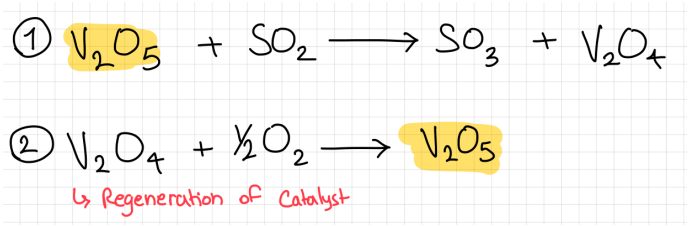
- Can be filtered off and are easy to **separate** from any liquid or gaseous products
- Suited to **continuous** processes rather than batch processes

Disadvantages:

- The effectiveness of a heterogeneous catalyst can be decreased by the presence of **impurities** in the gas involved in the reaction.
- The impurities can:
  - Adsorb onto catalyst surface and occupy active sites
  - Prevent bond weakening in the reactants
  - 'Take up' the surface area of catalyst by forming strong bonds to surface of catalyst so are less likely to desorb from surface of catalyst

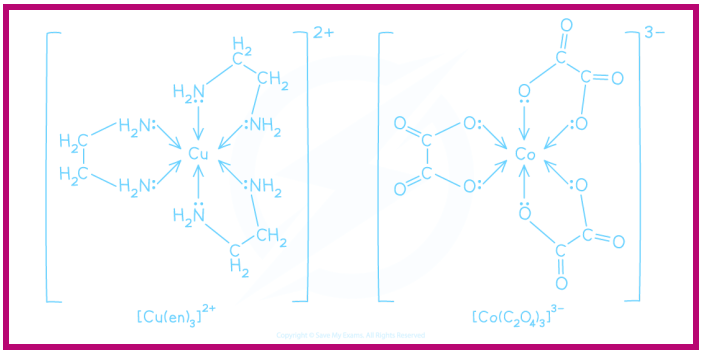
The contact process

Manufacture of sulfuric acid. Uses vanadium(V)oxide that is converted into vanadium(IV)oxide in the process and regenerated after. Decrease of +5 to +4



Catalytic converters & emissions

These are used in car exhaust boxes to reduce air pollution. Contain a mixture of finely divided platinum and rhodium supported on a ceramic base.



Carbon monoxide, nitrogen dioxide and unburnt hydrocarbons are sources of pollution from cars

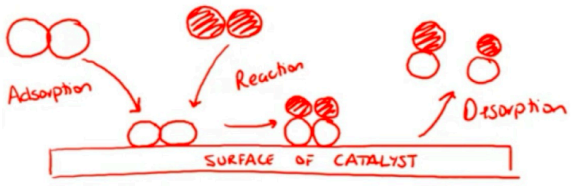
- Carbon monoxide is toxic and interferes with oxygen transport in the body
- Nitrogen monoxide is easily oxidised in the atmosphere to form nitrogen dioxide which is a respiratory irritant and contributes to the formation of acid rain

The transition metal catalysts facilitate the conversion of these pollutants into less harmful products

$$2NO\ (g) + 2CO\ (g) \rightarrow N_2\ (g) + 2CO_2\ (g)$$

$$CH_3CH_2CH_3\ (g) + 5O_2\ (g) \rightarrow 3CO_2\ (g) + 4H_2O\ (g)$$

It uses the surface absorption theory for this:



In order to **minimise** the **cost** and **maximise** the **efficiency** of the catalyst the following measures can be taken:

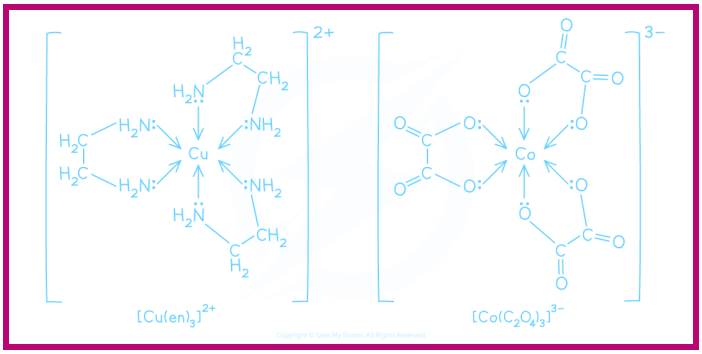
  - Increasing the surface area of the catalyst
  - Coating an inert surface medium with the catalyst to avoid using large amounts of the catalyst
- This is achieved by spreading the catalyst over a hollow matrix such as a honeycomb-like structure

Homogeneous catalyst

a catalyst that is in the same physical state as the reactant.
Either all **gases** or all **aqueous solutions**.

- The key feature of homogeneous catalysis is the formation of an intermediate species for which a specific formula can be written

Iron(III) ion catalyst



Transition element ions can adopt more than one **stable oxidation state**
This means that they can accept and lose electrons easily to go from one oxidation state to another
They can therefore catalyse **redox** reactions, by acting as both **oxidising agents** and **reducing agents**

When Fe(II) acts as a reducing agent, it will reduce another species and become oxidised itself

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

The Fe^{3+} formed in the catalytic cycle, can then also act as an oxidising agent by oxidising another species and getting reduced itself to reform the Fe^{2+} ion

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

Iron(II) ions catalyse the reaction between iodide ions and peroxodisulfate ions.

- The overall reaction is quite slow because **the repulsion of two negative ions coming together hinders the reaction**

$$S_2O_8^{2-} + 2I^- \rightarrow I_2 + 2SO_4^{2-}$$

- The reaction is quite slow even though it is **energetically favourable**. Both ions are negatively charged, so they are unlikely to make successful collisions with one another.
- Starch is often added to this reaction, which will form a blue-black colour showing the formation of iodine

With addition of Iron(II) ions:

$$S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$$

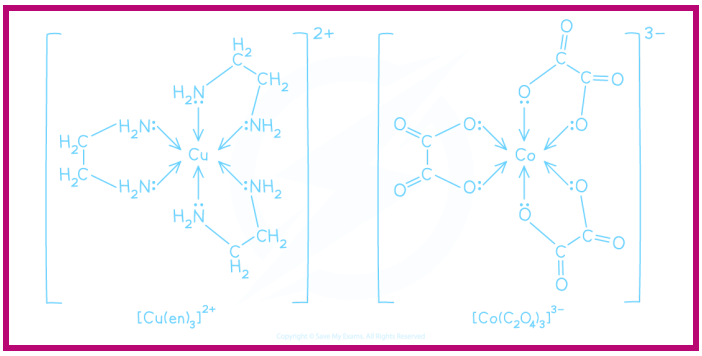
The iron(III) ions will oxidise iodide ions to iodine and then are reduced once again to iron(II):

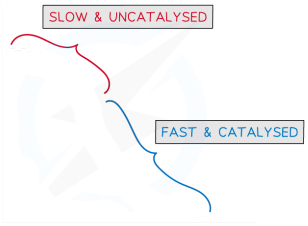
$$2I^- + 2Fe^{3+} \rightarrow I_2 + 2Fe^{2+}$$

Catalyst is **regenerated** at the end and repeats its job.

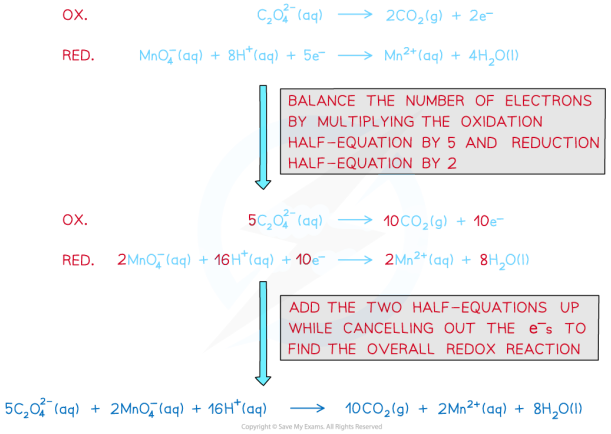
Manganese(II) ions as an Autocatalyst

Autocatalyst means that the reaction is sped up by the products formed by itself.





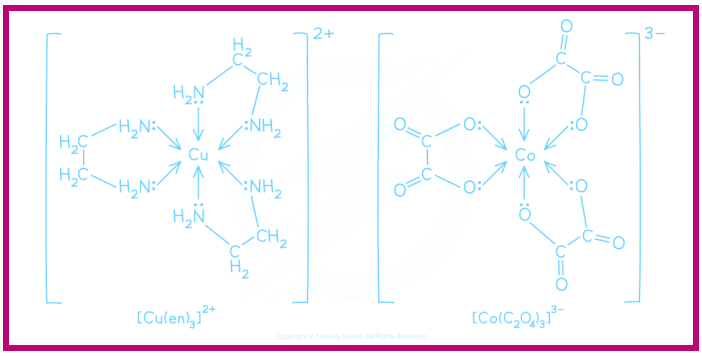
An example of autocatalyst is the reaction between **Manganate(VII)** ions and **Oxalate** ions.



as more manganese(II) is formed, the reaction speeds up more. The job of manganese(II) ions is to take part in a redox cycle between two different oxidation states: +2 → +3 → +2

$$4Mn^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightarrow 5Mn^{3+}(aq) + 4H_2O(aq)$$
$$2Mn^{3+}(aq) + C_2O_4^{2-}(aq) \rightarrow 2CO_2(g) + 2Mn^{2+}(aq)$$

This reaction is easily followed on a **colorimeter** as the rate at which the purple manganate(VII) ion is consumed accelerates with time.



Topic 18: Organic chemistry: Arenes

Benzene - structure and stability

Structure

Structure consists of 6 carbon atoms in a hexagonal ring, with alternating single and double carbon-carbon bonds.

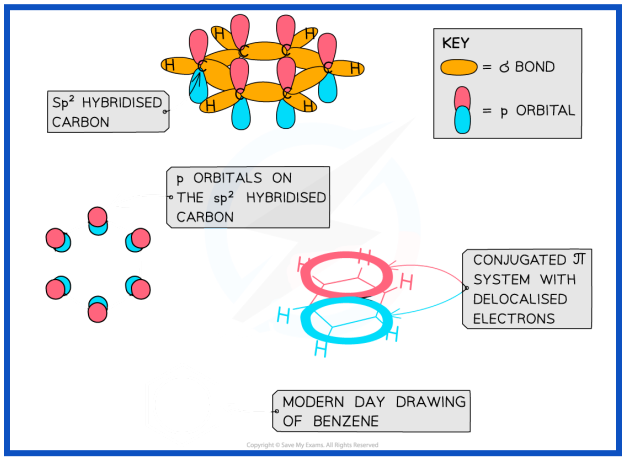
- This would suggest that benzene should react the same way an alkene does, but this is not the case.

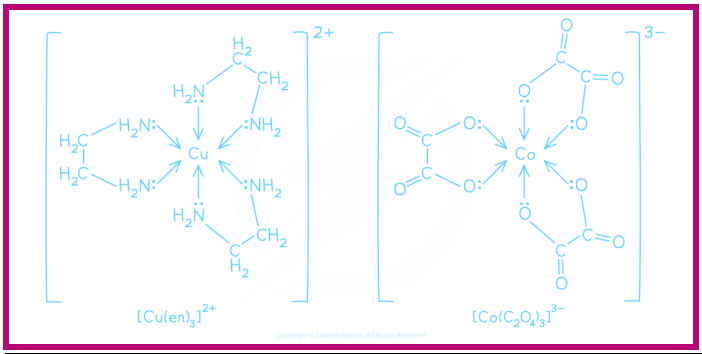
Each carbon atom forms three σ bonds using the **sp² orbitals**

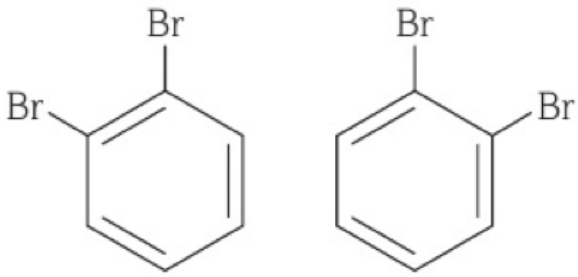
The remaining **p orbitals** overlap laterally with p orbitals of neighbouring carbon atoms to form a **π system**

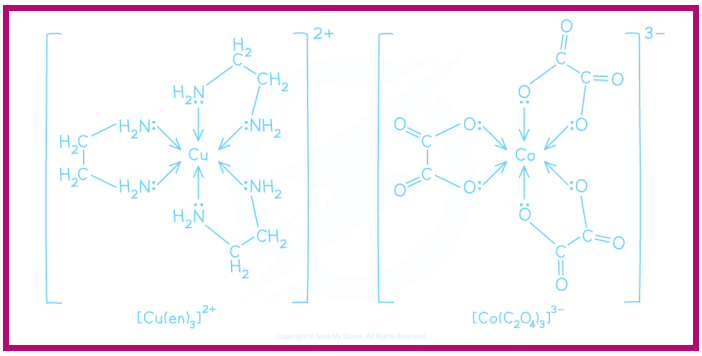
- This extensive sideways overlap of p orbitals results in the electrons being delocalised and able to freely spread over the entire ring causing a π system
    - The π system is made up of two ring-shaped clouds of electron density - one above the plane and one below it

The delocalisation of electrons means that all of the carbon-carbon bonds in these compounds are identical and have both **single** and **double bond** character





Problem with the kekule structure	how it is solved with new model
If a benzene ring contains three C=C, it should decolourise bromine water, but it doesn't.	no individual C=C bonds, so there is no addition reaction with bromine
if the kekule structure is correct, we should see structures like:  however only three are known to exist, suggesting that the bonds in the carbons are all the same	there are three, not four, isomers of $C_6H_4Br_2$ because when the bromine atoms are on adjacent carbon atoms, there is no difference in the arrangement of electrons between these atoms
The data from the X-ray diffractions about the length of the covalent bonds shows that bonds in benzene and cyclohexene are **not the same**, suggesting all the carbon-carbon bonds in benzene are all the same.	The carbon-carbon bonds are all the same length because they are identical and not individual C-C and C=C bonds.
Enthalpy change of hydrogenation of benzene ring is not three times that of cyclohexene, as previously thought.	When charge is spread around in a species, there is increased stability which explains the 152 kJ mol^{-1} greater stability of benzene compared with cyclohexa-1,3,5-triene
the infrared spectrum of benzene doesn't have stretched for C=C alkene, but for C=C of an typical aromatic	The infrared spectrum of benzene has a very strong absorption around 1500 which is typical of C=C in an aromatic compound. Absorption for C=C in non-aromatic compounds are between 1680 and 1645.



Evidence for delocalisation

This evidence of the bonding in benzene is provided by data from:

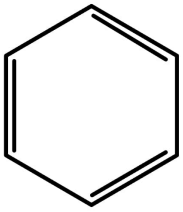
- Enthalpy changes of hydrogenation
- Carbon-carbon bond lengths from X-ray diffraction
- Saturation tests
- Infrared spectroscopy

Enthalpy changes of hydrogenation

- Hydrogenation of cyclohexene
  - Each molecule has one C=C double bond
  - The enthalpy change for the reaction of cyclohexene is -120 kJ mol^{-1}

$$C_6H_{10} + H_2 \rightarrow C_6H_{12} \quad \Delta H^{\ominus} = -120 \text{ kJ mol}^{-1}$$

- Hydrogenation of benzene
  - The Kekulé structure of benzene as cyclohexa-1,3,5-triene has three double C=C bonds:

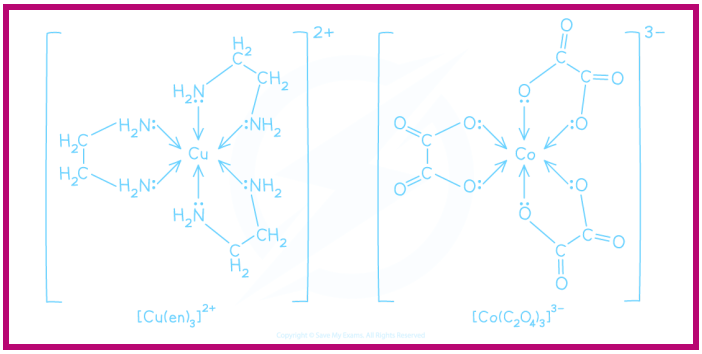


  - It would be expected that the enthalpy change for the hydrogenation of this structure would be three times the enthalpy change for the one C=C bond in cyclohexene

$$C_6H_6 + 3H_2 \rightarrow C_6H_{12} \quad \Delta H^{\ominus} = 3 \times -120 \text{ kJ mol}^{-1} = -360 \text{ kJ mol}^{-1}$$

- When benzene is reacted with hydrogen, the enthalpy change obtained is actually far less exothermic, $\Delta H^{\ominus} = -208 \text{ kJ mol}^{-1}$

Carbon-carbon bond lengths



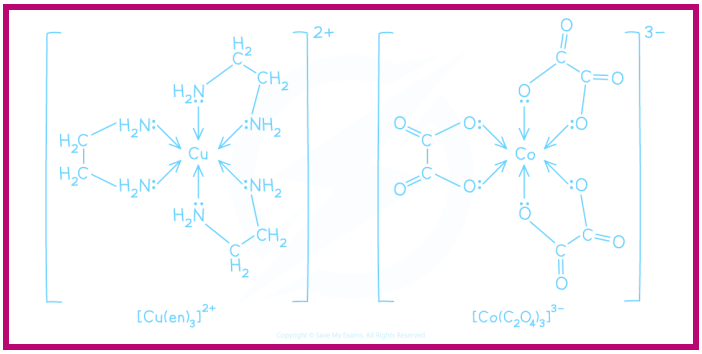
- Cyclohexene contains two different carbon-carbon bonds
    - The single carbon-carbon bond (C-C) has a bond length of 154 pm
    - The double carbon-carbon bond (C=C) has a bond length of 134 pm
- The Kekulé structure of benzene as cyclohexa-1,3,5-triene has three single C-C and three double C=C bonds
    - It would be expected that benzene would have an equal mixture of bonds with lengths of 134pm and 154 pm
- All of the carbon-carbon bond lengths are 140 pm suggesting that they are all the same and also intermediate of the single C-C and double C=C bonds

Saturation tests

- Cyclohexene will decolourise bromine water as an electrophilic addition reaction takes place
- The Kekulé structure of benzene as cyclohexa-1,3,5-triene has three double C=C bonds
    - It would, therefore, be expected that benzene would easily decolourise bromine water
- Benzene does not decolourise bromine water suggesting that there are no double C=C bonds

Infrared spectroscopy

- Cyclohexene shows a peak at around 1650 cm^{-1} for the double C=C bond within its structure
- The Kekulé structure of benzene as cyclohexa-1,3,5-triene has three double C=C bonds
    - It would, therefore, be expected to also show a peak at around 1650 cm^{-1} for the double C=C bonds
- Benzene does not show a peak at around 1650 cm^{-1} for the double C=C bonds, instead, peaks are seen at around 1450, 1500 and 1580 cm^{-1} which are characteristic of double C=C bonds in arenes



Bromination resistance

$$C_6H_{10} + Br_2 \rightarrow C_6H_{10}Br_2$$

Alkenes tend to undergo bromination easily and this decolourises the bromine water, making it be used as a test for alkenes.

- It produces an area of high electron density allowing it to repel the electron in the bromine molecule
- so, a dipole is introduced, making one bromine atom δ+ and one δ- bromine atom.
- the δ+ bromine atom is attracted to the π bond in the cyclohexene, and leaves a carbocation in the intermediate molecule which the bromine ion is attracted to

In benzene, there are no localised areas of high electron density, preventing it from being able to polarise the bromine molecule

In order for benzene to undergo electrophilic substitution with bromine, a halogen carrier must be present in the reaction e.g. $AlBr_3$

Benzene - reactions

Reaction with oxygen

Hydrocarbons will burn in air or oxygen to produce carbon dioxide and water providing sufficient oxygen is available

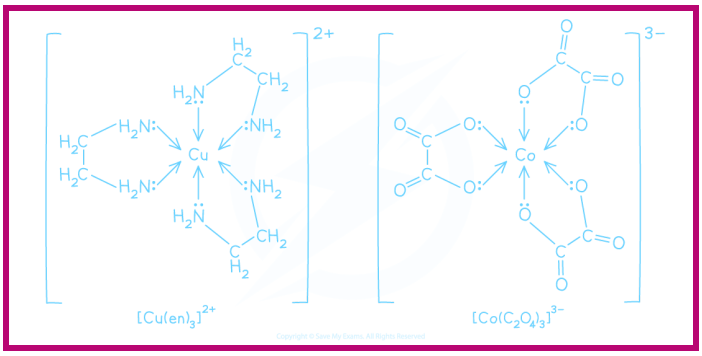
$$2C_6H_6\ (l) + 15O_2\ (g) \rightarrow 12CO_2\ (g) + 6H_2O\ (g)$$

- Insufficient oxygen leads to incomplete combustion
- This would lead to a dark misty flame as there would be insufficient oxygen available.

Hydrogenation

Done by mixing hydrogen with benzene and heating under pressure with a **nickel catalyst**.

$$C_6H_6\ (l) + 3H_2\ (g) \rightarrow C_6H_{12}$$



Halogenation

Electrophilic addition is not possible, therefore these aromatic compounds will react with halogens in the presence of a **metal halide carrier** like iron(III)bromide or aluminum chloride
The metal halide carrier acts as a catalyst and creates the electrophile X^+

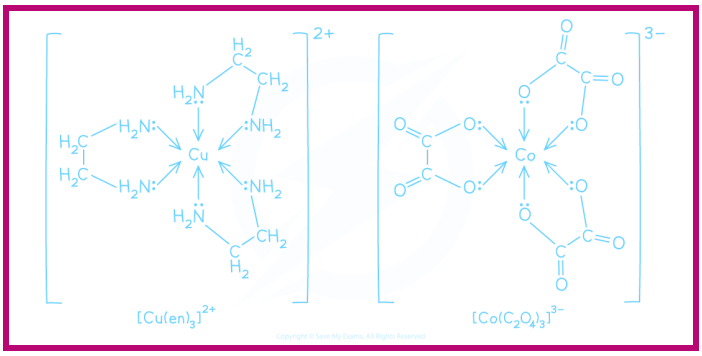
$$C_6H_6 + X_2 \rightarrow C_6H_5X + HX$$

Nitration

An example of a substitution reaction is the nitration.
A nitro group ($-NO_2$) replaces a hydrogen atom.

The benzene is reacted with a mixture of concentrated nitric acid (HNO_3) and concentrated sulfuric acid (H_2SO_4) at a temp between 25-60°C

Friedel-Craft reactions

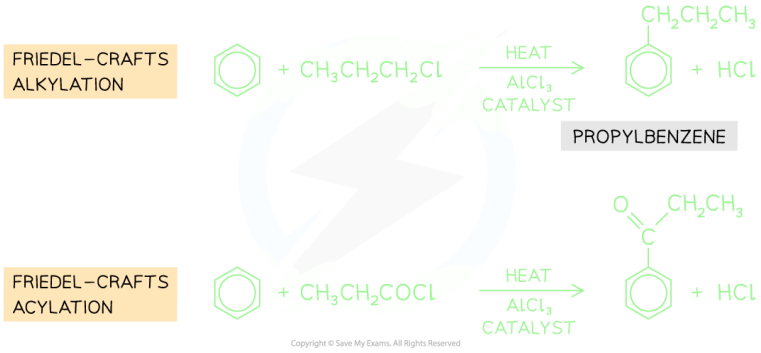


Substitution reactions. These are often unreactive due to the stability in arenes.

- used to substitute a hydrogen atom with an **alkyl group** or **acyl group**.

the Friedel-Crafts reactions consist of three steps:

- Generating the electrophile
- Electrophilic attack on the benzene ring
- Regenerating aromaticity of the benzene ring



Sulfonation

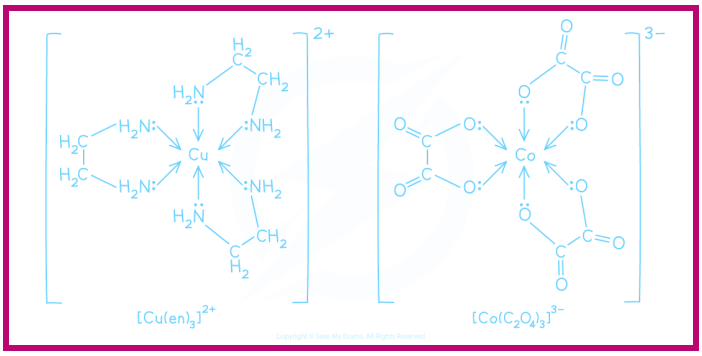
ANOTHER substitution reaction

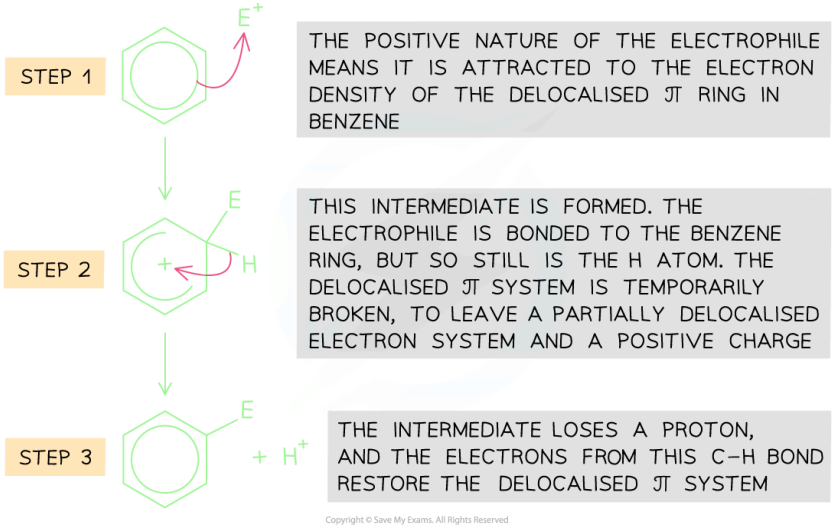
sulfonyl group (-SO_3H) replaces a hydrogen atom

Benzene is warmed with fuming sulfuric acid at temp of 40°C for around 30 minutes.

- Fuming sulfuric acid is made by dissolving sulfur trioxide in conc. sulfuric acid

Electrophilic substitution of benzene



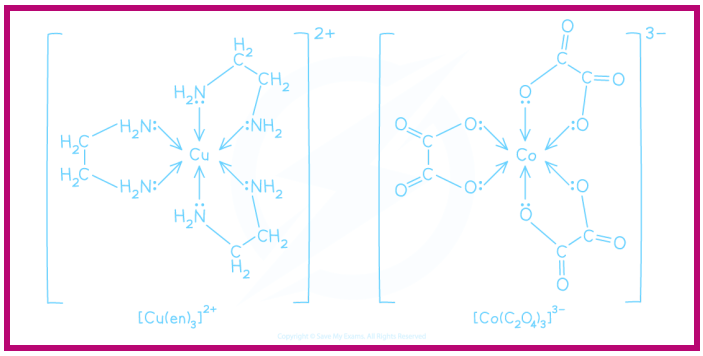


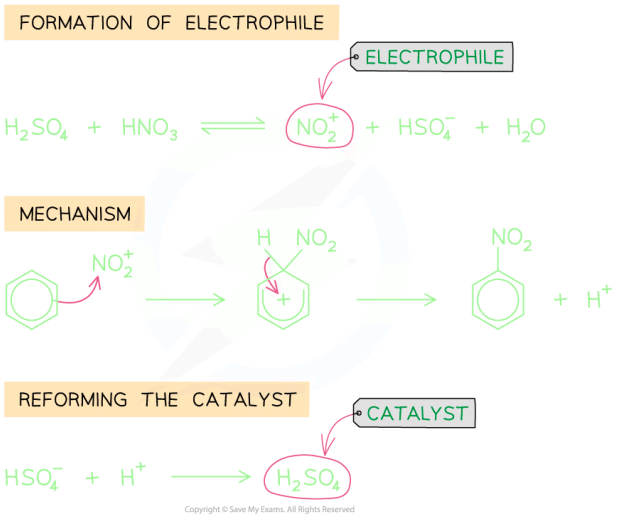
The delocalised π system is extremely stable and is a place of **high electron density**.
The **electrophilic substitution** reaction in arenes consists of **three steps**:

1. Generation of an **electrophile**
2. **Electrophilic attack**
3. Regenerating **aromaticity**

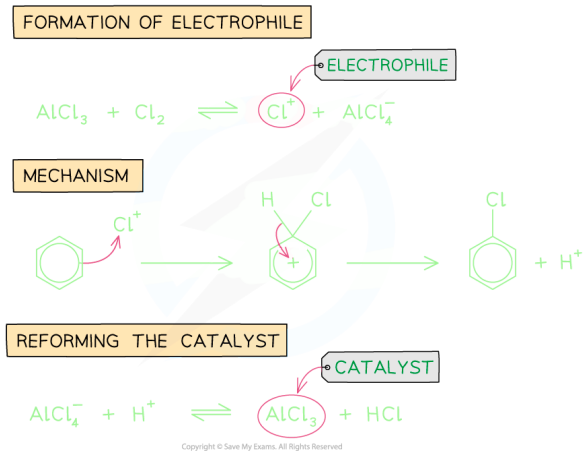
Nitration mechanism

1. Generation of electrophile
    a. NO_2^+ ion is generated by reacting conc. nitric acid (HNO_3) and conc. sulfuric acid (H_2SO_4)

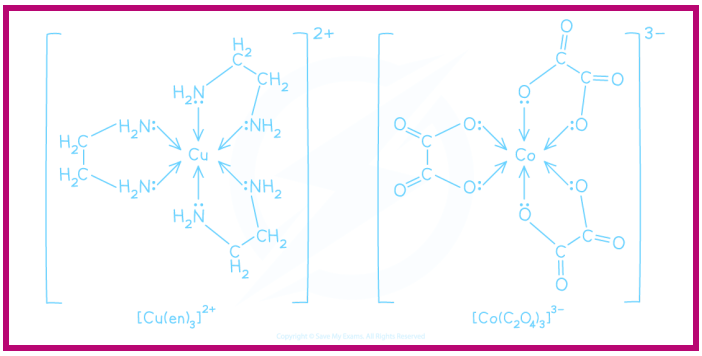


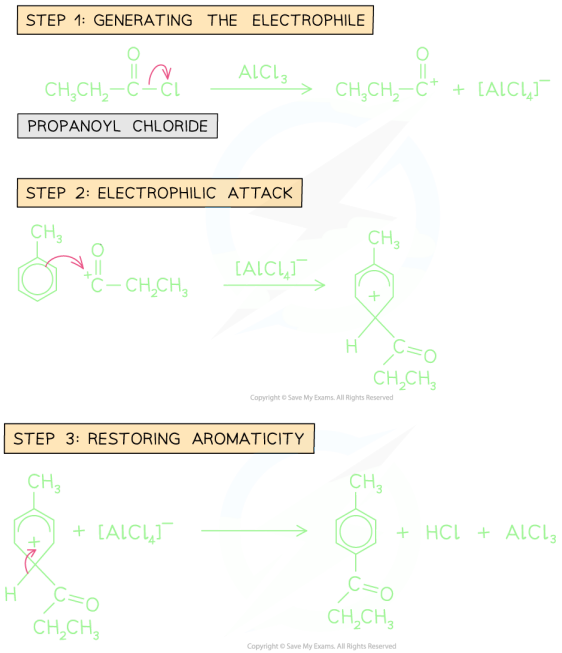


Halogenation mechanism



Friedel-craft mechanism





Phenol bromination

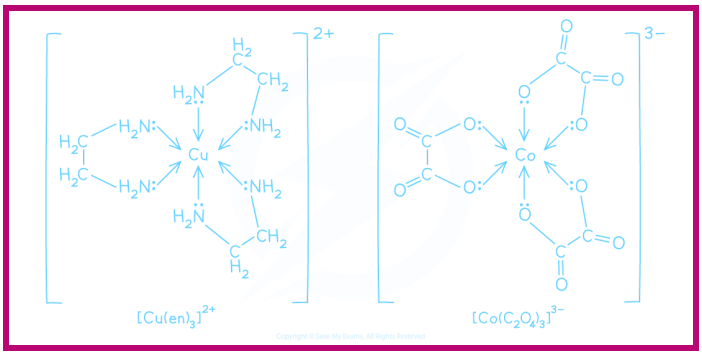
phenols are more readily reactive with electrophiles compared to benzene.

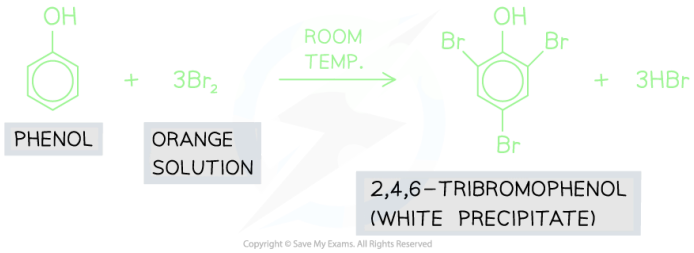
- this is bc one the the lone pairs of the electrons on the oxygen atom in the -OH overlaps with π bonding system
- This **increases the electron density** of the benzene ring making it more susceptible to electrophilic attack
- the -OH group in phenol is activating and directs incoming electrophiles to the 2, 4 and 6 position

Bromination

They go through electrophilic substitution reactions with **bromine water in room temp**.

- Phenol decolourises the orange bromine solution to form a **white ppt**.

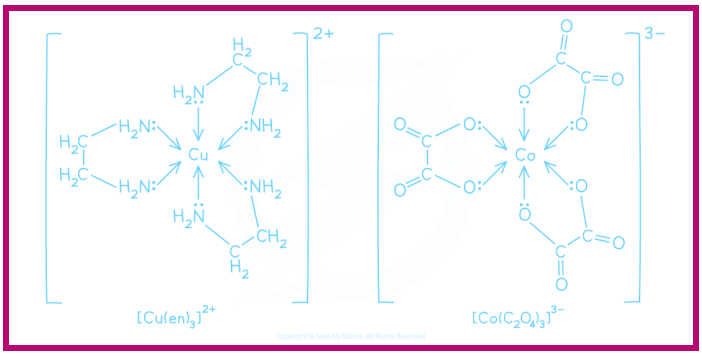


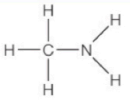
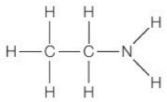
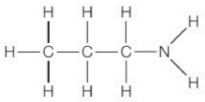
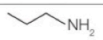
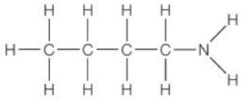
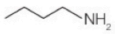
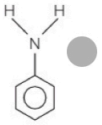


Topic 19: Organic Nitrogen compounds: Amines, Amides, Amino Acids and Proteins

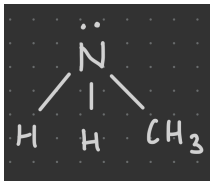
Amines ($-NH_2$)

STRUCTURAL FORMULA	NAME
CH_3NH_2	methylamine
$CH_3CH_2NH_2$	ethylamine
$CH_3CH_2CH_2NH_2$	propylamine
$CH_3CH_2CH_2CH_2NH_2$	butylamine
$C_6H_5NH_2$	phenylamine

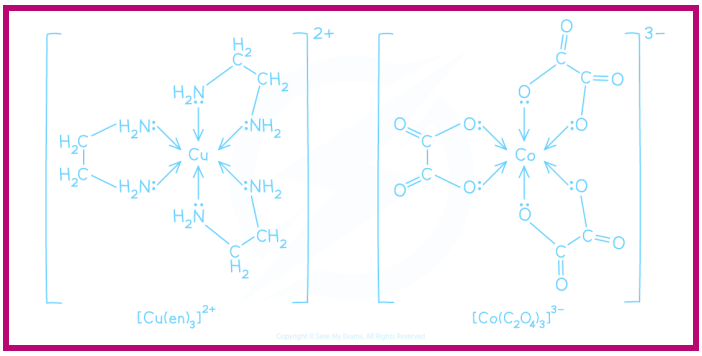


NAME	DISPLAYED FORMULA	SKELETAL FORMULA
methylamine		
ethylamine		
propylamine		
butylamine		
phenylamine		

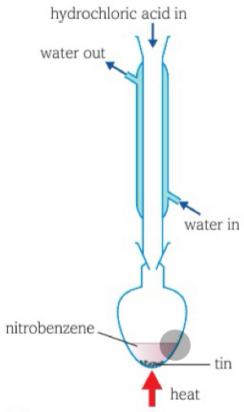
Primary Amine



- Used widely in drugs (ex. Amphetamines)
- Preparations of amines:
  - Aliphatic amines (Nitrogen is only bonded to a alkyl group) can be prepared by reducing a nitrile using $LiAlH_4$ in dry ether.
    - $CH_3CN + 4\ [H] \rightarrow CH_3CH_2NH_2$
  - Heating a halogenoalkane with ammonia (in a sealed container or with aqueous ammonia)
    - $CH_3Cl + NH_3 \rightarrow CH_3NH_2 + HCl$
- Preparations of Aromatic Amines:
  - Phenylamine is prepared by the reduction of nitrobenzene under reflux
    - Tin mixed with HCl is the reducing agent
    - Tin is oxidized from Tin (II) to Tin (III)



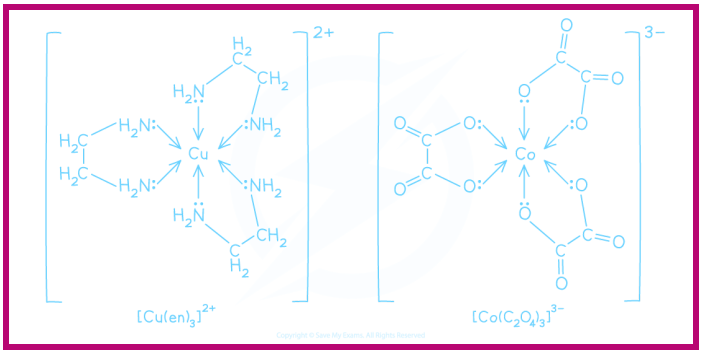
- $C_6H_5NO_2 + 6\,[H] \rightarrow C_6H_5NH_2 + H_2O$



- Amines with water
  - Short chain primary aliphatic amines are soluble in water as the form hydrogen bonds with the water.
  - As the HC chain gets longer the London forces become the predominant force, reducing the solubility.

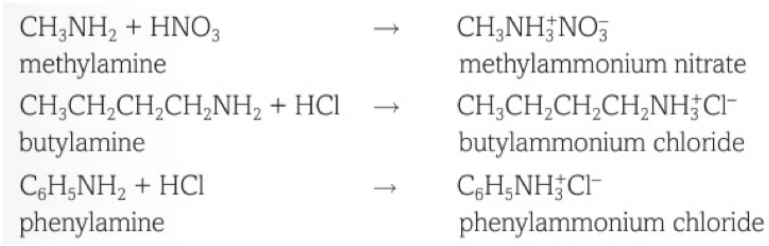
- Acid - Base reactions of Amines
  - Amines can react with water to form alkaline solutions, this is due to the lone pair on the nitrogen atom.
    - $CH_2NH_2 + H_2O = CH_2NH_3^+ + OH^-$
    - $NH_3 + H_2O = NH_4^+ + OH^-$
  - pK_b the basicity
  - the pK_b of water is 7.00 and any value lower than that indicates a basicity greater than water.
  - As the HC chain increases the pK_b value decreases which means it is more basic.
  - Phenylamine is an anomaly with a 9.38 pK_b value which means it is less basic.

Amines are more basic than water since they alky groups are more electron-donating making the lone pair on nitrogen more available for forming a dative covalent bond with H+ ions. And Phenol is less basic since the lone pair of electron on nitrogen is incorporated in the delocalised pi ring of electrons, decreasing it's availability for H+ ions.

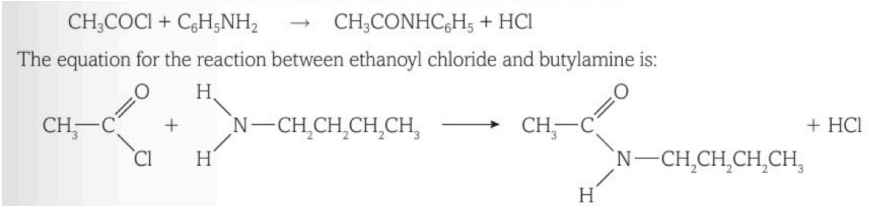


NAME	FORMULA	pK_b
ammonia	NH_3	4.75
methylamine	CH_3NH_2	3.36
ethylamine	$CH_3CH_2NH_2$	3.27
propylamine	$CH_3CH_2CH_2NH_2$	3.16
phenylamine	$C_6H_5NH_2$	9.38

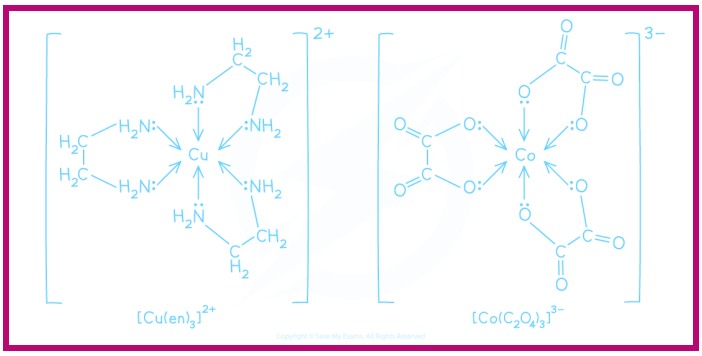
- Reactions with acids:
  - Even though they are all very basic they react with strong acids to form ionic salts.



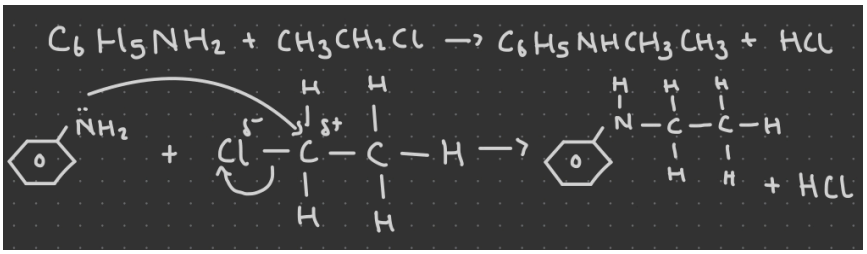
- Reaction of amine with ethanol chloride to form an amide (A carbonyl group is next to an NH group.
  - Addition-elimination reaction: a reaction in which two molecules join together and a small molecule is eliminated.



- Amines react with halogenoalkanes due to the presence of the electron deficient carbon on the halogenoalkane and the electron rich nitrogen atom on the amine.
  - It forms a secondary amine and the inorganic product is a hydrogen halide.

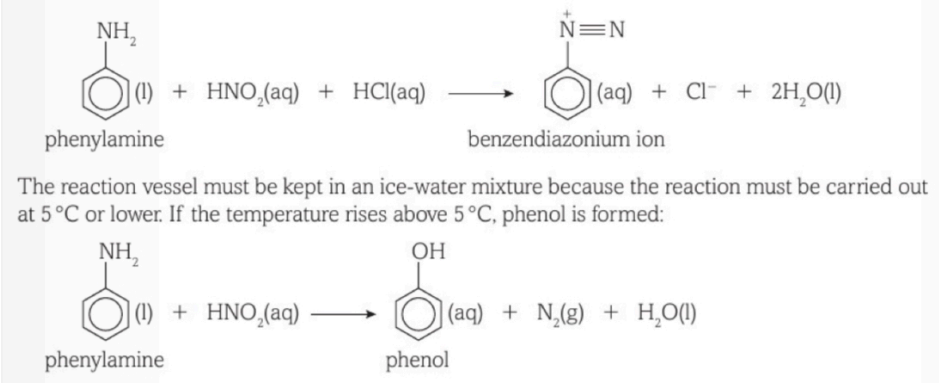


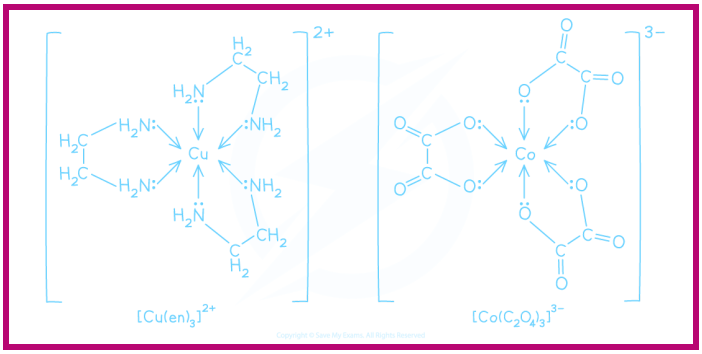
- For example: phenylamine + Chloroethane —-> forming a secondary amine.



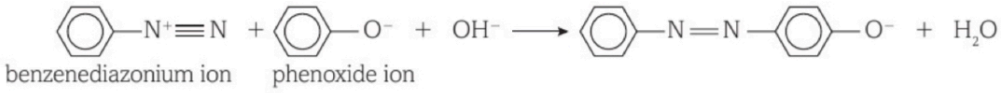
- Amines with copper (II) ion
  - With butylamine - a pale blue ppt is formed then with excess butylamine the ppt dissolves to a deep blue solution.
  - Pale blue: $[Cu(H_2O)_6]^{2+} + 2C_4H_9NH_2 \rightarrow [Cu(H_2O)_4(OH)_2] + 2C_4H_9NH_3^+$
  - Deep blue: $[Cu(H_2O)_4(OH_2)] + C_4H_9NH_2 \rightarrow [Cu(C_4H_9NH_2)_4(H_2O)_2]^{2+} + 2H_2O + 2OH^-$

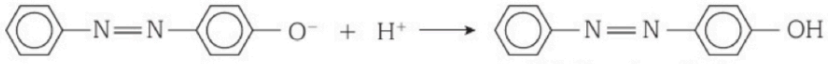
- Formation of Azo-dyes
  - Nitrous acid (HNO_2) can be prepared by mixing ice cold solutions of sodium nitrite and dilute HCl.
  - Then add it to phenylamine forming Diazonium ions.
    - Must be done at 5°C or else phenol will form.
  - The Diazonium ions carry a positive charge, they react readily in cold alkaline solution with aromatic phenols and amines.





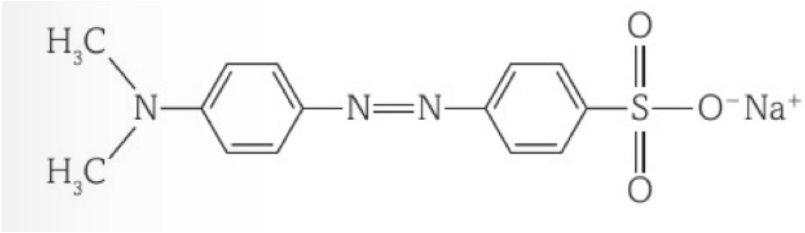
- Reactions of Diazonium ions and Phenols
  - Diazonium ions carry a positive charge and therefore can act as strong electrophiles.





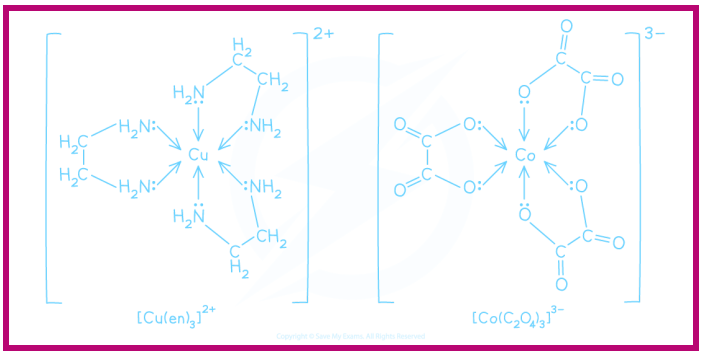
  - This is called a coupling reaction. - electrophilic sub
  - The compound formed is an energetically stable, yellow azo dye.

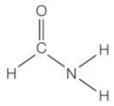
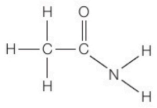
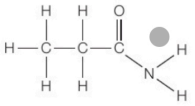
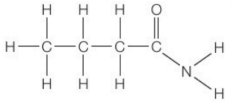
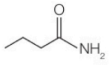
This is Methyl orange, it is also a kind of azo dye.



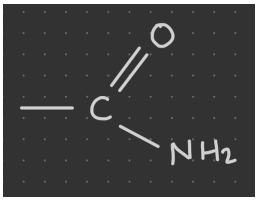
Amides (-$CONH_2$)

STRUCTURAL FORMULA	NAME
$HCONH_2$	methanamide
CH_3CONH_2	ethanamide
$CH_3CH_2CONH_2$	propanamide
$CH_3CH_2CH_2CONH_2$	butanamide



NAME	DISPLAYED FORMULA	SKELETAL FORMULA
methanamide		
ethanamide		
propanamide		
butanamide		

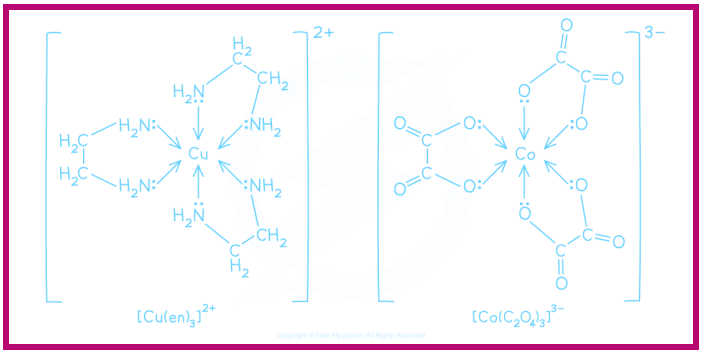
All are solids (except methylamide liquid)



- Preparations of amides:
  - Mix an acyl chloride with conc. (aq) ammonia.
  - The lone pair of electrons on the nitrogen of the ammonia molecule is strongly attracted to the electron deficient carbon atom of acyl chloride.

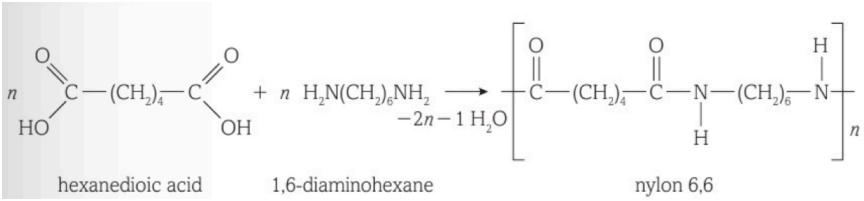
$$CH_3CH_2COCl + NH_3 \rightarrow CH_3CH_2CONH_2 + HCl$$

- Polyamide
  - They are formed in the condensation polymerisation reaction between dicarboxylic acids and diamines

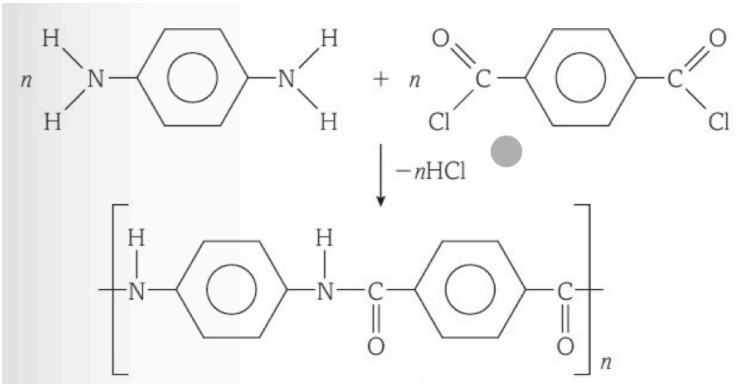


- They are semi- crystalline and very tough materials with good thermal and chemical resistance.
- The absorb moisture causing increased flexibility and resistance but also decreased strength and stiffness.
- (ex: HOOCCOOH + $H_2NCH_2NH_2$)

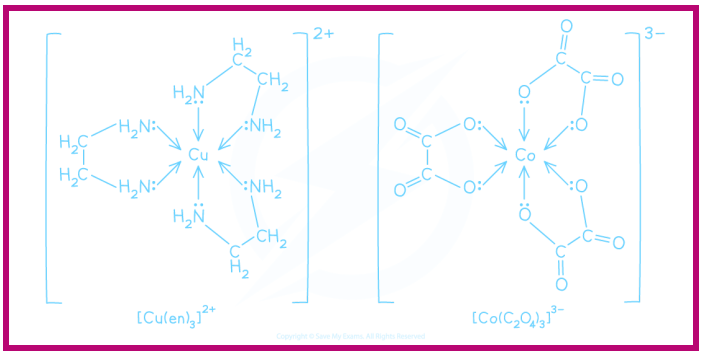
- Nylon is formed from hexanedioic acid and hexane- 1,6 -diamine
- Used to make clothes, fishing lines and carpets

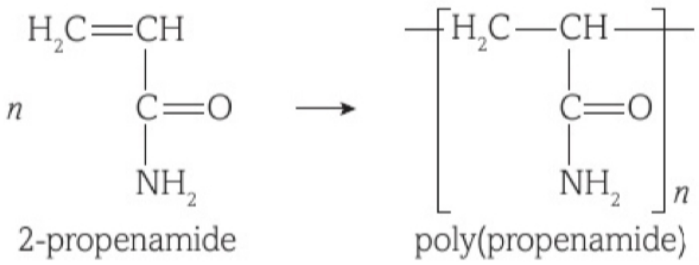


- Kevlar
- Used to make bulletproof and stab proof vests due to its strength.

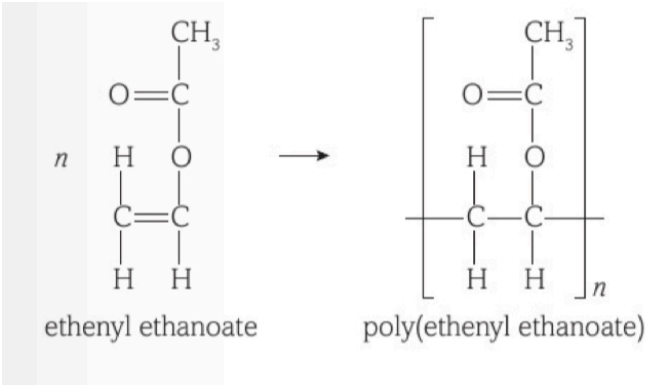


- poly (propenamides)
- Used as a thickener and siller in facial surgery. It is also used in water treatment and paper making

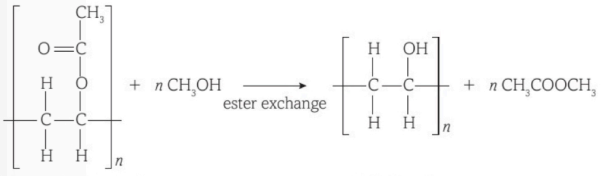




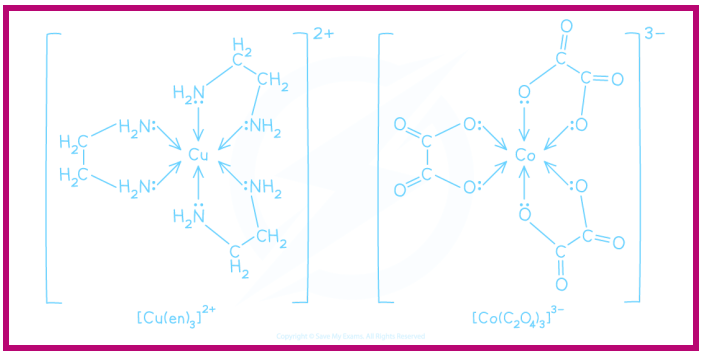
- poly (ethanol)
- Used to make disposable lays dry bags for hospitals, the laundry bags are soluble in water.
- Dirty bedding and clothes (may be covered in microorganisms) are placed into the bag. The bag is then placed in the washing machine without having to be touched, preventing possible contamination.
- It is made in two stages



In the second stage, poly(ethenyl ethanoate) is reacted with methanol to form poly(ethenol) and methyl ethanoate, in a process called ester exchange:



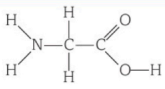
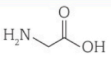
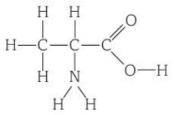
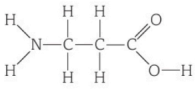
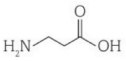
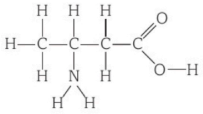
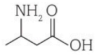
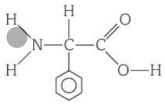
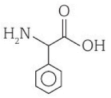
The amount of ester exchange can be controlled by altering the temperature.

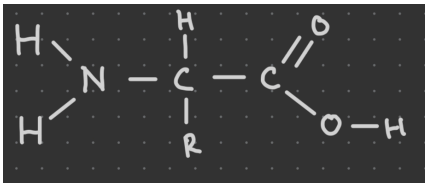


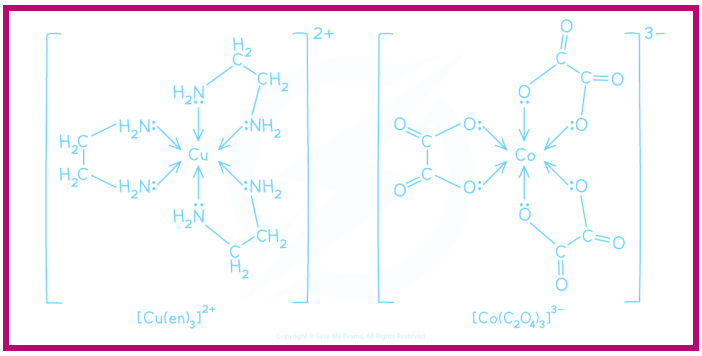
Amino Acids (-NH_2 and -COOH)

- Amino acids contain an amino (-NH2) group and a carboxylic acid (-COOH) group separated by a carbon atom.

STRUCTURAL FORMULA	NAME
H_2NCH_2COOH	2-aminoethanoic acid
$CH_3CH(NH_2)COOH$	2-aminopropanoic acid
$H_2NCH_2CH_2COOH$	3-aminopropanoic acid
$CH_3CH(NH_2)CH_2COOH$	3-aminobutanoic acid
$C_6H_5CH(NH_2)COOH$	2-aminophenylethanoic acid

NAME	DISPLAYED FORMULA	SKELETAL FORMULA
2-aminoethanoic acid		
2-aminopropanoic acid		
3-aminopropanoic acid		
3-aminobutanoic acid		
2-aminophenylethanoic acid		





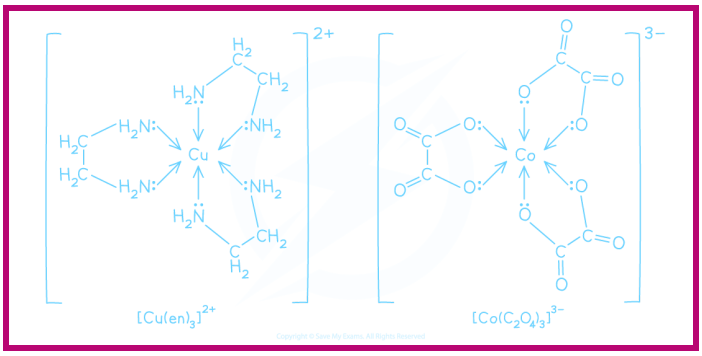
- Peptides
    - When 2 amino acids react together, an acid base reactions occurs.
    - It is a condensation reaction and the two amino acids are joined by an amide group (CO-NH)
    - Polypeptides are formed by condensation polymerisation of many amino acids.
    - Long chain, polypeptides are different to proteins, due to proteins' further levels of structure.
    - Hydrolysing proteins:
        - They can be broken down into their individual amino acids by prolonged heating with conc. HCl
        - The individual amino acids can be spotted on chromatography paper.
        - To identify colourless amino acids the paper must be sprayed with ninhydrin or another developing agent.
        - The Rf value can the be calculated and the amino acid identified.

$$R_f = \frac{\text{distance travelled by spot}}{\text{distance travelled by solvent}}$$ — the value should be less than one

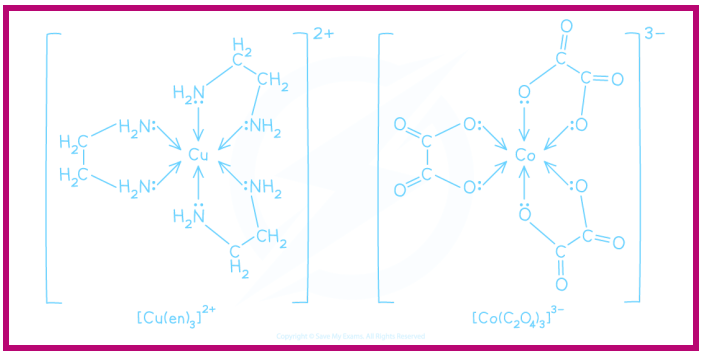
Topic 20: Organic Synthesis

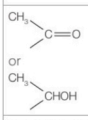
Organic analysis

- Mass spectrometry allows us to determine the accurate relative molecular mass of a compound.
    - The fragmentation patterns also allow us to suggest possible groups that may be present in the compound.
    - Ex. A peak *m/z* value of 15 and indicate a CH_3 group
- Infrared spectroscopy allows us to identify particular functional groups and features in the organic compound.
    - Ex. An absorption between 1740 and 1720 cm^{-1} indicates the presence of C=O group in an aldehyde



- ^{13}C NMR spectroscopy allows us to identify the number of different carbon environments in a compound.
    - Ex. Ethanol, CH_3CH_2OH has two peaks, indicating two different carbon environments.
    - Ex. 1-methyl ethyl propanoate $CH_3CH_2COOCH(CH_3)_2$ this indicates it has five peaks.
        - There are six carbon atoms but only has 5 carbon peaks because the two methyl groups on the right hand side are identical environments.
- Proton NMR spectroscopy allows us to identify groups of hydrogen atoms in a compound.
    - Splitting patterns also allow us to identify the number of hydrogens on an adjacent carbon atom.
    - Ex. If there are three hydrogen atoms in the same environment it indicates a $-CH_3$ group is present



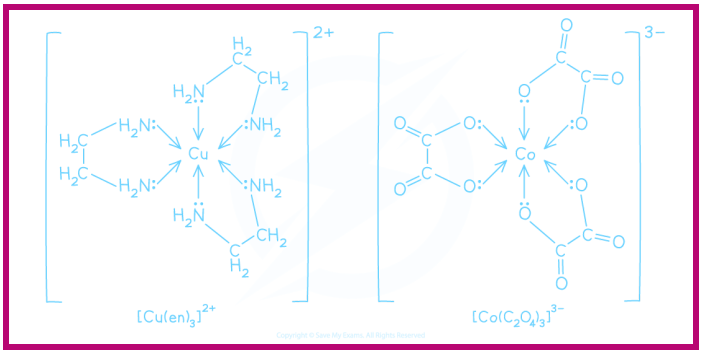
FUNCTIONAL GROUP	TEST	OBSERVATION	NOTES
Alkene (C=C)	add $Br_2(aq)$	bromine decolourises immediately	aldehydes and ketones decolourise $Br_2(aq)$, but very slowly phenols decolourise $Br_2(aq)$ immediately and also produce a white precipitate
Halogenoalkanes (R–X), where X = Cl, Br or I	warm with NaOH(aq) and then add dilute HNO_3, followed by a few drops of $AgNO_3(aq)$	R–Cl produces a white precipitate R–Br produces a cream precipitate R–I produces a yellow precipitate	the precipitate is insoluble in dilute $NH_3(aq)$ the precipitate is insoluble in dilute $NH_3(aq)$, but soluble in concentrated $NH_3(aq)$ the precipitate is insoluble in both dilute $NH_3(aq)$ and concentrated $NH_3(aq)$
Hydroxy group (–OH)	add solid PCl_5	misty fumes	both alcohols and carboxylic acids, but not phenols, produce misty fumes
Primary alcohol (RCH_2OH)	add acidified $K_2Cr_2O_7$ solution and warm	solution turns from orange to green	the organic product of this reaction produces a silver mirror with Tollens' reagent
Secondary alcohol (R_2CHOH)	add acidified $K_2Cr_2O_7$ solution and warm	solution turns from orange to green	the organic product does not produce a silver mirror with Tollens' reagent Ketone
Carbonyl group 	add 2,4-dinitrophenylhydrazine	orange precipitate	both aldehydes and ketones produce an orange precipitate
Aldehydes 	add Tollens' reagent and warm	silver mirror forms	Fehling's or Benedict's solutions can also be used ketones do not react with Tollens' reagent, Fehling's solution or Benedict's solution
	add an alkaline solution of iodine and warm Iodoform test	yellow precipitate forms	this is known as the triiodomethane (or iodoform) test
Carboxylic acids (R–COOH)	add $NaHCO_3(aq)$ or $Na_2CO_3(aq)$ and warm if necessary	bubbles of gas	
Phenol 	add bromine water	bromine immediately decolourises and a white precipitate forms	phenylamine produces the same observation however, phenol is soluble in NaOH(aq) but insoluble in dilute HCl; phenylamine is insoluble in NaOH(aq) but soluble in dilute HCl

Organic synthesis

- Multi (four step) synthesis reactions.
- A —-> B —-> C —-> D —> E

Extending a carbon chain:

- Reacting a halogenoalkane with a cyanide ion forms a nitrile with one more carbon atom than the halogenoalkane.
- The addition of hydrogen cyanide to a carbonyl compound.
- The alkylation of benzene, which introduces an alkyl group into a benzene ring



Grignard reagent

- They are an organometallic compound containing magnesium.
- They are made by heating a halogen with magnesium and dry ether.
- R—Br + Mg —> R—Mg—Br
- Reactions of grignard reagent:
    - With carbon dioxide: RMgBr —> RCOOH (Carboxylic acid)
    - With methanal: RMgBr —> RCH2OH (Primary alcohol)
    - With an aldehyde (R'CHO): RMgBr —> RR'CHOH (Secondary alcohol)
    - With a ketone (R'COR") —> RMgBr —> RR'R"COH (Tertiary alcohol)

examples of Grignard reagent:

Formation of Propan-1-ol: from methanal (CH_2OH) and bromoethane (CH_3CH_2)

$$CH_3CH_2Br \xrightarrow{Mg/ether} CH_3CH_2MgBr \xrightarrow[\text{then } H_2O/H^+]{HCHO} CH_3CH_2CH_2OH$$

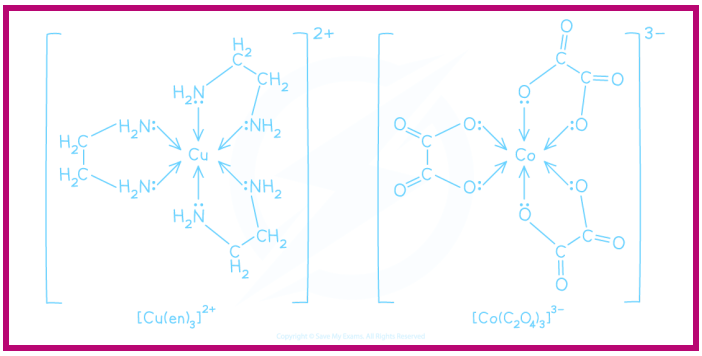
Formation of Pentan-2-ol: from ethanal ($CH_3CH(OH)$) and 1-bromopropane ($CH_3CH_2CH_2$)

$$CH_3CH_2CH_2Br \xrightarrow{Mg/ether} CH_3CH_2CH_2MgBr \xrightarrow[\text{then } H_2O/H^+]{CH_3CHO} CH_3CH(OH)CH_2CH_2CH_3$$

Formation of 2-Methylpropan-2-ol: from peopanone ($(CH_3)_2COH$) and bromoethane (CH_3)

$$CH_3Br \xrightarrow{Mg/ether} CH_3MgBr \xrightarrow[\text{then } H_2O/H^+]{CH_3COCH_3} (CH_3)_3COH$$

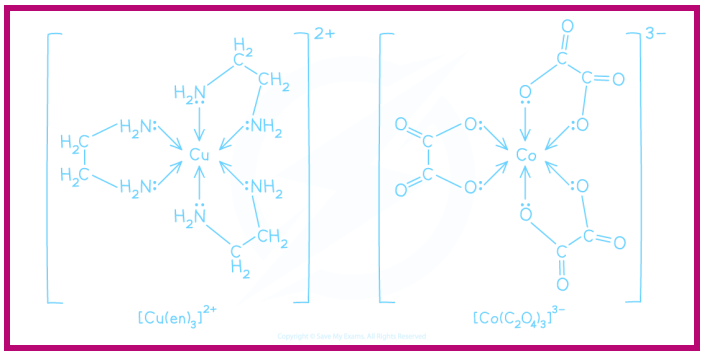
Converting one functional group to another:



CONVERSION	EQUATION	REAGENT	CONDITIONS
Alkene to halogenoalkane	$CH_2{=}CH_2 + HX \rightarrow CH_3CH_2X$	hydrogen halide	mix the gases at room temperature
Halogenoalkane to alcohol	$RX + NaOH \rightarrow ROH + NaX$	aqueous sodium hydroxide	heat under reflux
Halogenoalkane to nitrile	$RX + KCN \rightarrow RCN + KX$	alcoholic potassium cyanide	heat under reflux
Halogenoalkane to amine	$RX + 2NH_3 \rightarrow RNH_2 + NH_4X$	aqueous ammonia	heat under pressure
Alcohol to chloroalkane	$ROH + PCl_5 \rightarrow RCl + HCl + POCl_3$	phosphorus(V) chloride	room temperature
Alcohol to bromoalkane	$ROH + HBr \rightarrow RBr + H_2O$	50% concentrated sulfuric acid and potassium bromide	warm
Alcohol to iodoalkane	$3ROH + PI_3 \rightarrow 3RI + H_3PO_3$	red phosphorus and iodine	heat under reflux
Primary alcohol to aldehyde	$RCH_2OH + [O] \rightarrow RCHO + H_2O$	potassium dichromate(VI) and dilute sulfuric acid	add the reagent to hot alcohol and allow the aldehyde to distil off as it is formed
Primary alcohol to carboxylic acid	$RCH_2OH + 2[O] \rightarrow RCOOH + H_2O$	potassium dichromate(VI) and dilute sulfuric acid	heat under reflux
Secondary alcohol to ketone	$RCH(OH)R' + [O] \rightarrow RCOR' + H_2O$	potassium dichromate(VI) and dilute sulfuric acid	heat under reflux
Aldehyde to primary alcohol	$RCHO + 2[H] \rightarrow RCH_2OH$	lithium aluminium hydride in dry ether	room temperature
Ketone to secondary alcohol	$RCOR' + 2[H] \rightarrow RCH(OH)R'$	lithium aluminium hydride in dry ether	room temperature
Aldehyde and ketone to 2-hydroxynitrile	$RCHO + HCN \rightarrow RCH(OH)CN$ $RCOR' + HCN \rightarrow RR'C(OH)CN$	potassium cyanide in dilute sulfuric acid	10–20 °C
Carboxylic acid to primary alcohol	$RCOOH + 4[H] \rightarrow RCH_2OH + H_2O$	lithium aluminium hydride in dry ether	room temperature
Carboxylic acid to ester	$RCOOH + R'OH \rightarrow RCOOR' + H_2O$	alcohol and concentrated sulfuric acid	heat
Acyl chloride to carboxylic acid	$RCOCl + H_2O \rightarrow RCOOH + HCl$	water	room temperature
Acyl chloride to ester	$RCOCl + R'OH \rightarrow RCOOR' + HCl$	alcohol	room temperature
Acyl chloride to primary amide	$RCOCl + 2NH_3 \rightarrow RCONH_2 + NH_4Cl$	aqueous ammonia	room temperature
Acyl chloride to secondary amide (*N*-substituted amide)	$RCOCl + R'NH_2 \rightarrow RCONHR' + HCl$	amine	room temperature

CONVERSION	EQUATION	REAGENT	CONDITIONS
Nitrile to primary amine	$RCN + 4[H] \rightarrow RCH_2NH_2$	lithium aluminium hydride in dry ether	room temperature
Nitration of benzene	$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$	concentrated nitric acid and concentrated sulfuric acid	heat under reflux between 50 and 60 °C
Sulfonation of benzene	$C_6H_6 + H_2SO_4 \rightarrow C_6H_5SO_3H + H_2O$	fuming sulfuric acid	40 °C
Bromination of benzene	$C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$	liquid bromine with iron (to form iron(III) bromide)	dry and room temperature
Friedel–Crafts alkylation of benzene	$C_6H_6 + RX \rightarrow C_6H_5R + HX$	halogenoalkane	dry, in the presence of anhydrous aluminium halide
Friedel–Crafts acylation of benzene	$C_6H_6 + RCOCl \rightarrow C_6H_5COR + HCl$	acyl chloride	dry, in the presence of anhydrous aluminium chloride

Hazard, Risks and Control Measures

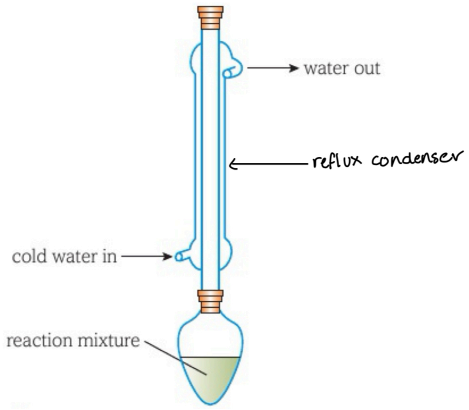


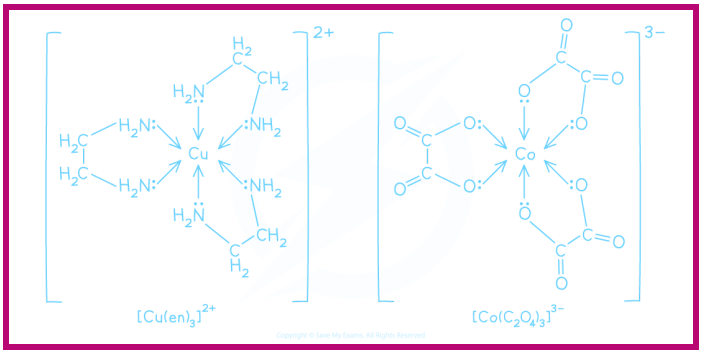
SYMBOL	MEANING	
	Health hazard	includes warnings on skin rashes, eye damage and ingestion
	Corrosive	can cause skin burns and permanent eye damage
	Flammable	can catch fire if heated or comes into contact with a flame
	Acute toxicity	can cause life-threatening effects, even in small quantities

Practical Techniques in organic chemistry:

Heating under reflux:

- This is used to heat volatile compounds, so they don't escape from the reaction mixture.
- Can be heated by a Bunsen burner.
- Anti Bumping granules are used for smoother boiling. Prevent vigorous uneven boiling.

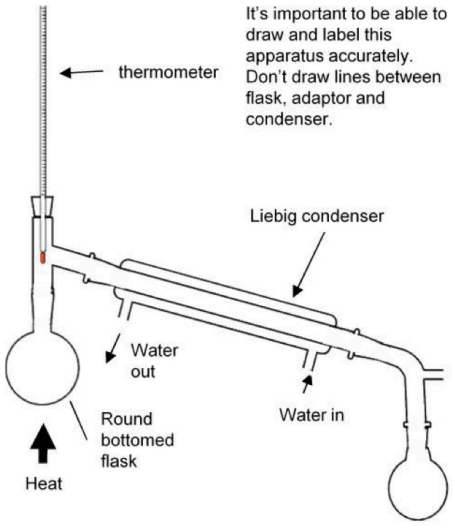




- Methods of separations:
-

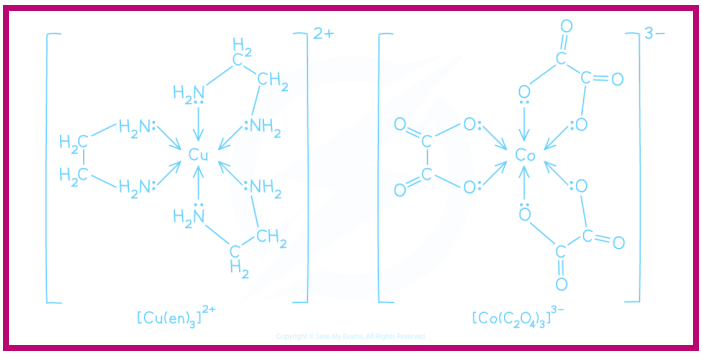
Simple distillation:

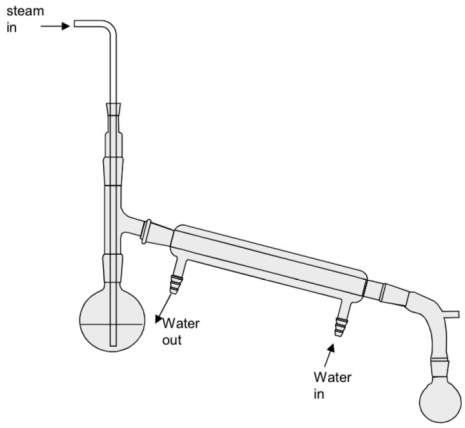
- this separation technique is used to obtain a liquid from a reaction mixture that has a boiling point much lower than the other substances in the reaction mixture.
    - The liquid with the lowest boiling temp evaporates or boils off first and passes into the condenser. To be collected in the receiver separately from the other liquids.



Steam Distillations:

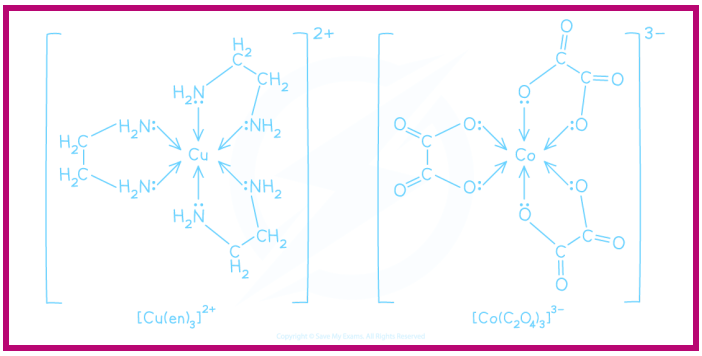
- This is used to separate an insoluble liquid from an aqueous solution.
    - The insoluble liquid is removed from its reaction mixture at temperatures below its normal boiling temperature - lowering the chance of decomposition.
    - Steam is passed into the mixture and the product is distilled off with water.

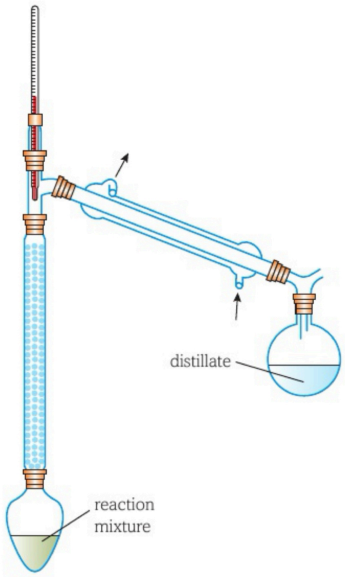




Fractional distillation:

- Uses the same apparatus as simple distillation, but with a fractionating column between the heating flask and the still head.
    - The column is usually filled with glass beads or broken pieces of glass. These act as surfaces on which the vapour leaving the column can condense.
    - This means the vapour experiences several repeated distillations as it passes up the column, providing a better separation.
    - It is used when the difference in boiling temperatures is small and when there are several compounds to be separated from a mixture.

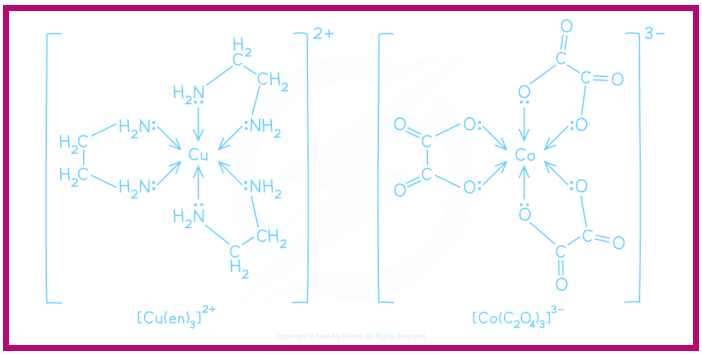


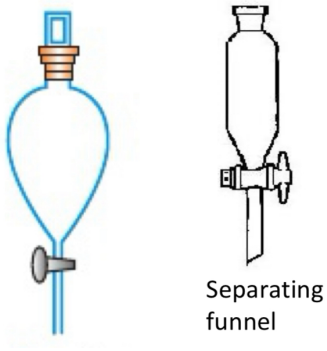


Solvent extraction:

- Using a solvent to remove the desired organic product from the other substances in the reaction mixture.
    - The solvent added should be immiscible (not forming a mixture) with the solvent containing the desired organic compound.

- Method of solvent extraction:
    - Place the reaction mixture in the separation funnel, then add the chosen solvent - it should form a separate layer.
    - Place the stopper in the neck of the funnel and gently mix, put a finger on the stopper, invert, open the tap. Mix in a circular motion, close the tap and return the funnel to its normal position.
    - Allow the contents to settle in two layers.
    - Remove the stopper and open the tap to allow the lower layer to drain into a flask, then do the same to allow the upper layer to drain into a separate flask.



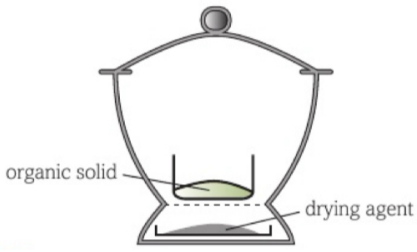


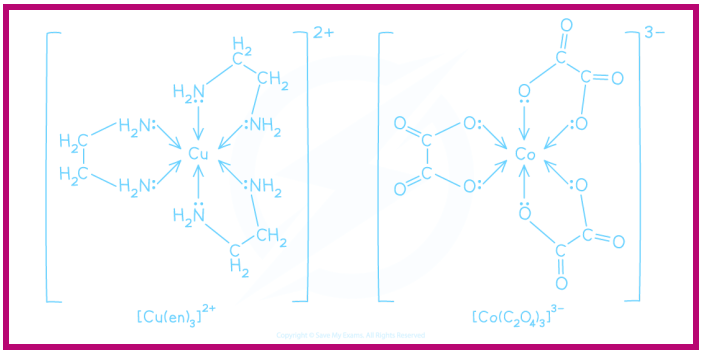
Washing:

- It is also used to remove impurities from a liquid and solid.
    - Washing could involve the use of water, an organic solvent or sodium carbonate solution to remove any excess acid that may be present.

Drying:

- leaving an organic compound in a warm place or in a desiccator with a suitable drying agent.
    - Water may be an impurity that needs to be removed by a dying agent.
    - The drying agent mustn't react with the organic liquid
    - Several drying agents are available, usually anhydrous salts.
    - Ex. Calcium chloride, magnesium sulfate and sodium sulfate.
    - These salts absorb the water as crystallisation
    - the drying agent is removed by recantation (pouring the organic liquid off the solid drying agent or by filtration.



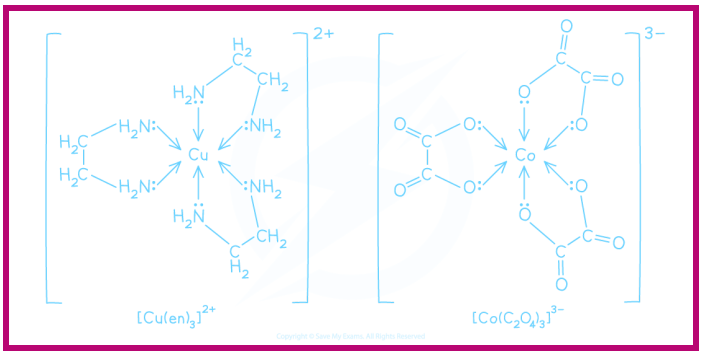


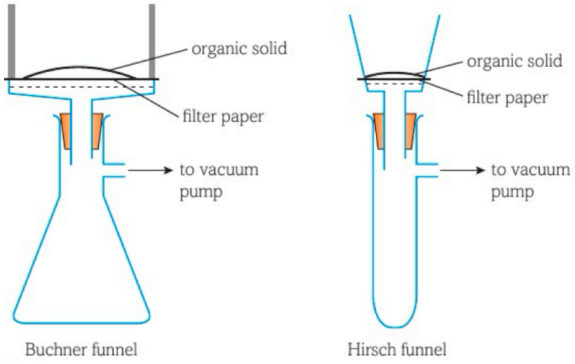
Filtration >:(

- organic solid needs to be filtered at some stage. Happens as a part of recrystallisation.
- usually a **buchner** and **hirsch** funnel used.
- use of **vacuum pump** means that the methods described as filtration are happening under reduced pressure

Recrystallisation

- used for purification. A solid compound is dissolved in a suitable solvent that can dissolve most or all impurities and very little of the compound that is being purified.
- Steps:
    - Add the impure solid to a conical flask
    - add some of the chosen solvent and warm until the mixture nears the boiling temperature of the mixture.
    - if there is still some undissolved solid, add further solvent and warm until the mixture boils again.
    - continue adding further solvent and heating until all of the soluble solid has dissolved
    - if insoluble impurities are present, then hot filtration could be done using fluted filter paper in a heated funnel
    - allow liquid to cool until crystals of the organic solid have formed
    - more crystals can be obtained by cooling the solution below room temperature in an ice bath
    - the mixture is then filtered to remove soluble impurities using a buchner funnel or a hirsch funnel
    - the crystals are washed with a small amount of ice-cold solvent and then dried in a desiccator or warm oven.





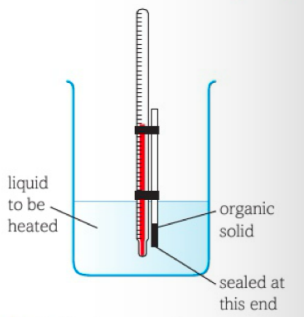
Testing for purity

Determination of melting temperature

For solids, impurities reduce the melting temp. If you measure the melting temp of your organic compound and then compare it with known values of the pure compound.

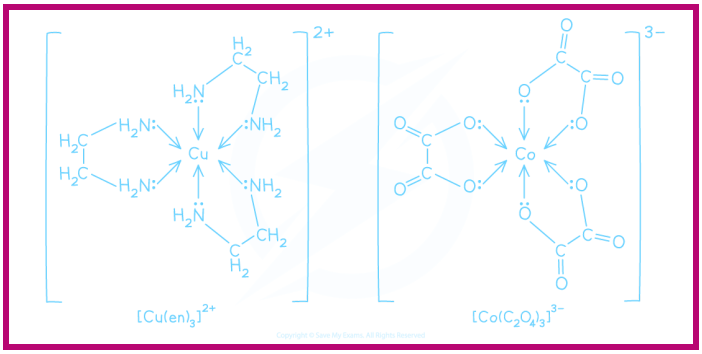
Traditional method of measuring melting temp:

- place some of the solid in a small capillary tube attached to the bulb of a thermometer and then place the assembly in a liquid that has a boiling temperature above that of the melting temp of the solid.



Determination of boiling temperature

For liquids, impurities **increase** the boiling temperature.



If you measure the boiling temperature of your organic compound, you can compare it to the values of the pure compound and then estimate how pure the compound is.

Apparatus used depends on the volume of liquid available, and whether it is toxic or flammable.

- simple distillation apparatus usually used in most cases

Why doesn't work all the time

- May not be enough proof because you cannot measure the exact boiling temperature of organic compound accurately
- The thermometer might read too low or too high. Might wrongly assume that the compound is pure.
- same organic compounds may have the same boiling temperature.
    - Ex. 1-chloro pentane and 2-methylpropan-1-ol boil at the same temperature of 108°C.