Your notes

Cambridge (CIE) A Level Chemistry

General Characteristic Chemical Properties of the First Set of Transition Elements, Titanium to Copper

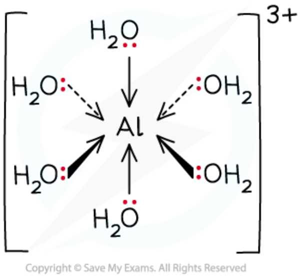
Contents

Your notes

Complex formation

What is a complex?

- A **complex** is a molecule or ion formed by a **central metal atom or ion** surrounded by one or more **ligands**
- A ligand is a species with a lone pair of electrons that can be donated to the metal ion
  - Ligands form **dative covalent bonds** with the metal by donating their lone pair of electrons
- For example, $[Al(H_2O)_6]^{3+}$ (aq):



Al(III) is the central metal ion with 6 water ligands, each donating a lone pair

Transition metal complex formation

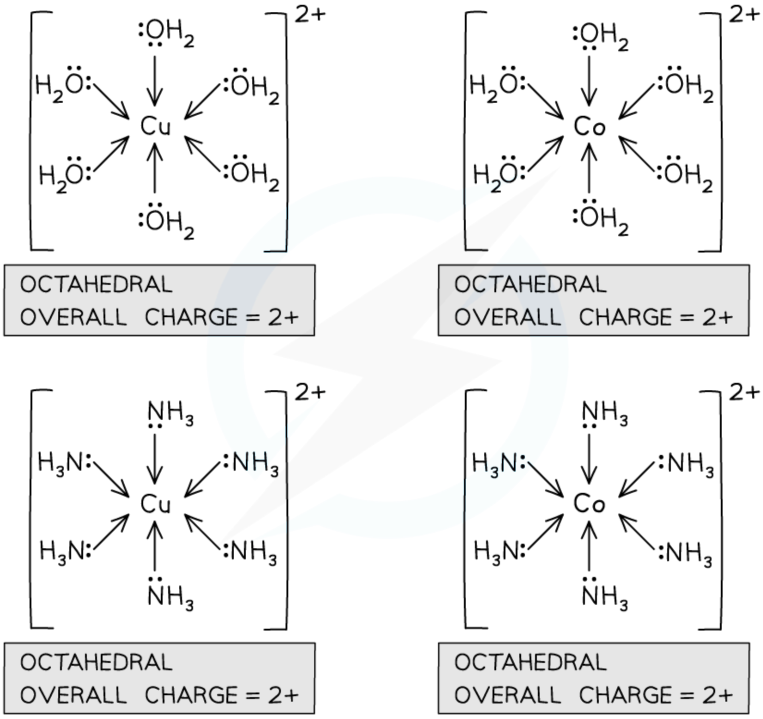
- Transition metal ions readily form **complexes** with **ligands**
- Copper(II) and cobalt(II) ions will be used as examples of the central metal ions, in the complexes with:
  - Water (H_2O)
  - Ammonia (NH_3)
  - Hydroxide (OH^-)
  - Chloride (Cl^-)

Co(II) and Cu(II) complexes with water & ammonia

- Water and ammonia are **neutral** ligands
  - Water donates a lone pair from the oxygen atom
  - Ammonia donates a lone pair from the nitrogen atom
- Water and ammonia are small ligands
  - Up to 6 water or ammonia ligands can fit around a central metal ion

- This results in 6 dative covalent bonds
- 6 dative covalent bonds give:
  - An octahedral shape
  - A coordination number of 6
    - The **coordination number** of a complex is the number of dative covalent bonds formed between the central metal ion and the ligands

Cobalt(II) and copper(II) complexes with water and ammonia



Cobalt(II) and copper(II) form octahedral complexes with ammonia and water ligands

- The overall charge of a complex is the sum of the charge on the central metal ion, and the charges on each of the ligands
- For a cobalt(II) or copper(II) complex with 6 water or ammonia ligands:
  - The central metal ion has a charge of **2+**
  - The ligands have a charge of **0**
  - So, the **overall charge** of the complex is (2+) + (6 x 0) = **2+**

Complexes with hydroxide & chloride ions

- Hydroxide ions, OH^-, and chloride ions, Cl^-, are **negatively** charged ligands
  - Each donates a lone pair of electrons to form a dative covalent bond with the central metal ion

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Hydroxide complexes

- Hydroxide ions are small ligands
  - Up to 6 hydroxide ions can fit around a central metal ion
  - This results in:
    - 6 dative covalent bonds
    - An octahedral shape
    - A coordination number of 6

Examiner Tips and Tricks

Although up to 6 hydroxide ions can fit around a central metal ion, in many examples only 2 hydroxide ions are present alongside 4 water ligands

Chloride complexes

- Chloride ions are large ligands
  - Up to 4 chloride ligands can fit around a central metal ion
  - This results in 4 dative covalent bonds
- 4 dative covalent bonds give:
  - A tetrahedral shape
  - A coordination number of 4

Charges of Co(II) complexes with hydroxide and chloride ligands

- Co(II) ions commonly form complexes with 2 hydroxide ion ligands
  - The remaining ligands are water
- For this cobalt(II) complex:
  - The central metal ion has a charge of **2+**
  - The water ligands have a charge of **0**
  - The 2 hydroxide ligands have a charge of 2 x (-1) = **-2**
  - So, the **overall charge** of the complex is (2+) + (4 x 0) + (-2) = **0**

$$[Co(H_2O)_4(OH)_2]$$

- Co(II) ions commonly form complexes with 4 chloride ion ligands
- For this cobalt(II) complex:

- The central metal ion has a charge of **2+**
- The 4 chloride ligands have a charge of 4 x (-1) = **-4**
- So, the **overall charge** of the complex is (2+) + (-4) = **-2**

$[CoCl_4]^{2-}$

Charges of Cu(II) complexes with hydroxide and chloride ligands

- Cu(II) ions commonly form complexes with 2 hydroxide ion ligands
  - The remaining ligands are water
- For this copper(II) complex:
  - The central metal ion has a charge of **2+**
  - The water ligands have a charge of **0**
  - The 2 hydroxide ligands have a charge of 2 x (-1) = **-2**
  - So, the **overall charge** of the complex is (2+) + (4 x 0) + (-2) = **0**

$[Cu(H_2O)_4(OH)_2]$

- Cu(II) ions commonly form complexes with 4 chloride ion ligands
- For this copper(II) complex:
  - The central metal ion has a charge of **2+**
  - The 4 chloride ligands have a charge of 4 x (-1) = **-4**
  - So, the **overall charge** of the complex is (2+) + (-4) = **-2**

$[CuCl_4]^{2-}$

Comparing copper(II) and cobalt(II) complexes with chloride and water / hydroxide ions

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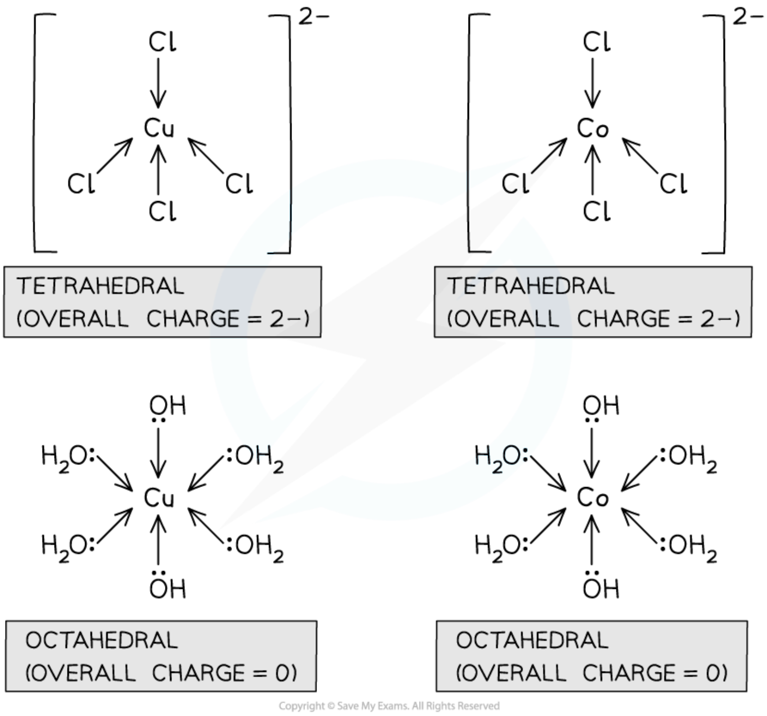

Cobalt(II) and copper(II) form tetrahedral complexes with chloride and octahedral complexes with water and hydroxide ligands

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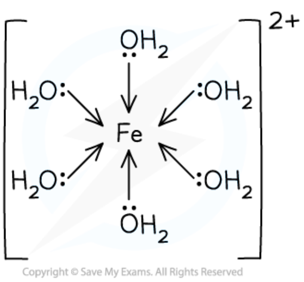
Define Ligand

- A **ligand** is a molecule or ion that has **one** or **more** lone pairs of electrons
- These lone pairs of electrons are donated by the ligand, to form **dative covalent bonds** to a central metal atom or ion

Examples of ligands table

Ligand name	Ligand formula
Water	H_2O
Ammonia	NH_3
Chloride	Cl^-
Cyanide	CN^-
Thiocyanate	SCN^-
Ethanedioate (ox)	$^-COO\text{–}COO^-$ $C_2O_4^{2-}$
1,2-diaminoethane	$H_2NCH_2CH_2NH_2$

Example of a complex formed between a central Fe^{2+} ion and water ligands



The complex of a central Fe^{2+} ion and water ligands is formed with dative covalent bonds

Types of Ligands

- Different **ligands** can form different numbers of dative bonds to the central metal ion in a complex.

- Some ligands can form **one** dative bond to the central metal ion
- Other ligands can form **two** dative bonds, and some can form **multiple** dative bonds

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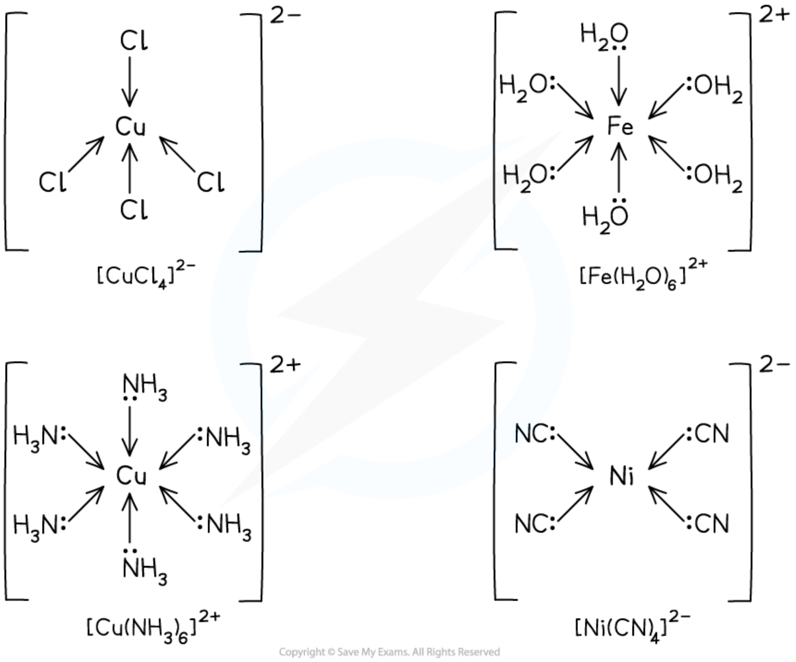
Monodentate ligands

- **Monodentate** ligands can form only **one** dative bond to the central metal ion
- Examples of monodentate ligands are:
  - Water (H_2O) molecules
  - Ammonia (NH_3) molecules
  - Chloride (Cl^-) ions
  - Cyanide (CN^-) ions

Examples of complexes with monodentate ligands



Smaller monodentate ligands tend to form octahedral complexes, while larger monodentate ligands tend to form tetrahedral complexes

Bidentate ligands

- **Bidentate** ligands can each form **two** dative bonds to the central metal ion
- This is because each ligand contains **two** atoms with lone pairs of electrons
- Examples of bidentate ligands are:
  - 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'**

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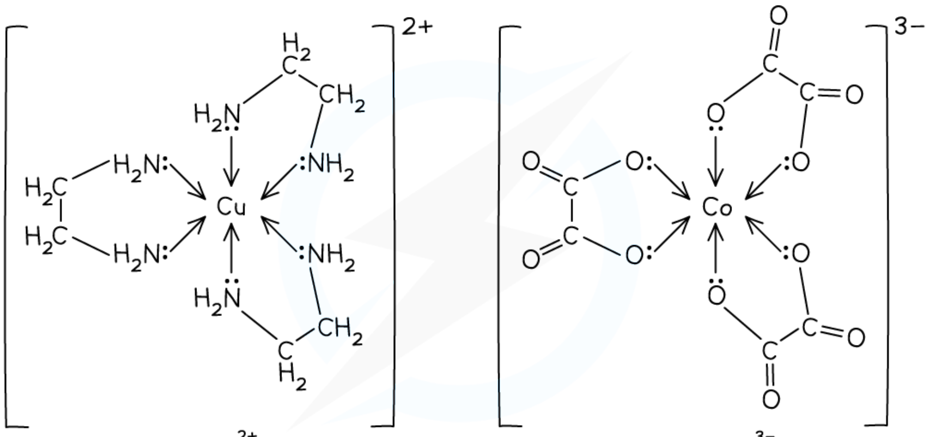
Examples of complexes with bidentate ligands



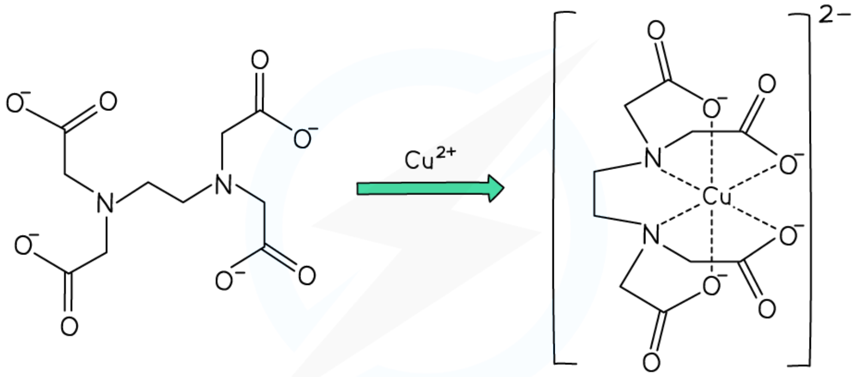
$[Cu(en)_3]^{2+}$ $[Co(C_2O_4)_3]^{3-}$

The en and ox bidentate ligands form coordinate bonds through the lone pairs on the nitrogen and oxygen atoms respectively

Polydentate ligands

- Some ligands contain more than two atoms with lone pairs of electrons
- These ligands can form more than two dative bonds to the central metal ion and are said to be **polydentate** ligands
- An example of a polydentate ligand is $EDTA^{4-}$, which is a **hexadentate** ligand as it forms 6 dative covalent bonds to the central metal ion

Example of a polydentate ligand complex



EDTA LIGAND

COPPER (II) – EDTA COMPLEX

The $EDTA^{4-}$ ligand forms 6 coordinate bonds to the central metal ion

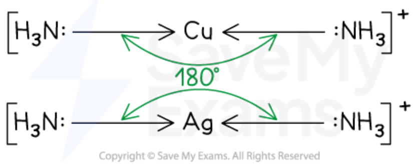
Geometry of the Transition Element Complexes

- Depending on the **size of the ligands** and the **number of dative bonds** to the central metal ion, transition element complexes have different geometries
  - Dative bonds can also be referred to as **coordinate bonds**, especially when discussing the geometry of a complex

Linear

- Central metal atoms or ions with **two coordinate bonds** form **linear** complexes
- The bond angles in these complexes are 180°
- The most common examples are a copper (I) ion, (Cu^+), or a silver (I) ion, (Ag^+), as the central metal ion with two coordinate bonds formed to two ammonia ligands

Examples of a linear complex

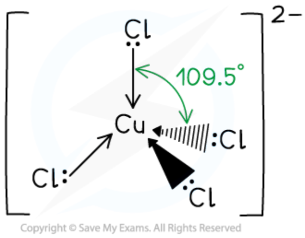


A linear complex has a bond angle of 180°

Tetrahedral

- When there are **four coordinate bonds** the complexes often have a **tetrahedral** shape
  - Complexes with four **chloride ions** most commonly adopt this geometry
  - Chloride ligands are large, so only four will fit around the central metal ion
- The bond angles in tetrahedral complexes are 109.5°

Example of a tetrahedral complex

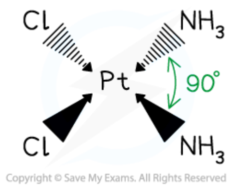


Tetrahedral complexes have a bond angle of 109.5°

Square planar

- Sometimes, complexes with **four coordinate bonds** may adopt a **square planar** geometry instead of a tetrahedral one
  - Cyanide ions (CN^-) are the most common ligands to adopt this geometry
  - An example of a square planar complex is **cisplatin**
- The bond angles in a square planar complex are 90°

Example of a square planar complex



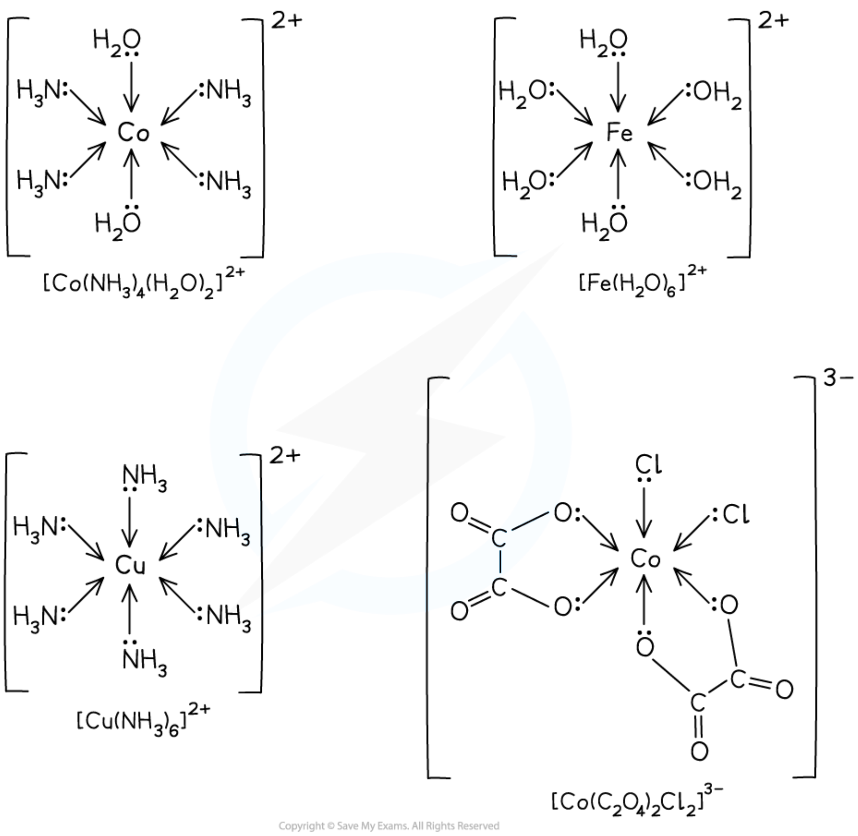
Cisplatin is an example of a square planar complex with a bond angle of 90°

Octahedral

- **Octahedral** complexes are formed when a central metal atom or ion forms **six coordinate bonds**
- This could be six coordinate bonds with **six** small, **monodentate** ligands
  - Examples of such ligands are **water** and **ammonia** molecules and **hydroxide** and **thiocyanate** ions
- It could be six coordinate bonds with **three bidentate** ligands
  - Each bidentate ligand will form two coordinate bonds, meaning six coordinate bonds in total
  - Examples of these ligands are **1,2-diaminoethane** and the **ethanedioate ion**
- It could be six coordinate bonds with **one polydentate** ligand
  - The polydentate ligand, for example $EDTA^{4-}$, forms all six coordinate bonds
- The bond angles in an octahedral complex are 90°

Examples of octahedral complexes

Your notes



Octahedral complexes have bond angles of 90°

Types of ligands table

Geometry	Number of coordinate bonds	Bond angle (°)	Ligand(s) involved
Linear	2	180	Ammonia, NH_3
Tetrahedral	4	109.5	Chloride ion, Cl^-
Square planar	4	90	Cyanide ion, CN^-
Octahedral	6	90	Water, H_2O Ammonia, NH_3 Hydroxide ion, OH^- Thiocyanate ion, SCN^- Ethanedioate ion, $C_2O_4^{2-}$ 1,2–diaminoethane, $NH_2CH_2CH_2NH_2$ $EDTA^{4-}$

Coordination Number & Predicting Complex Ion Formula & Charge

Your notes

- The **coordination number** of a complex is the number of coordinate bonds that are formed between the **ligand(s)** and the central metal atom or ion
- Some ligands can form only one coordinate bond with the central metal ion (**monodentate ligands**), whereas others can form two (**bidentate ligands**) or more (**polydentate ligands**)
- It is **not** the number of ligands which determines the coordination number, it is the number of coordinate (dative) bonds

Predicting complex ion formula & charge

- The formula and charge of a complex ion can be predicted if the following are known:
  - The central metal ion and its charge/oxidation state
  - The ligands
  - The coordination number/geometry

Your notes

Ligand Exchange

- **Ligand exchange** (or **ligand substitution**) is when one **ligand** in a complex is replaced by another
- Ligand exchange forms a new complex that is **more stable** than the original one
- The ligands in the original complex can be **partially** or **entirely** substituted by others
- There are no changes in coordination number, or the geometry of the complex if the ligands are of a **similar size**
- But, if the ligands are of a **different size**, for example, water ligands and chloride ligands, then a change in coordination number and the geometry of the complex will occur

Substitution in copper(II) complexes

- When a transition element ion is in solution, it can be assumed that it exists as a **hexaaqua** complex ion (i.e. it has six water ligands attached to it)
  - For example, $Cu^{2+}(aq)$ is $[Cu(H_2O)_6]^{2+}(aq)$
- The $[Cu(H_2O)_6]^{2+}$ (aq) complex ion is **blue** in colour
- Upon **dropwise** addition of sodium hydroxide (NaOH) solution, a **light blue precipitate** is formed
- **Partial** ligand substitution of two water ligands by two hydroxide ligands has occurred

$[Cu(H_2O)_6]^{2+}$ (aq)	+ $2OH^-$ (aq) →	$[Cu(H_2O)_4(OH)_2]$ (s)	+ $2H_2O$ (l)
Blue solution		Pale blue precipitate	

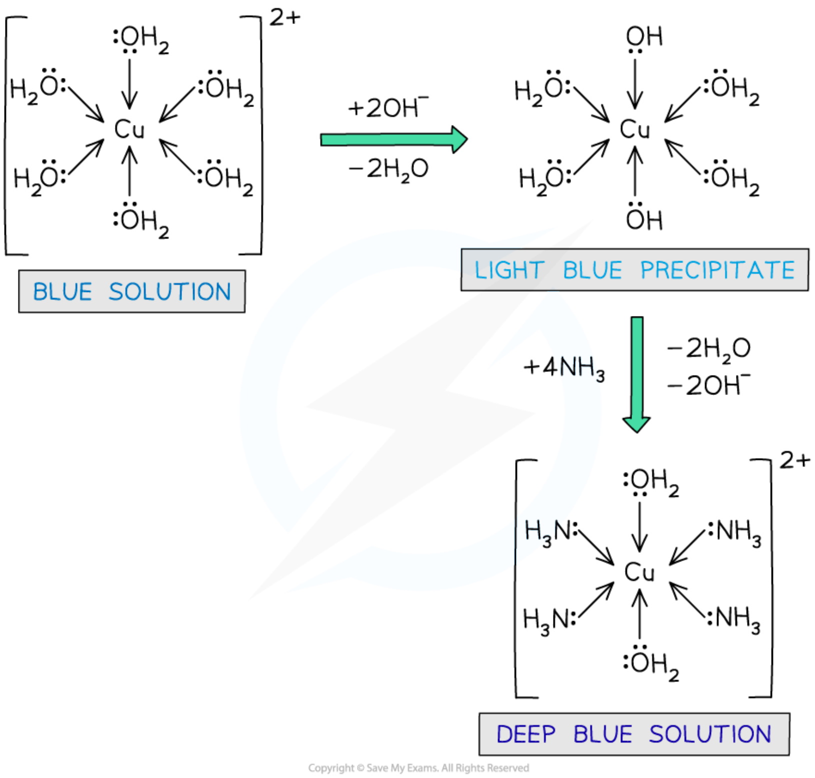
- Upon addition of **excess concentrated** ammonia (NH_3) solution, the pale blue precipitate dissolves to form a **deep blue solution**
- Again, **partial** ligand substitution has occurred

$[Cu(H_2O)_4(OH)_2]$ (s)	+ $4NH_3$ (aq) →	$[Cu(NH_3)_4(H_2O)_2]^{2+}$ (aq)	+ $2H_2O$ (l) + $2OH^-$ (aq)
Pale blue precipitate		Deep blue solution	

- If you were to add **concentrated ammonia** (NH_3) solution **dropwise** to the $[Cu(H_2O)_6]^{2+}$ (aq), rather than sodium hydroxide (NaOH) solution, the same **light blue precipitate** would form

- Again, the pale blue precipitate will **dissolve** to form a deep blue solution, if **excess** ammonia solution is then added

Examples of ligand exchange with copper(II) complexes



Water ligands are exchanged by hydroxide and ammonia ligands in the copper(II) complex

- The water ligands in $[Cu(H_2O)_6]^{2+}$ can also be substituted by **chloride** ligands, upon addition of **concentrated** hydrochloric acid (HCl)
- The **complete** substitution of the water ligands causes the **blue** solution to turn **yellow**

$[Cu(H_2O)_6]^{2+}$ (aq)	**+ $4Cl^-$ (aq) →**	**$[CuCl_4]^{2-}$ (aq)**	**+ $6H_2O$ (l)**
Blue solution		**Yellow solution**	

- The **coordination number** has changed from **6 to 4**, because the chloride ligands are larger than the water ligands, so only 4 will fit around the central metal ion
- The geometry of the complex has also changed from **octahedral to tetrahedral**
- This is a reversible reaction, and some of the $[Cu(H_2O)_6]^{2+}$ complex ion will still be present in the solution
    - The mixture of blue and yellow solutions in the reaction mixture will give it a **green** colour

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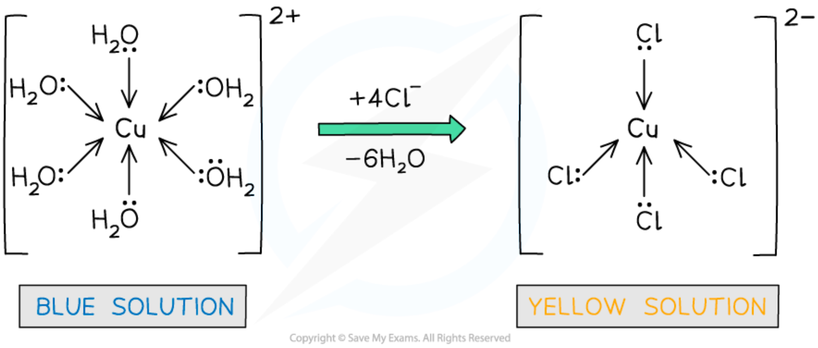
- Adding **water** to the solution will cause the **chloride** ligands to be **displaced by the water** molecules, and the $[Cu(H_2O)_6]^{2+}$ (aq) ion and the **blue solution** will return

Example of ligand exchange with copper(II) complexes and chloride ions



Water ligands are exchanged by chloride ligands in the copper(II) complex

Substitution in cobalt(II) complexes

- The $[Co(H_2O)_6]^{2+}$(aq) complex ion is **pink** in colour
- Upon **dropwise** addition of sodium hydroxide (NaOH) solution, a **blue** precipitate is formed
- **Partial** ligand substitution of two water ligands by two hydroxide (OH^-) ligands has occurred
  - If the alkali is added in **excess**, the blue precipitate will turn **red** when warmed

$[Co(H_2O)_6]^{2+}$ (aq)	**+ $2OH^-$ (aq) →**	**$[Co(H_2O)_4(OH)_2]$ (s)**	**+ $2H_2O$ (l)**
Pink solution		**Blue precipitate**	

- If **excess concentrated** ammonia solution is added to $[Co(H_2O)_6]^{2+}$, a **brown** solution will also be formed
  - There will be no precipitate formed in this instance, as the ammonia has been added in excess and not dropwise
- **Complete** ligand substitution of the water ligands by ammonia ligands has occurred

$[Co(H_2O)_6]^{2+}$ (aq)	**+ $6NH_3$ (aq) →**	**$[Co(NH_3)_6]^{2+}$ (aq)**	**+ $6H_2O$ (l)**
Pink solution		**Brown solution**	

- The ammonia ligands make the cobalt(II) ion so **unstable** that it readily gets **oxidised** in air to cobalt(III), $[Co(NH_3)_6]^{3+}$

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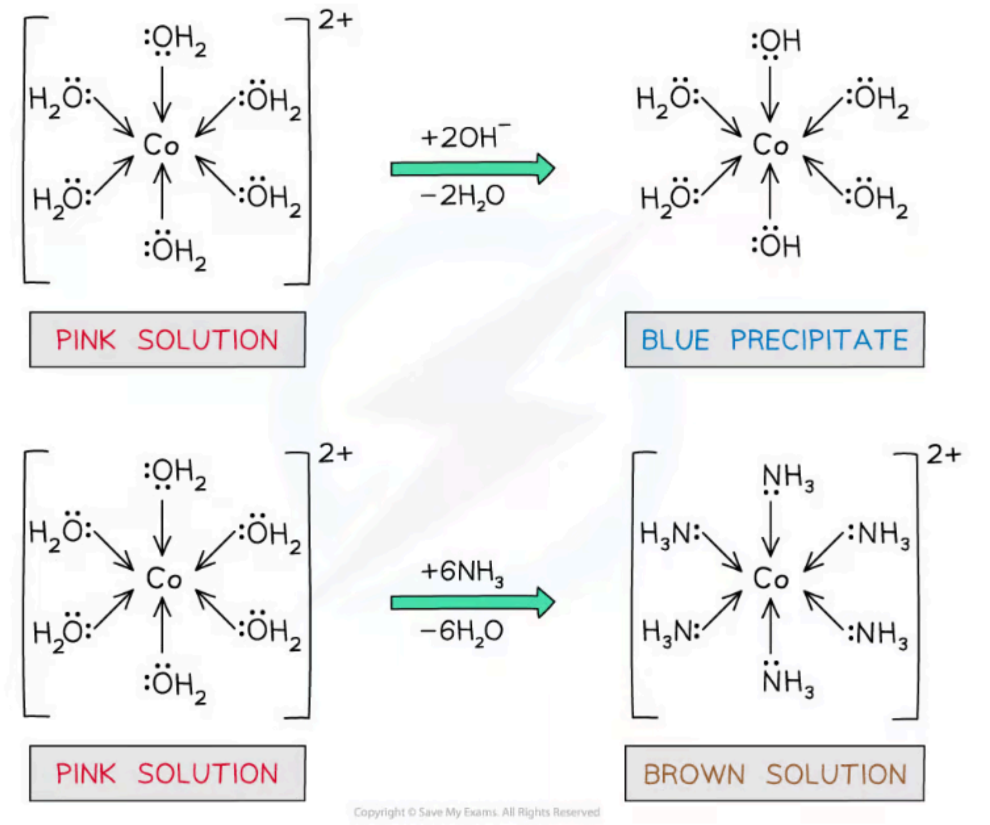
Examples of ligand exchange with cobalt(II) complexes



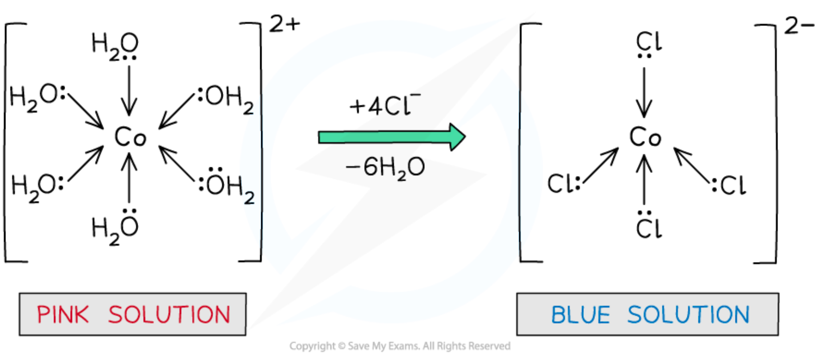
Water ligands are exchanged by hydroxide and ammonia ligands in the cobalt(II) complex

- The water ligands in $[Co[H_2O)_6]^{2+}$ can also be substituted by **chloride** ligands, upon addition of **concentrated** hydrochloric acid
- The **complete** substitution of the water ligands causes the **pink** solution to turn **blue**

$[Co(H_2O)_6]^{2+}$ (aq)	+ $4Cl^-$ (aq) →	$[CoCl_4]^{2-}$ (aq)	+ $6H_2O$ (l)
Pink solution		Blue solution	

- Like with $[Cu(H_2O)_6]^{2+}$ above, the **coordination number** has changed from **6 to 4**, because the chloride ligands are larger than the water ligands, so only 4 will fit around the central metal ion
- The geometry of the complex has also changed from **octahedral** to **tetrahedral**
- Adding **water** to the solution will cause the **chloride** ligands to be **displaced by the water** molecules, and the $[Co(H_2O)_6]^{2+}$ (aq) ion and the **pink solution** will return

Example of ligand exchange with cobalt(II) complexes and chloride ions



Water ligands are exchanged by chloride ligands in the cobalt(II) complex

Feasibility of Redox Reactions Using Standard Electrode Values

- Transition elements can form ions with various oxidation states
- The change in their oxidation states involves the **transfer** of electrons
- Transition elements are often involved in **redox reactions**
- A redox reaction is a reaction in which one species is **oxidised** (loses electrons) and another is **reduced** (gains electrons)
- The **standard electrode potentials** (E^{θ}) of the two species can be used to predict the **feasibility** of redox reactions involving transition elements and their ions

Predicting the feasibility of redox reactions

- The standard electrode potential (E^{θ}) of a species gives an indication of how well it can be reduced
- In the exam, you will be provided with a half equation and the standard electrode potential (E^{θ})
- The half equations are always written as a reduction equation
  - They are equilibrium reactions, as they demonstrate the equilibrium reached when the species in the equation gains electrons at the same rate as it loses electrons
- The **more positive** the standard electrode potential (E^{θ}) of a species is, the more readily that element will be reduced (gain electrons)
  - This is always when compared to the standard hydrogen electrode
  - The opposite is of course true; the more negative the standard electrode potential (E^{θ}) of a species is, the more readily that element will be oxidised (lose electrons)
- The feasibility of a reaction can be predicted using these values
- For example, the feasibility of Fe^{3+} being reduced to Fe^{2+} when reacted with Cu^{2+} can be predicted using their standard electrode potentials

Standard electrode potentials of Fe(III) & Cu(II) table

Half equation	Standard electrode potential, E^{θ} (V)
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$Cu^{2+} + e^- \rightleftharpoons Cu^+$	+0.15

- The table above shows that yes, the reaction is feasible and Fe^{3+} is more likely to get **reduced** to Fe^{2+}
  - Fe^{3+} has a **more positive** standard electrode potential
  - Fe^{3+} will gain electrons more readily than Cu^{2+}
  - Therefore, Fe^{3+} is the better **oxidising agent**
  - The reaction for this half equation will therefore proceed in the forward direction (reduction)

$$\mathbf{Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \quad \mathit{E}^\theta = +0.77\,V}$$

- Since it is feasible that the Fe^{3+} will be reduced and this half equation will move in the forward direction, this means that the half equation for copper will move in the backward direction (oxidation)
  - Cu^{2+} equation has a **less positive** (or more negative) standard electrode potential
  - The Cu^+ will therefore be oxidised to Cu^{2+}
  - The reaction for this half equation will therefore be in the reverse direction

$$\mathbf{Cu^{2+} + e^- \rightleftharpoons Cu^+ \quad \mathit{E}^\theta = +0.15\,V}$$

- Combining these two half-equations to get the overall equation gives (after cancelling the electrons on both sides):

$$\mathbf{Fe^{3+} + Cu^+ \rightleftharpoons Fe^{2+} + Cu^{2+}}$$

- The standard cell potential is:
  - $E^\theta = E^\theta_{reduction} - E^\theta_{oxidation}$
  - $E^\theta = (+0.77) - (+0.15)$
  - $E^\theta = +0.62\,V$
- The positive value of $E_{cell}{}^\theta$ (+0.62 V) suggests that the reaction is likely to proceed
- The changes in the transition element ions' oxidation states are therefore **feasible**
- Standard electrode potentials (E^θ) are only predictions about the feasibility of a reaction; they do not guarantee that a reaction will definitely occur
  - For example, a reaction may be feasible according to these rules but have a very large activation energy barrier meaning that, in reality, it will not occur

Your notes

The Permanganate & Oxalate Redox System

- The oxidation states of transition element ions can change during **redox reactions**
  - A species will either be oxidised or reduced, depending on what reaction is occurring
- To find the concentration of specific ions in solution, a titration can be performed
- There are three particular redox titrations that need to be learnt:
  - Iron (II) (Fe^{2+}) and permanganate (MnO_4^-) in acid solution given suitable data
  - Permanganate (MnO_4^-) and ethanedioate ($C_2O_4^{2-}$) in acid solution given suitable data
  - Copper (II) (Cu^{2+}) and iodide (I^-) given suitable data
- The first redox titration involving transition element ions, that needs to be learned, is the titration of permanganate (MnO_4^-) and ethanedioate, sometimes known as oxalate ($C_2O_4^{2-}$) in acid solution given suitable data

Reaction of MnO_4^- & $C_2O_4^{2-}$ in acid

- The reaction of MnO_4^- with ethanedioate, $C_2O_4^{2-}$ is an example of a redox reaction in which the ethanedioate ions ($C_2O_4^{2-}$) get **oxidised** by manganate(VII) (MnO_4^-) ions
- A titration reaction can be carried out to find the concentration of the **toxic** ethanedioate ions
- As before, the endpoint is when all of the ethanedioate ions have reacted with the MnO_4^- ions, and the first permanent pink colour appears in the flask
  - At this point, the MnO_4^- is very slightly in **excess**
- The two half-reactions that are involved in this redox reaction are as follows:

$$C_2O_4^{2-}\ (aq) \rightarrow 2CO_2\ (g) + 2e^-$$

- The $C_2O_4^{2-}$ (aq) loses 2 electrons to form $2CO_2$ (g)
  - The oxidation number of carbon changes from +3 in $C_2O_4^{2-}$ (aq) to +4 in CO_2 (g)
  - Since there is an increase in oxidation number, this is the oxidation reaction

$$MnO_4^-\ (aq) + 8H^+\ (aq) + 5e^- \rightarrow Mn^{2+}\ (aq) + 4H_2O\ (l)$$

- The oxidation number of manganese changes from +7 in MnO_4^- (aq) to +2 in Mn^{2+} (aq)
  - Since there is a decrease in oxidation number, this is the reduction reaction
- The half equations are combined to get the overall equation:

$$\text{Oxidation: } C_2O_4^{2-}(aq) \rightarrow 2CO_2(g) + 2e^-$$

$$\text{Reduction: } MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

- Both half equations must have the same number of electrons, so:
  - The oxidation half equation is multiplied by 5
  - The reduction half equation is multiplied by 2

$$\text{Oxidation: } 5C_2O_4^{2-}(aq) \rightarrow 10CO_2(g) + 10e^-$$

$$\text{Reduction: } 2MnO_4^-(aq) + 16H^+(aq) + 10e^- \rightarrow 2Mn^{2+}(aq) + 8H_2O(l)$$

- The reactants and products from each half equation can be combined together:

$$5C_2O_4^{2-}(aq) + 2MnO_4^-(aq) + 16H^+(aq) + 10e^- \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g) + 10e^-$$

- Any species that appear on both sides of the overall equation can be cancelled out
  - In this case, there are $10e^-$ on both sides, which can be cancelled:

$$5C_2O_4^{2-}(aq) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$$

- This is an example of an **autocatalysis reaction**
- This means that the reaction is catalysed by one of the products as it forms
- In this reaction, the Mn^{2+} ions formed act as the **autocatalyst**
- The more Mn^{2+} formed, the faster the reaction gets, which then forms even more Mn^{2+} ions and speeds the reaction up even further
- Transition element ions can act as autocatalysts because they can change their oxidation states during a reaction

The Ferrous & Permanganate Redox System

- The second redox titration involving transition element ions, that needs to be learned, is the titration of permanganate (MnO_4^-) and iron(II) ions (Fe^{2+})

Reaction of MnO_4^- & Fe^{2+} in acid

- The concentration of Fe^{2+} ions can be determined by titrating a known **volume** of Fe(II) ions with a known **concentration** of MnO_4^- ions
- During the reaction of MnO_4^- with Fe^{2+}, the **purple** colour of the manganate(VII) ions disappears
- The end-point is when all of the Fe^{2+} ions have reacted with the MnO_4^- ions, and the first trace of a permanent **pink** colour appears in the flask
  - At this point, the MnO_4^- is very slightly in **excess**
- The two half-reactions that are involved in this redox reaction are as follows:

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

Your notes

- The Fe^{2+} (aq) loses an electron to form Fe^{3+} (aq)
  - The oxidation number of iron changes from +2 in Fe^{2+} (aq) to +3 in Fe^{3+} (aq)
  - So, this is the oxidation reaction

$$\mathbf{MnO_4^- (aq) + 8H^+ (aq) + 5e^- \rightarrow Mn^{2+} (aq) + 4H_2O (l)}$$

- The oxidation number of manganese changes from +7 in MnO_4^- (aq) to +2 in Mn^{2+} (aq)
  - Since there is a decrease in oxidation number, this is the reduction reaction
- The half equations are combined to get the overall equation:

$$\text{Oxidation: } \mathbf{Fe^{2+} (aq) \rightarrow Fe^{3+} (aq) + e^-}$$

$$\text{Reduction: } \mathbf{MnO_4^- (aq) + 8H^+ (aq) + 5e^- \rightarrow Mn^{2+} (aq) + 4H_2O (l)}$$

- Both half equations must have the same number of electrons, so:
  - The oxidation half equation is multiplied by 5
  - The reduction half equation does not need any changes

$$\text{Oxidation: } \mathbf{5Fe^{2+} (aq) \rightarrow 5Fe^{3+} (aq) + 5e^-}$$

$$\text{Reduction: } \mathbf{2nO_4^- (aq) + 8H^+ (aq) + 5e^- \rightarrow Mn^{2+} (aq) + 4H_2O (l)}$$

- The reactants and products from each half equation can be combined together:

$$\mathbf{5Fe^{2+} (aq) + MnO_4^- (aq) + 8H^+ (aq) + 5e^- \rightarrow Mn^{2+} (aq) + 4H_2O (l) + 5Fe^{3+} (aq) + 5e^-}$$

- Any species that appear on both sides of the overall equation can be cancelled out
  - In this case, there are $5e^-$ on both sides, which can be cancelled:

$$\mathbf{5Fe^{2+} (aq) + MnO_4^- (aq) + 8H^+ (aq) \rightarrow Mn^{2+} (aq) + 4H_2O (l) + 5Fe^{3+} (aq)}$$

The Cupric & Iodide Redox Systems

- The third redox titration involving transition metal ions, that needs to be learnt, is the titration between copper(II) ions (Cu^{2+}) - sometimes known as cupric ions - and iodide ions (I^-)

Reaction of Cu^{2+} & I^-

- The reaction of Cu^{2+} with I^- is an example of a redox reaction in which the copper ions (Cu^{2+}) **oxidise** the iodide ions (I^-) and as a result are themselves **reduced**
- The two half-reactions that are involved in this redox reaction are as follows:

$$\mathbf{2I^- (aq) \rightarrow I_2 (aq) + 2e^-}$$

- The $2I^-$ (aq) loses an electron each to form I_2 (aq)
  - The oxidation number of iodine changes from -1 in I^- (aq) to 0 in I_2 (aq)
  - So, this is the oxidation reaction

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

- The Cu^{2+} (aq) gains an electron to form Cu^+ (aq)
  - The oxidation number of copper changes from +2 in Cu^{2+} (aq) to +1 in Cu^+ (aq)
  - Since there is a decrease in oxidation number, this is the reduction reaction
- The half equations are combined to get the overall equation:

Oxidation: $2I^- (aq) \rightarrow I_2 (aq) + 2e^-$

Reduction: $Cu^{2+} (aq) + e^- \rightarrow Cu^+ (aq)$

- Both half equations must have the same number of electrons, so:
  - The oxidation half equation does not need any changes
  - The reduction half equation is multiplied by 2

Oxidation: $2I^- (aq) \rightarrow I_2 (aq) + 2e^-$

Reduction: $2Cu^{2+} (aq) + 2e^- \rightarrow 2Cu^+ (aq)$

- The reactants and products from each half equation can be combined together:

$$2I^- (aq) + 2Cu^{2+} (aq) + 2e^- \rightarrow 2Cu^+ (aq) + I_2 (aq) + 2e^-$$

- Any species that appear on both sides of the overall equation can be cancelled out
  - In this case, there are $2e^-$ on both sides, which can be cancelled:

$$2I^- (aq) + 2Cu^{2+} (aq) \rightarrow 2Cu^+ (aq) + I_2 (aq)$$

- When **excess** iodide ions are reacted with Cu(II), a precipitate of copper(I) iodide and **iodine** is formed:
  - $2Cu^{2+} (aq) + 4I^- (aq) \rightarrow I_2 (aq) + 2CuI (s)$ **Reaction 1**
- A titration reaction can be carried out to find an unknown concentration of the copper(II) solution
- This is done by finding the amount of iodine which is liberated during the reaction, through a titration:

1. A known concentration of **sodium thiosulfate solution** is added to the mixture formed in Reaction 1 from a burette
   - The I_2 formed in Reaction 1 will react with the thiosulfate ions
     - $I_2 (aq) + 2S_2O_3^{2-} (aq) \rightarrow 2I^- (aq) + S_4O_6^{2-} (aq)$ **Reaction 2**
   - As the iodine is used up, the **brownish** colour of the solution gets **lighter**
   - When most of the iodine colour is gone, starch is added, which turns deep **blue/black** with the remaining I_2 (aq)
   - **Step 5:** Titrate further until the blue/black colour disappears, i.e. when all of the iodine has reacted

Your notes

        - By knowing the number of moles of thiosulfate ions added in the titration, you can use the molar ratios from the reaction equations and work backwards to calculate the number of moles of Cu(II)
    - Look at Reaction 2 It can be concluded that half the number of moles of I_2 reacts when compared to the moles of thiosulfate that react
    - Now look at Reaction 1
        - The number of moles of I_2 which react in Reaction 2, is the moles formed in Reaction 1
        - The number of moles of Cu(II) is twice that of I_2 (aq), i.e. the same number of moles as thiosulfate ions added in the titration
    - Divide the number of moles of Cu(II) by the volume in dm^3 to get the concentration of Cu(II)

Calculations of Other Redox Systems

Calculations of Other Redox Systems

- You are required to perform calculations involving **redox reactions** of transition elements
- These include:
    - Constructing redox equations
    - Calculating oxidation states
    - Selecting suitable **oxidising agents** and **reducing agents**
    - Calculating cell potentials

Your notes