AN INTRODUCTION TO THE CHEMISTRY OF TRANSITION ELEMENTS

Content

- General physical and characteristic chemical properties of the first set of transition elements, scandium to copper
- Colour of complexes

Learning Outcomes

Candidates should be able to:

(a) explain that a transition element is a d block element whose atom has an incomplete d subshell, or which can give rise to cations with an incomplete d subshell

(b) state the electronic configuration of a first row transition element and of its ions

(c) explain why the atomic radii and first ionisation energies of the transition metal atoms are relatively invariant

(d) contrast, qualitatively, the melting point and density of the transition elements with those of calcium as a typical s block element

(e) describe the tendency of transition elements to have variable oxidation states

(f) predict from a given electronic configuration, the likely oxidation states of a transition element

(g) describe and explain the use of Fe^{3+}/Fe^{2+}, MnO_4^-/Mn^{2+} and $Cr_2O_7^{2-}/Cr^{3+}$ as examples of redox systems (see also ***REDOX AND ELECTROCHEMISTRY***)

(h) predict, using $E^{\ominus}$ values, the likelihood of redox reactions (see also ***ELECTROCHEMISTRY***)

(i) define the terms *ligand* and *complex* as exemplified by the complexes of copper(II) ions with water, ammonia and chloride ions as ligands (including the transition metal complexes found in the **Qualitative Analysis Notes**)

(j) explain qualitatively that ligand exchange may occur, as exemplified by the formation of the complexes in (i), including the colour changes involved, and CO/O_2 exchange in haemoglobin

(k) describe, using the shape and orientation of the d orbitals, the splitting of degenerate d orbitals into two energy levels in octahedral complexes

(l) explain, in terms of d orbital splitting and d-d transition, why transition element complexes are usually coloured [knowledge of the relative order of ligand field strength is not required]

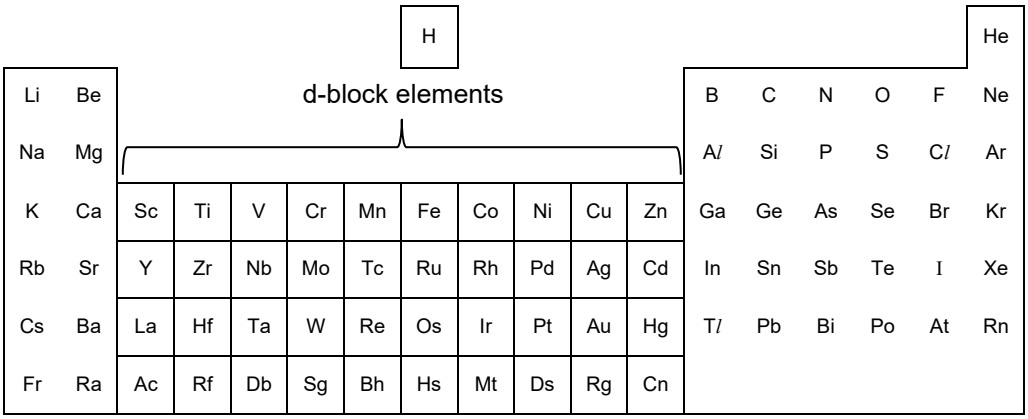
(m) explain how some transition elements and/or their compounds can act as catalysts (see also ***REACTION KINETICS***)

1 Introduction

Success Criteria:

- I know the definition of a transition element.
- I can state the electronic configuration of a first row transition element and of its ions.

A transition element is d block element whose atom has an incomplete d subshell, ***or*** which can give rise to cations with an incomplete d subshell.
For A−Level syllabus, we study the chemistry of first row transition elements.
(*e.g.* from **scandium to copper**)



The electronic configurations of d-block elements (first row) are:

Note:
Ground state electronic configurations of Cr and Cu atom are [Ar] $3d^5\ 4s^1$ and [Ar] $3d^{10}\ 4s^1$ respectively

Element	Atomic no.	Electronic configuration	Electronic configuration of 1 stable ion	
Scandium	21	[Ar] $3d^1\ 4s^2$	Sc^{3+}	[Ar] $\mathbf{3d^0}\ 4s^0$
Titanium	22	[Ar] $3d^2\ 4s^2$	Ti^{2+}	[Ar] $3d^2\ 4s^0$
Vanadium	23	[Ar] $3d^3\ 4s^2$	V^{3+}	[Ar] $3d^2\ 4s^0$
Chromium*	24	[Ar] $3d^5\ 4s^1$	Cr^{3+}	[Ar] $3d^3\ 4s^0$
Manganese	25	[Ar] $3d^5\ 4s^2$	Mn^{2+}	[Ar] $3d^5\ 4s^0$
Iron	26	[Ar] $3d^6\ 4s^2$	Fe^{2+}	[Ar] $3d^6\ 4s^0$
Cobalt	27	[Ar] $3d^7\ 4s^2$	Co^{3+}	[Ar] $3d^6\ 4s^0$
Nickel	28	[Ar] $3d^8\ 4s^2$	Ni^{2+}	[Ar] $3d^8\ 4s^0$
Copper*	29	[Ar] $\mathbf{3d^{10}}\ 4s^1$	Cu^{2+}	[Ar] $3d^9\ 4s^0$
Zinc	30	[Ar] $\mathbf{3d^{10}}\ 4s^2$	Zn^{2+}	[Ar] $\mathbf{3d^{10}}\ 4s^0$

Quick recall:

- For d−block elements, electrons occupy the 4s subshell first before the 3d subshell as the empty 4s subshell is of lower energy than the empty 3d subshell.
- When filled with electrons, the 4s subshell has a higher energy than the 3d subshell. Hence, during the formation of positive ions, the 4s electrons are removed first.

Q: Why is zinc not considered as transition elements even though it is a d-block element?

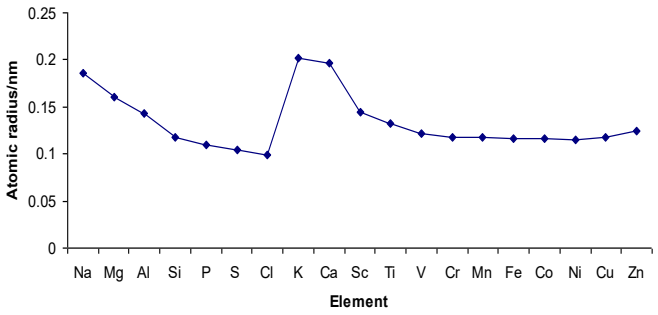
- Zn atom has complete d-subshell: Zn: [Ar] $3d^{10}\,4s^2$
- It has only one known oxidation state: Zn^{2+} , with an incomplete d subshell.
  Zn^{2+}: [Ar] $3d^{10}$
- As such, the melting point of Zn (420 °C) is much lower than the others (> 1500 °C).

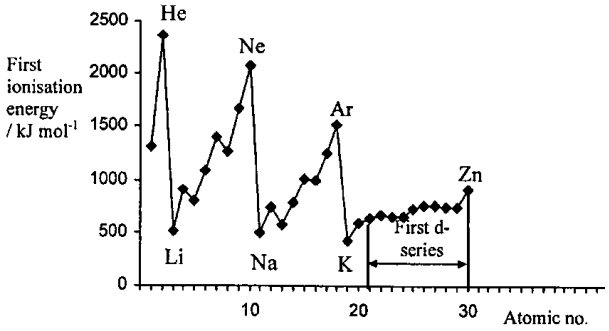
2 Physical Properties of Transition Elements

Success Criteria:

- I can explain why the atomic radii and first ionization energies of transition elements of the same period remain relatively constant.
- I can explain why the melting points and densities of transition elements are higher than typical s block elements.

2.1 Atomic radii & First Ionisation Energy





	Across Period 3 Elements (Na to C*l*)	Across Transition Elements (Sc to Cu)
Atomic radii	Decrease significantly	Remain relatively constant
1st I.E.	Increase significantly	Remain relatively constant
Reasons	• Nuclear charge <u>increases</u> • Electrons are added to <u>same valence shell</u> • Shielding effect <u>remains approximately constant</u> • Nuclear attraction for the valence electrons <u>increases significantly</u>	• Nuclear charge <u>increases</u> • Electrons are added to the <u>inner principal quantum shell (3d subshell)</u> • Shielding effect for valence shell 4s electrons <u>increases due to the increase in no. of inner shell (3d) electrons</u> • Nuclear attraction for the valence electrons <u>is almost constant</u>

2.2 Melting Point and Density

Differences between an s-block metal, Ca, and a d-block transition element, Fe

	Calcium [Ar] $4s^2$	**Iron** [Ar] $\mathbf{3d^6}$ $4s^2$
Melting point / °C	850	1535
Density / g cm^{-3}	1.54	7.86

2.2.1 Melting Point

All transition elements have much **higher melting and boiling points** than the s-block metals due to **stronger metallic bonds**.

The **small energy difference** between the 3d and 4s subshells allows transition elements to contribute **3d AND 4s electrons** to the sea of delocalised electrons for metallic bonding. Whereas calcium only contributes its 4s electrons for metallic bonding.

The strength of the metallic bond is proportional to the **number of delocalised electrons**. More energy is required to overcome the stronger metallic bonding in transition elements than calcium. Transition elements have higher melting point than calcium.

2.2.2 Density

Transition elements are **denser** than the s-block elements in the same period.

Transition elements have smaller atomic size (atomic radii in *Data Booklet*) and thus more atoms per unit volume. Furthermore, the transition element atoms are of high atomic mass compared to s-block elements.

Hence transition elements have greater mass per unit volume (higher density) as compared to s-block elements.

Checkpoint 1 

Which element is most likely to be a transition element?

	m.p./°C	b.p./°C	density/g cm^{-3}
A	1900	3400	6.1
B	157	2000	7.3
C	1280	2970	1.9
D	3730	4200	2.2

3 Chemical Properties of Transition Elements

Transition elements show great similarities in their chemical properties due to

1) Close similarity in energies of the 3d and 4s orbitals.
2) Stable ions with incomplete d subshell.

3.1 Variable oxidation states

The s-block elements are only able to exhibit oxidation states of +1 (Group 1) or +2 (Group 2). Once the outermost electrons in the s orbital are removed, subsequent removal of electrons would be from an inner electronic shell. This would require a much larger amount of energy and hence removal of additional electrons is not favorable.

Transition elements exhibit ***variable oxidation states*** in their compounds due to the ***close similarity in energy*** of the 3d and 4s orbitals. Hence, both 3d and 4s electrons can be removed to form stable ions of different oxidation states.

e.g. Fe^{2+}, Fe^{3+} Mn^{2+}, MnO_2, MnO_4^- Cr^{3+}, $Cr_2O_7^{2-}$ V^{2+}, V^{3+}, VO^{2+}, VO_2^+

The table below summarises the known oxidation states of Sc to Zn.

Note:
In general, Highest possible O.N. = no of unpaired d-electrons + 4s electrons

Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
$3d^1\ 4s^2$	$3d^2\ 4s^2$	$3d^3\ 4s^2$	$3d^5\ 4s^1$	$3d^5\ 4s^2$	$3d^6\ 4s^2$	$3d^7\ 4s^2$	$3d^8\ 4s^2$	$3d^{10}\ 4s^1$	$3d^{10}\ 4s^2$
	+1	+1	+1	+1	+1	+1	+1	**+1**	
+2	**+2**	**+2**	**+2**	**+2**	**+2**	**+2**	**+2**	**+2**	**+2**
+3	**+3**	**+3**	**+3**	+3	**+3**	**+3**	+3	+3	
	+4	**+4**	+4	**+4**	+4	+4	+4		
		+5	+5	+5	+5	+5			
			+6	+6	+6				
				+7					

***Highlighted cell indicates the common oxidation states of the various transition elements.*

The first row transition elements beyond manganese are more commonly found in the lower oxidation state due to the increasing difficulty to remove a 3d electron as nuclear charge increases.

3.2 Formation of Complexes

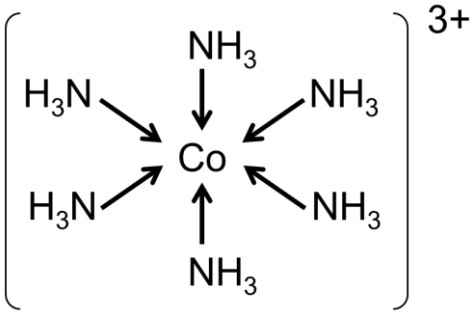
Success Criteria:

- I can draw octahedral complexes.
- I can determine the charge(s)/oxidation state of the transition metal cation and the overall charge of the complex ion, given the charge of the ligands.
- I can deduce the formula of a complex ion from its given name.

A **complex** contains a central metal ion/atom linked to **ligands** by dative bonds *(also known as coordinate bonds*). If the species carries an overall **charge**, it is often called a **complex ion**.

Note:
Based on definition, ligands act as Lewis bases (electron pair donor) while the central metal ion/atom acts as Lewis acid (electron pair acceptor).

Ligands are ions or neutral molecules that possess at least a lone pair of electrons available for donation into a low-lying vacant orbital of a central metal ion/atom **(formation of dative bond).**
E.g.**:** CN^-, **:**$C\mathit{l}^-$, **:**NH_3, **:**OH^-, H_2O**:** , $H_2N\text{-}CH_2CH_2\text{-}NH_2$



$[Co(NH_3)_6]^{3+}$ complex ion

Note:
The formula of complex is represented by the square bracket "[ ]".

The molecules/anions inside the square bracket are the ligands

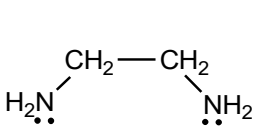
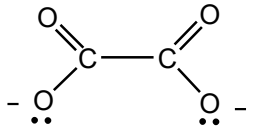
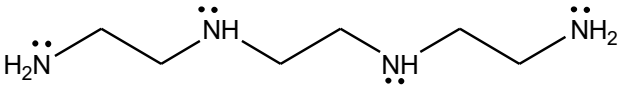
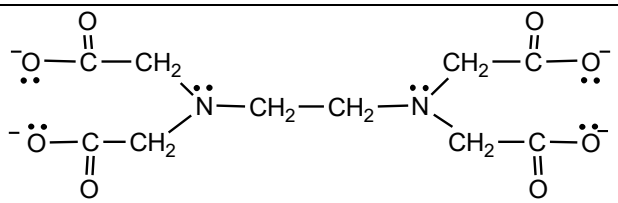
Transition metals ions are capable of forming stable complex ions because their high charge to size ratio (high polarising power) results in strong attraction for ligands, forming dative covalent bonds.

The lone pair of electrons on the ligand is donated into the low-lying vacant orbitals (any energetically accessible orbital, e.g. 3d, 4s, 4p or 4d) of the central transition metal ion to form a dative covalent bond.

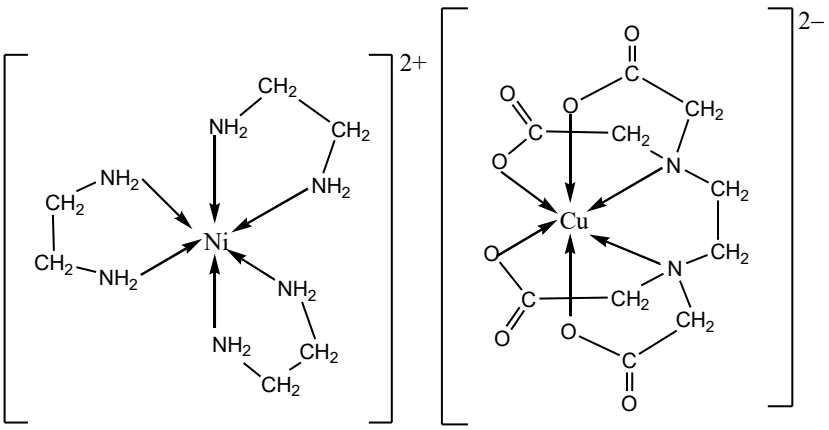
Complex formation is not confined to d-block elements; main group metal ions can also form complexes, e.g. $[A\mathit{l}(OH)_4]^-$
(Relate to Qualitative Analysis Notes and K_{sp})

3.2.1 Types of Ligands

Ligands are classified according to the number of coordinate bonds (dative bonds) each ligand forms with the central metal ion/atom. (**−dentate**)

Type of Ligand	No. of coordinate bonds formed	Examples of *common ligands found in complex ions*
Monodentate	1	H_2O: , :NH_3 , $^-$:C≡N, :Cl^-, :SCN^-, :OH^-, :C≡O
Bidentate	2	 Ethane−1,2−diamine (en)  ethanedioate
Tetradentate	4	 Triethylenetetramine
Hexadentate	6	 **E**thylene-**d**iamine-**t**etra-**a**cetate (edta^{4-})

Polydentate ligands are sometimes called **chelating agents** because of their ability to hold a metal ion like the claws of a crab. Chelating ligands form stable complex species with the central metal ion as the pincer-like grip of these ligands to hold the cation very securely.

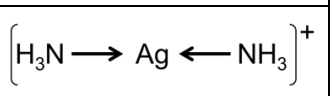
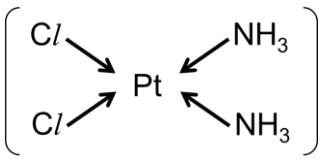
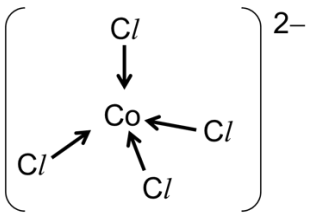
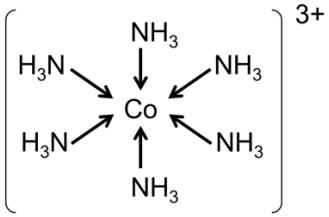


Chelate complexes ions of $[Ni(en)_3]^{2+}$ and $[Cu(edta)]^{2-}$

e.g. edta^{4-} is used to bind metal ions in the practice of chelation therapy, especially for treatment of mercury and lead poisoning.

3.2.2 Co-ordination Number and Shapes of Complexes

Co-ordination number indicates the number of co-ordinate bonds (dative bonds) that the central metal ion formed with ligands.

Co-ordination Number	Shape	Examples	Illustration
2	Linear	$[CuCl_2]^-$ $[Ag(NH_3)_2]^+$	
4	Square planar	$[Ni(CN)_4]^{2-}$ $[Pt(Cl)_2(NH_3)_2]$	
4	Tetrahedral (more common than square planar)	$[CoCl_4]^{2-}$ $[CuCl_4]^{2-}$	
6	Octahedral	$[Co(NH_3)_6]^{3+}$ $[Cu(H_2O)_6]^{2+}$ $[Fe(CN)_6]^{3-}$	

Common co-ordination numbers and complexes

Note:
For H2 syllabus, there is no need to differentiate between square planar and tetrahedral if the coordination number is 4.

Checkpoint 2

1) Which species does **not** act as a ligand in the formation of complexes?

A CH_3NH_2 **B** SCN^- **C** NH_4^+ **D** CO

2) The oxidation state and coordination number of cobalt in $[Co(NH_3)_5Cl]Cl_2$ are, respectively,

A +2 and 5 **B** +2 and 6 **C** +3 and 5 **D** +3 and 6

General guidelines for coordination numbers (C. No.) in complexes:

Coordination number **(C. No.)** = 6 is the most common, all complex ions with H_2O ligands can be assumed to have coordination number **(C. No.)** = 6.

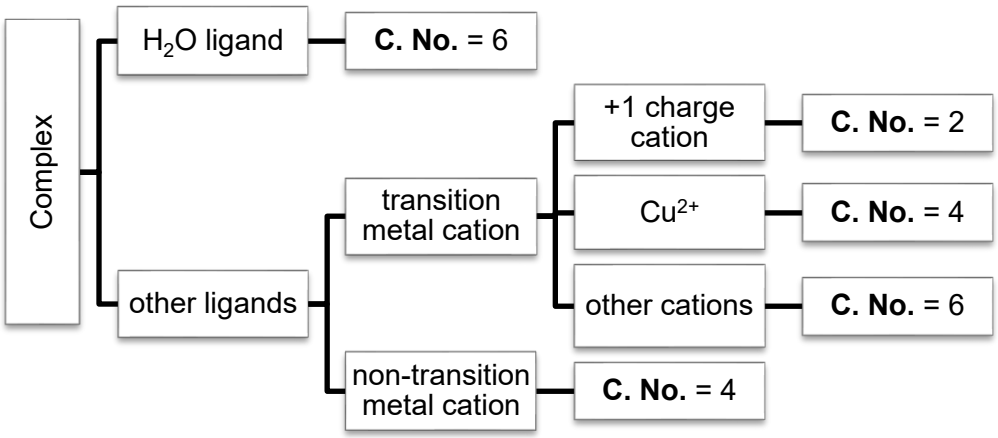
Exceptions:

1) Transition metal cation with +1 charge (Ag^+, Cu^+) forms complexes with coordination number = 2,

E.g. Ag^+ and NH_3 gives $[Ag(NH_3)_2]^+$, Cu^+ and Cl^- gives $[CuCl_2]^-$

2) Cu^{2+} and non-transition metal cations form complexes with coordination number = 4 when ligand is NOT H_2O

E.g. Cu^{2+} with NH_3 gives $[Cu(NH_3)_4]^{2+}$, Zn^{2+} with OH^- gives $[Zn(OH)_4]^{2-}$



Checkpoint 3

Give the formula of the complex ions formed by these cations and ligands

	Cations and ligands	C. No.	Complex ion
(a)	Zn^{2+} and NH_3		
(b)	Al^{3+} and H_2O		
(c)	Al^{3+} and OH^-		
(d)	Ag^+ and CN^-		
(e)	Fe^{2+} and CN^-		
(f)	Fe^{3+} and $C_2O_4^{2-}$ (bidentate ligand)		
(g)	Fe^{3+} and $edta^{4-}$ (hexadentate ligand)		
(h)	Cu^+ and Cl^-		
(i)	Cu^{2+} and Cl^-		
(j)	Cu^{2+} and H_2O		

3.2.3 Understanding Systematic Name of Complexes (Naming of complex is not required, but need to deduce formula of complex from the given name)

The systematic name of a complex is obtained by following the sequence:

1. The ligands are named first, in alphabetical order and the metal ion is named last.

2. The names of anionic ligands end with the letter 'o', whereas a neutral ligand is usually called by the name of the molecule.
   Exceptions: H_2O (aqua) and NH_3 (ammine).

3. When more than one ligand of a particular kind is present, the prefixes, di–, tri–, tetra–, penta–, hexa– is used.

4. The oxidation number of a metal is written in Roman numerals following the name of the metal.

5. If the complex is anionic, its name ends in –ate.
   E.g. anion complex of Cu $\rightarrow$ cuprate
   anion complex of Fe $\rightarrow$ Ferrate

Worked Example 1

Deduce the formula of the following complexes.

Name of complex	Ligands	Cation	Formula of complex
Hexacyanoferrate(III)	$6 \times CN^-$	Fe^{3+}	$[Fe(CN)_6]^{3-}$
Tetrachlorocuprate(II)	$4 \times Cl^-$	Cu^{2+}	$[CuCl_4]^{2-}$
Tetraamminecopper(II)	$4 \times NH_3$	Cu^{2+}	$[Cu(NH_3)_4]^{2+}$
Hexaaquachromium(III)	$6 \times H_2O$	Cr^{3+}	$[Cr(H_2O)_6]^{3+}$
Diamminesilver(I)	$2 \times NH_3$	Ag^+	$[Ag(NH_3)_2]^+$

3.2.4 Qualitative Analysis of Cations and Complex Ions Formation

In Qualitative Analysis of cations, precipitates of certain metal hydroxides are observed to be soluble in presence of excess NaOH(aq) or NH_3(aq) due to the formation of soluble complex ion in the presence of OH^- or NH_3 ligands.

1) When NaOH(aq) is added to M^{n+}, metal hydroxide, $M(OH)_n$ (s), is formed.
In excess NaOH(aq), soluble OH^- complex can be formed.

2) When NH_3(aq) is added to M^{n+}, $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
metal hydroxide, $M(OH)_n$ (s), is formed.
In excess NH_3(aq), soluble NH_3 complex can be formed.

cation	reaction with	
	NaOH(aq)	NH_3(aq)
Al^{3+}(aq) Colourless solution	White ppt of **$Al(OH)_3$** soluble in excess NaOH to form colourless solution with complex ion **$[Al(OH)_4]^-$**	White ppt of **$Al(OH)_3$** insoluble in excess NH_3
Cr^{3+}(aq) Green solution	Grey-green ppt of **$Cr(OH)_3$** soluble in excess NaOH to give dark green solution with complex ion **$[Cr(OH)_6]^{3-}$**	Grey-green ppt of **$Cr(OH)_3$** insoluble in excess NH_3
Cu^{2+}(aq) Blue solution	Pale blue ppt of **$Cu(OH)_2$** insoluble in excess NaOH	Pale blue ppt of **$Cu(OH)_2$** soluble in excess NH_3 to give dark blue solution with complex ion **$[Cu(NH_3)_4]^{2+}$**
Fe^{2+}(aq) Pale green solution	green ppt of **$Fe(OH)_2$** insoluble in excess NaOH. On standing, green ppt turns reddish brown ppt **$Fe(OH)_3$**	green ppt of **$Fe(OH)_2$** insoluble in excess NH_3. On standing, green ppt turns reddish brown ppt **$Fe(OH)_3$**
Fe^{3+}(aq) Yellow solution	Reddish-brown ppt of **$Fe(OH)_3$** insoluble in excess NaOH	Reddish-brown ppt of **$Fe(OH)_3$** insoluble in excess NH_3
Mg^{2+}(aq) Colourless solution	White ppt of **$Mg(OH)_2$** insoluble in excess NaOH	White ppt of **$Mg(OH)_2$** insoluble in excess NH_3
Mn^{2+}(aq) Colourless solution	Off-white ppt of **$Mn(OH)_2$** insoluble in excess NaOH. On standing, off-white ppt turns brown ppt **$Mn(OH)_3$**	Off-white ppt of **$Mn(OH)_2$** insoluble in excess NH_3. On standing, off-white ppt turns brown ppt **$Mn(OH)_3$**
Zn^{2+}(aq) Colourless solution	White ppt of **$Zn(OH)_2$** soluble in excess NaOH to give colourless solution with complex ion **$[Zn(OH)_4]^{2-}$**	White ppt of **$Zn(OH)_2$** soluble in excess NH_3 to give colourless solution with complex ion **$[Zn(NH_3)_4]^{2+}$**

Note:
White ppt of **AgCl** is soluble in excess NH_3 to give colourless solution with complex ion **$[Ag(NH_3)_2]^+$**

3.3 Ligand exchange reactions

Success Criteria:

- I can explain how ligand exchange leads to formation of different complexes with different colours, particularly for the complexes of copper(II) ions with water, ammonia and chloride ions as ligands.
- I know that CO is a strong ligand and can readily displace oxygen in oxyhaemoglobin (HbO_2) to form carboxyhaemoglobin (HbCO).

Note:
The formation of a new complex is usually accompanied by
- ***Change in colour*** of solution
- ***Dissolution*** of precipitate

- Formation of complexes depends on the stability of the complexes and involves competition between ligands for the central metal cations.

- Competition between ligands often takes place in qualitative analysis, leading to **ligand exchange** reactions (**reversible reaction**).

$$\text{e.g. } [M(H_2O)_6]^{2+} + 6L^- \rightleftharpoons [ML_6]^{4-} + 6H_2O$$

- When a **new ligand** is added in **high concentration**, the position of the equilibrium would shift to the **right**, **favouring the ligand exchange** reaction and lead to the formation of the new complex ions.

3.3.1 Complexes of Cu^{2+} with water, ammonia and chloride ligands

Copper(II) salts dissolve in water to give a blue solution, which is attributed to the complex ion $[Cu(H_2O)_6]^{2+}$, commonly known as $Cu^{2+}(aq)$.

Note:
C. No. = 6 for Cu^{2+} with H_2O ligands.
C. No. = 4 for Cu^{2+} with other ligands.

1) When **excess** ammonia solution is added to aqueous copper(II) sulfate, ammonia molecules displace the water molecules from the hydrated copper(II) ions forming $[Cu(NH_3)_4]^{2+}(aq)$ in the ligand exchange reaction.

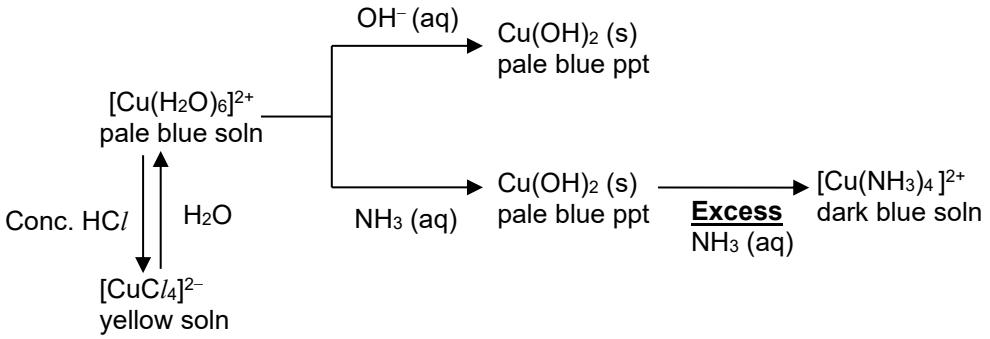
$$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + 6\,H_2O(l)$$
pale blue solution — deep blue solution

Note:
In some textbooks, $[Cu(NH_3)_4]^{2+}$ may be expressed as $[Cu(NH_3)_4(H_2O)_2]^{2+}$. Both formulae are accepted by Cambridge.

2) When **excess** chloride ion is added to aqueous copper(II) sulfate, chloride ion displace the water molecules from the hydrated copper(II) ions forming $[CuCl_4]^{2-}(aq)$ in the ligand exchange reaction.

$$[Cu(H_2O)_6]^{2+}(aq) + 4\,Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}aq) + 6\,H_2O(l)$$
pale blue solution — yellow solution

Ligand Exchange Reactions of Cu^{2+}



Worked Example 2 *N2010/III/5b*

Describe the colour changes when dilute aqueous ammonia is added to a solution containing $Cu^{2+}(aq)$ until the ammonia is in excess, giving the formulae of all relevant copper compounds. [4]

Answer

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$

Blue solution pale blue ppt

When dilute NH_3 is added to a blue $Cu^{2+}(aq)$ solution, a blue ppt of $Cu(OH)_2$ is observed.

$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$ ….(1)

$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + 6H_2O(l)$

Pale blue solution dark blue solution

When **excess** dilute NH_3 is added, a dark blue solution of $[Cu(NH_3)_4]^{2+}$ complex is formed.

This lowers concentration of $Cu^{2+}(aq)$, causing the equilibrium of (1) to shift to the right, causing the pale blue $Cu(OH)_2$ ppt to dissolve.

Worked Example 3 *N2010/III/5d*

When concentrated hydrochloric acid is added to a solution containing $Cu^{2+}(aq)$, the colour changes to a pale yellow-green. No gas is evolved.

No such colour changes occur when concentrated sulfuric acid is added to $Cu^{2+}(aq)$. Dilution of the yellow-green solution with water produced the original pale blue colour. Suggest an explanation of these observations. [3]

Answer

$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$ --------- (1)
Blue solution yellow solution

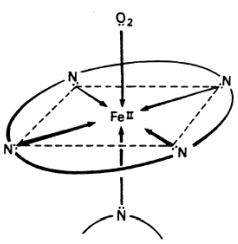
Concentrated HCl provides high concentration of Cl^- which favours ligand exchange with H_2O in the hydrated complex, $[Cu(H_2O)_6]^{2+}$. Formation of a new complex causes the colour to change. An equilibrium mixture that contains blue $[Cu(H_2O)_6]^{2+}$ and yellow $[CuCl_4]^{2-}$ produces a yellow-green mixture.

When conc H_2SO_4 is added, there is no ligand exchange/ new complex formation. Therefore, no colour change occurs.

During dilution, adding H_2O shifts position of equilibrium (1) to the left (H_2O displace Cl^- ligands) upon dilution, therefore the original blue solution is formed.

3.3.2 Ligand Exchange (CO/O_2) in Haemoglobin

Haemoglobin is the vital oxygen-carrying constituent of blood. It is a complex molecule where each of the four polypeptide chains is bound to one haem group, giving a total of four haem groups per molecule. Each of the haem group is a complex ion containing a hexacoordinated Fe^{2+}.



Five of the coordination sites of the haem group are occupied by nitrogen. Oxygen is reversibly bonded at the 6th site. The $Fe^{2+}-O_2$ coordinate bond is weak, thus allowing oxygen to be transported from one part of the body to another and released to the cells easily.

Ligands such as carbon monoxide (CO) binds more strongly than O_2 with iron ion in haemoglobin to form very stable complexes ($Fe^{2+}-CO$ coordinate bond is stronger than $Fe^{2+}-O_2$ coordinate bond); *i.e.* CO readily displaces oxygen in oxyhaemoglobin (HbO_2) to form carboxyhaemoglobin (HbCO).

$$HbO_2 + CO \rightleftharpoons HbCO + O_2$$

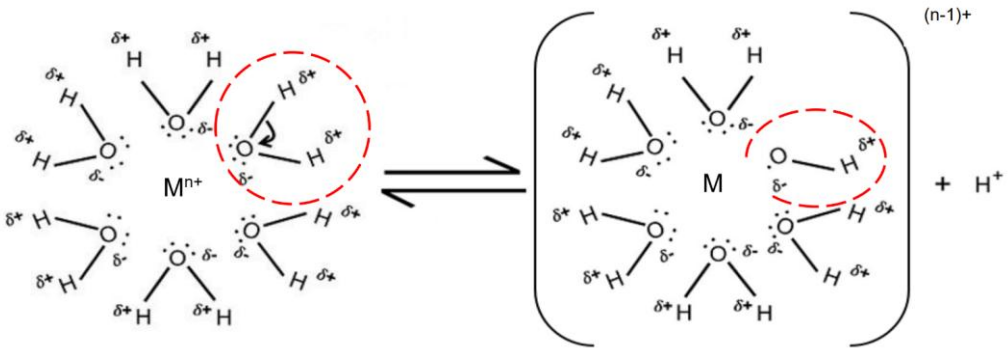
This cuts down the supply of oxygen to the body and accounts for the toxic nature of carbon monoxide and cyanide.

A patient suffering from carbon monoxide poisoning can be treated by being given pure oxygen to breathe.

3.3.3 Acidity of aqua complexes

In aqueous solutions, metal ions with high charge density such as Fe^{3+} form aqua complexes with water ligands. Such metal ions undergo hydrolysis to give weakly acidic solutions.

Note that the metal ions are not limited to transition metal ions, Al^{3+} and Mg^{2+} also undergo hydrolysis in water to give acidic solutions (covered in Periodic Table).



Metal ions with high charge density have high polarising power. They polarise the electron cloud of H_2O and weaken the O−H covalent bond in H_2O, causing one of the six H_2O ligands in the aqua complex to dissociate into OH^- ligand and free H^+.

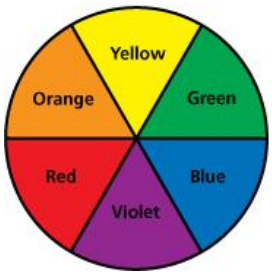
$$[Fe(H_2O)_6]^{3+}(aq) \rightleftharpoons [Fe(H_2O)_5OH]^{2+}(aq) + H^+(aq)$$

$$[Cr(H_2O)_6]^{3+}(aq) \rightleftharpoons [Cr(H_2O)_5OH]^{2+}(aq) + H^+(aq)$$

3.4 Colour of complexes

Transition element compounds in their solid (hydrated crystal form) and aqueous states are usually coloured. Their colour is due to the *uneven absorption* of light in the *visible region* of the electromagnetic spectrum.

Note:



Colours directly opposite each other on the colour wheel are said to be complementary colours.

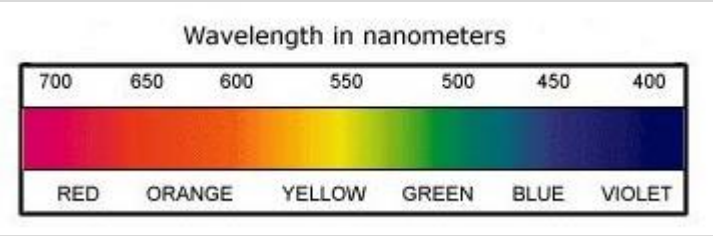
If energy is absorbed in the visible region of the electromagnetic spectrum, then a **colour which is the *complement* of the colour absorbed will be observed**. (Reflected light rays are detected by our eyes.)

The following table shows the relationship between the colour of light absorbed and the observed colour of a compound/ion.

Colour of light absorbed	**Wavelength of light absorbed / nm**	**Observed colour**
Violet	400	Yellow
Blue	450	Orange
Green	500	Red
Yellow	550	Violet
Orange	600	Blue
Red	700	Green

For Your Information (FYI)

The visible region of the electromagnetic spectrum refers to electromagnetic radiation with wavelengths from 400 nm to 700 nm.



The formula for calculating the energy of the electromagnetic radiation is given below, where *h* refers to *Plank's constant*, *c* refers to the speed of light and λ refers to the wavelength of the light.

$$\Delta E = \frac{hc}{\lambda}$$

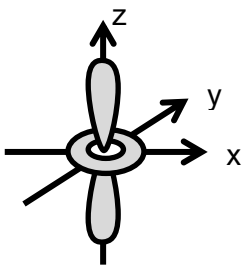
h = 6.63 × 10^{-34} J s, c = 3.00 × 10^{8} m s^{-1} (can be obtained from the Data Booklet)

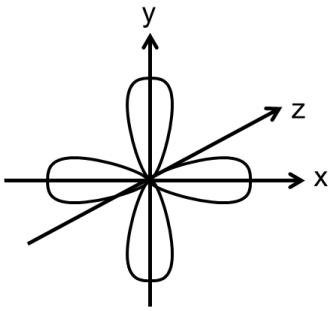
3.4.1 Shapes of d-orbitals (Recap)

There are a total of five d-orbitals in each d-subshell.

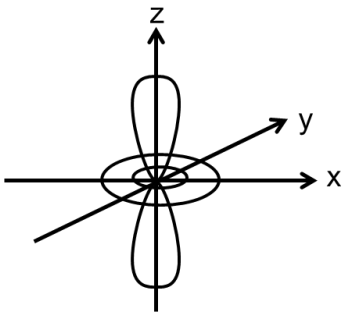
- Two of the orbitals have electron density concentrated **along** the x, y and z axes.

Note:
The actual representation of d_{z^2} orbital.





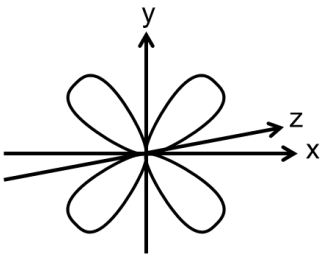
$d_{x^2-y^2}$ orbital



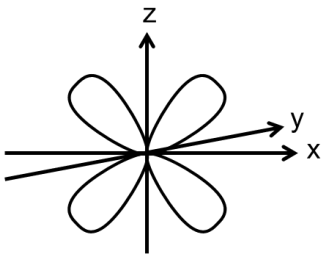
d_{z^2} orbital

- The other three orbitals have electron density concentrated **between** the x, y and z axes.
  E.g. d_{xy} orbital has electron density concentrated between the x and y axes.

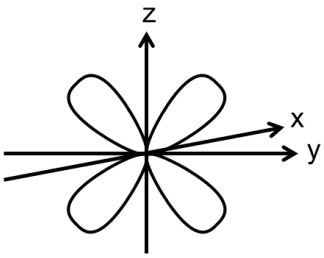
Note:
The lobes of d_{xy}, d_{yz}, d_{xz} orbitals lie between the respective axes while the lobes of $d_{x^2-y^2}$ lie along the x and y axes.



d_{xy} orbital



d_{xz} orbital



d_{yz} orbital

3.4.2 Explanation for Colour of Transition Metal Compounds

Success Criteria:

- I can explain the splitting of degenerate d orbitals into two energy levels in octahedral complexes.
- I can explain d-d transition is required for transition metal compounds to give coloured solids and aqueous solutions.
- I know that the **colour** of transition elements complexes (solids and aqueous solutions) **observed** is the ***complement of the colour*** **absorbed**.

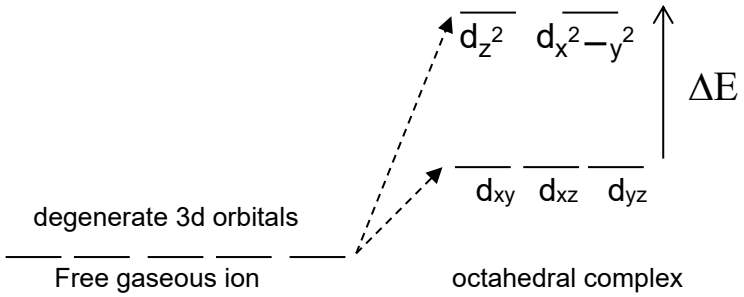
d−splitting (in context of an Octahedral complexes)

- For isolated gaseous transition metal atoms/ions, all the five 3d-orbitals are degenerate (at the same energy level). In forming **octahedral** complexes, six ligands approach the central metal atom/ion ***along the x, y and z axes***, resulting in electrostatic repulsion between the electrons in the 3d orbitals and the lone pairs on the ligands. The energy of an electron in any of the 3d-orbitals will be higher than it is in an isolated atom because of the electronic repulsion.

Note:
For complexes of other shapes, the d-splitting is different as the ligands approach the metal atom/ion from different orientations and electrons in each d-orbital are repelled to different extent.

- The ***energy of an electron*** in the **$3d_{x^2-y^2}$ and $3d_{z^2}$** orbitals will ***be raised by a greater extent*** as compared to the electrons in the **$3d_{xy}$, $3d_{xz}$ and $3d_{yz}$** orbitals. This is due to the ***stronger inter-electronic repulsion*** arising as a result of the ***"head-on" approach*** between the ligand lone pair and the electrons in the $3d_{x^2-y^2}$ orbital and the $3d_{z^2}$orbital.

- Hence, the five 3d-orbitals are split into two energy levels as shown in the figure below. The difference in energy between the two energy levels, ***ΔE***, also called the ***crystal field splitting energy*** and its magnitude is determined by the nature or strength of the approaching ligand as well as the number of electrons in the d orbitals.



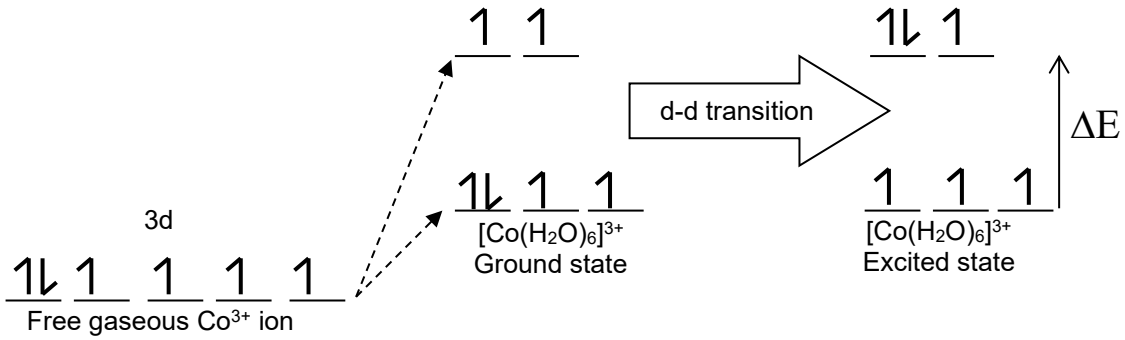
Splitting of 3d-orbitals into two energy levels in an octahedral environment

d-d transition of electrons

- The difference in energy between the two energy levels, ***ΔE***, often falls in the energy range of ***visible light***.

- Consequently, when light falls on a transition metal compound/ion, light of a particular wavelength ($\Delta E = \frac{hc}{\lambda}$) may be absorbed to promote the electrons from the lower energy d-orbitals to the higher energy d-orbitals. This is known as the ***d-d transition***.

E.g. d-d transition of $[Co(H_2O)_6]^{3+}$ **[Ar] 3d^6**



Colour observed

- The colour observed is the **complement** of the **colour absorbed**. Thus, the transition metal compound/ion will have a characteristic colour.

(IMPORTANT!)
Summarised explanation for colour of transition element compounds:

The colour of a transition element compound in the hydrated crystal form or in the aqueous solution is explained as:

- In the **presence of ligands, electronic repulsion** between lone pair electrons of ligands and the electrons in d orbitals causes the **degenerate d-orbitals** of the transition metal ion **to split into two different energy levels with a small energy gap, ∆E (d splitting).**

- As the **3d subshell is partially filled**, electrons in the **lower energy d-orbitals** can **absorb light of a certain wavelength in the visible light spectrum** with energy corresponding to the energy gap, ∆E, and be **promoted to the higher energy d-orbitals (d−d transition).**

- The colour observed is the **complement of the colour absorbed**.

3.4.3 Factors Affecting Colours of Transition Metal Complexes

Factor 1 : Number of d-electrons present

Complexes of the same transition metal in different oxidation states show different colours.

E.g. $Fe^{2+}(aq)$ or $[Fe(H_2O)_6]^2$ pale green $Fe^{3+}(aq)$ or $[Fe(H_2O)_6]^{3+}$ yellow

- Different numbers of electrons in the d-orbitals have a different degree of repulsion with the lone pairs in the ligands, splitting the 3d orbitals with different energy gaps $(\Delta E = \frac{hc}{\lambda})$.
- A different wavelength of the visible light is absorbed during d-d transition.
- A different complementary colour is observed.

Factor 2: Nature of Ligands

Complexes of the same transition metal with different ligands show different colours.

E.g. $[Cu(H_2O)_6]^{2+}$ blue $[Cu(NH_3)_4]^{2+}$ deep blue

- Different ligands cause different degree of repulsion with the electrons in the 3d orbitals, splitting the 3d orbitals with different energy gaps $(\Delta E = \frac{hc}{\lambda})$.
- A different wavelength of the visible light is absorbed during d-d transition.
- A different complementary colour is observed.

Worked Example 4

Why are Sc^{3+}, Cu^+ and Zn^{2+} compounds white and form colourless solutions?

Answer

The electronic configuration for the ions are:

Sc^{3+}: [Ar] $3d^0$ Cu^+: [Ar] $3d^{10}$ Zn^{2+}: [Ar] $3d^{10}$

For Sc^{3+}, there are no electrons in the 3d subshell,

- in the presence of ligands, d splitting **does not occur.**
- no d-d transition is possible,
- light from the visible light spectrum is not absorbed, and the solution appears colourless.

For Cu^+ and Zn^{2+}, the 3d subshell is fully filled,

- in presence of ligands, d splitting occurs.
- **since 3d subshell is fully filled,** no d-d transition is possible,
- light from the visible light spectrum is not absorbed, and the solution appears colourless.

3.4.4 Common transition metal compounds and their colours

Transition Metal	Oxidation no. of central metal cation	Formula	Colour
Manganese (Mn)	+2	$[Mn(H_2O)_6]^{2+}$	Pale pink solution
		$Mn(OH)_2$	Off-white **ppt**
	+4	MnO_2	Brown **ppt**
	+7	MnO_4^-	Purple solution
Iron (Fe)	+2	$[Fe(H_2O)_6]^{2+}$	Pale green solution
		$Fe(OH)_2$	Dirty green **ppt**
	+3	$[Fe(H_2O)_6]^{3+}$	Yellow solution
		$Fe(OH)_3$	Reddish brown **ppt**
		$[Fe(SCN)(H_2O)_5]^{2+}$	Blood red solution
Copper (Cu)	+1	$CuCl$, CuI	White **ppt**
	+2	$[Cu(H_2O)_6]^{2+}$	Blue solution
		$Cu(OH)_2$	Pale blue **ppt**
		$[Cu(NH_3)_4]^{2+}$	Deep blue solution
		$[CuCl_4]^{2-}$	Yellow solution
Chromium (Cr)	+3	$[Cr(H_2O)_6]^{3+}$	Green solution
		$Cr(OH)_3$	Grey-green **ppt**
		$[Cr(OH)_6]^{3-}$	Dark Green solution
	+6	$*CrO_4^{2-}$	Yellow solution
		$*Cr_2O_7^{2-}$	Orange solution

***Chromate(VI) to dichromate(VI) interconversion** is not a redox reaction as there is no change in oxidation number. It is an "acid-base" reaction.

$$\underset{\text{yellow}}{2\,CrO_4^{2-}} + 2\,H^+ \rightleftharpoons \underset{\text{orange}}{Cr_2O_7^{2-}} + H_2O$$

3.5 Catalytic activity

Success Criteria:

- I can differentiate and explain the mode of actions of heterogenous catalysts and homogeneous catalyst.

Transition metals and their compounds are commonly used as catalysts. A **catalyst** is a substance which alters *the rate of a reaction*, without itself undergoing any permanent chemical change. It speeds up the rate of reaction by providing an *alternative pathway which involves a lower activation energy* than the uncatalysed reaction.

	Catalyst and reactants	**Reason for catalytic ability**
Heterogeneous Catalyst	Different phases	Incomplete d-subshell
Homogeneous Catalyst	Same phase	Variable oxidation states of transition metal cation

3.5.1 Heterogeneous Catalysis

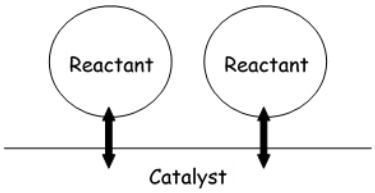
Transition elements and their compounds can act as heterogeneous catalysts **due to the presence of an incomplete d-subshell** which can act as electron acceptors from the reactants. Thus, weak interactions are formed between the reactant particles and the catalyst surface, thereby lowering the activation energy.

Mode of action in heterogeneous catalysis:

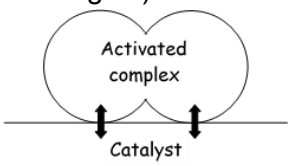
Note:
Adsorption is the adhesion of particles to a surface.

This is different from "absorption" where particles are drawn into the material.

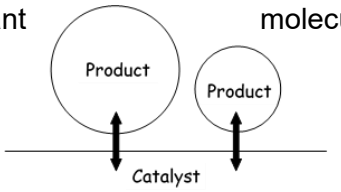
Step 1: **Adsorption** of reactant molecules onto the active sites of the catalyst surface through weak interactions.



Step 2: **Reaction** at the catalyst surface occurs at a faster rate as reactant molecules are brought closer together in the correct orientation for reaction and existing bonds within the reactant molecules are weakened, thereby reducing E_a)



Step 3: **Desorption** of product molecules from the catalyst surface. Catalyst is regenerated and there are vacant active sites available for adsorbing other reactant molecules.



Examples of heterogeneous catalyst

Note:
Transition metals are particularly effective as heterogeneous catalysts since they have partially filled d-orbitals which can be utilized in bonding.

solid catalyst	Reaction catalysed (usually involves gaseous reactants)
Fe or Fe_2O_3	**Haber process**: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
V_2O_5	**Contact process**: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
Ni	**Hardening of vegetable oils to manufacture margarine** $RCH{=}CH_2 + H_2 \longrightarrow RCH_2CH_3$
Pt, Pd or Rh	**Removal of polluting substance from the car exhaust (catalytic converter)** $2CO(g) + 2NO(g) \longrightarrow 2CO_2(g) + N_2(g)$

3.5.2 Homogeneous catalysis

Transition metal cations can act as homogeneous catalysts as the transition elements **can exhibit variable oxidation states**. The ease of inter-conversion of the oxidation states enables the ions of transition elements to provide chemical reactions with an alternative pathway of lower activation energy.

E.g. $S_2O_8^{2-}(aq) + 2I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_2(aq)$

[O] $2\,I^-(aq) \longrightarrow I_2(aq) + 2e^-$ $\quad E^\ominus(I_2/I^-) = +0.54$ V

[R] $S_2O_8^{2-}(aq) + 2e^- \longrightarrow 2SO_4^{2-}(aq)$ $\quad E^\ominus(S_2O_8^{2-}/SO_4^{2-}) = +2.01$ V

Since $E^\ominus_{cell} = +2.01 - 0.54 = +1.47$ V > 0, hence the reaction is expected to occur spontaneously.
However, the rate of this reaction is very slow. There is high activation energy due to the collision of two negatively-charged ions (experiencing electrostatic repulsion).

A possible *catalysed pathway* with Fe^{2+} as the catalyst involves 2 steps.

Step 1: Formation of intermediate (Fe^{2+} colliding with $S_2O_8^{2-}$)

	$E^\ominus$/V
$Fe^{3+}(aq) + e^- \rightleftharpoons$ **Fe^{2+}**(aq)	+0.77
$S_2O_8^{2-}$ $(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq)$	+2.01

Overall: $S_2O_8^{2-}(aq) + 2Fe^{2+}(aq) \longrightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)$

$E^\ominus_{cell} = +2.01 - 0.77 = +1.24$ V

Step 2: Regeneration of catalyst

	$E^\ominus$/V
Fe^{3+} $(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$I_2(aq) + 2e^- \rightleftharpoons$ **$2I^-$**(aq)	+0.54

Note:
If Fe^{3+} is used instead, the two steps above will take place in the reverse order and the net effect will still be the same.

Overall: $2I^-(aq) + 2Fe^{3+}(aq) \longrightarrow I_2(aq) + 2\,Fe^{2+}(aq)$

$E^\ominus_{cell} = +0.77 - 0.54 = +0.23$ V

(a) This two-step reaction provides a lower energy pathway because both steps involve collision between oppositely-charged ions.

(b) Other transition metal cations can also catalyse the reaction as long as their $E^\ominus$ values are between +0.54 V and +2.01 V.

Annex: Cis-Trans isomerism in Complex ions

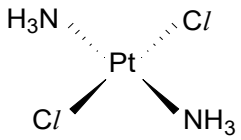
Transition metal complexes can show both cis-trans isomerism in both square planar and octahedral monodentate complexes.

Cis-trans isomerism: Square planar complexes

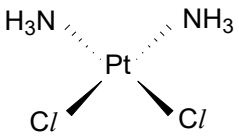
Cis-trans isomerism occurs in square planar complexes with two different pairs of ligands.

- Trans isomer – occurs when the pairs are *opposite* to each other.
- Cis isomer – Occurs when the pairs are *adjacent* to each other.

Example: $Pt(NH_3)_2Cl_2$



trans



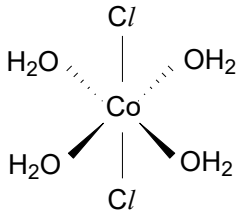
cis

Cis-trans isomerism: Octahedral monodentate complexes

In cis-trans isomerism, the octahedral complex must have two different types of monodentate ligands.

The ligands are in different positions relative to one another.

Example: $CoCl_2(H_2O)_4$



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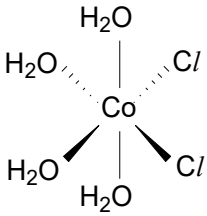


cis

- Trans isomer – occurs when the chloride ions are at *opposite* ends of the complex.
- Cis isomer – occurs when the chloride ions are on the *same* side of the complex.

An Introduction to the Chemistry of Transition Elements Tutorial

Self Attempt Questions:

Physical Properties of Transition Elements

1 **(a)** What do you understand by the term transition metal?

(b) **(i)** State the electronic configuration of V, Cr and Cr^{3+}.

(ii) Explain why the 1st ionisation energies of vanadium and chromium are similar.

(c) Explain why chromium has a higher melting point (1907 °C) than calcium (842 °C).

2 Which oxidation states can be found for chromium in its compounds?

1 +3 **2** +6 **3** +7

A All of the above **B** **1** and **2** only **C** **2** and **3** only **D** **1** only

3 The cation of a transition metal M forms a complex ion with formula $[M(CN)_6]^{4-}$. The same cation also forms a complex ion with formula $[M(NH_3)_4]^{x}$.
What is the value of ***x***?

A 4− **B** 2− **C** 2+ **D** 3+

4 Which property is true for all ligands in complex ions?

1 Ligands have at least one lone pair of electrons.
2 Ligands form dative bonds.
3 Ligands are only negative ions.

A All of the above **B** **1** and **2** only **C** **2** and **3** only **D** **1** only

5 A crystalline salt, ***Z***, was dissolved in water and then aqueous sodium hydroxide was added until present in excess. A white precipitate was formed, which turned brown on exposure to the air.
Which could be ***Z***?

A $Al_2(SO_4)_3$ **B** $MnSO_4$ **C** $FeSO_4$ **D** $Fe_2(SO_4)_3$

Answer key to MCQ:

2	3	4	5
B	C	B	B

Discussion Questions:
Oxidation Number, Ligands and Complexes

6 Which type of bonds are present in the compound $[Cu(NH_3)_4]C\mathit{l}_2$?

1 Dative covalent **2** Ionic **3** Hydrogen bonding

A All of the above **B** **1** and **2** only **C** **2** and **3** only **D** **1** only

7 Chromium(III) chloride combines with ammonia to form compound **X** in which the coordination number of chromium is 6. When solution **X** is treated with an excess of aqueous $AgNO_3$, only two thirds of the total chloride present is precipitated as $AgC\mathit{l}$.

What is the formula of compound **X**?

A $Cr(NH_3)_3C\mathit{l}_3$ **B** $Cr(NH_3)_4C\mathit{l}_3$ **C** $Cr(NH_3)_5C\mathit{l}_3$ **D** $Cr(NH_3)_6C\mathit{l}_3$

8 The anti-cancer drug 'cisplatin' is a complex of platinum with both ammonia and chloride as ligands. It has the formula $[Pt(NH_3)_2C\mathit{l}_2]$.

(i) Give the oxidation number and coordination number of platinum in 'cisplatin'.

(ii) State and draw the shape of the complex, given that it is polar and have cis-trans isomers.

Redox Reactions

9 When excess zinc powder is added to aqueous solution of ammonium vanadate(V), NH_4VO_3, a series of colour changes occurs.

Explain this observation with appropriate equations and $E^{\ominus}$ values from the *Data Booklet*.

10 The decomposition of hydrogen peroxide is very slow and can be catalysed by a *homogeneous* catalyst.

(i) By considering relevant $E^{\ominus}$ values from the *Data Booklet*, show by means of equations, how $Mn^{2+}(aq)$ ions can act as a *homogenous* catalyst in this reaction.

(ii) Suggest another suitable transition metal ion that can also act as a *homogenous* catalyst in this reaction.

11 ***N2007/I/36*** Use of the Data Booklet is relevant to this question.
Which compound is chemically stable when left to stand in the atmosphere?

1 A solution of potassium hexacyanoferrate(III)
2 A solution of chromium(II) chloride
3 A mixture of aqueous sodium hydroxide and iron(II) sulfate

A All of the above **B** **1** and **2** only **C** **2** and **3** only **D** **1** only

Ligand Exchange Reactions and Qualitative Analysis

12 A student dissolved some cobalt(II) chloride crystals in water. A pink solution was formed. She then added concentrated hydrochloric acid to this solution. A blue solution containing a complex ion with coordination number = 4 was formed.

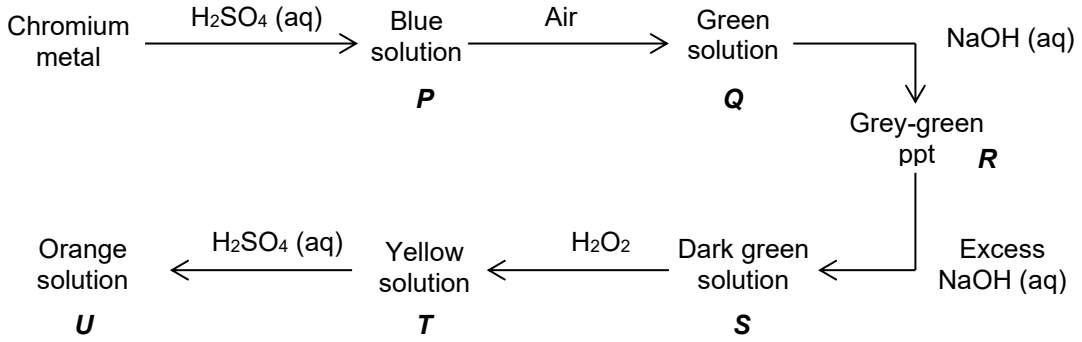
(i) Give the formula of the complex ion in each solution.

(ii) Write a balanced equation to illustrate the equilibrium that exists between these two complex ions in solution.

(iii) The student added an excess of aqueous silver nitrate, $AgNO_3(aq)$, to the blue solution. A white precipitate formed and the solution turned pink. Suggest an explanation for these observations.

(iv) Another sample of pink aqueous solution of cobalt(II) chloride changes to purple when a crystal of ammonium thiocyanate, NH_4SCN, is added to it.
Why is a different colour observed when SCN^- ions are added to the cobalt(II) solution?

13 The following sequence of reactions involving chromium illustrates many of the characteristic properties of transition metals.

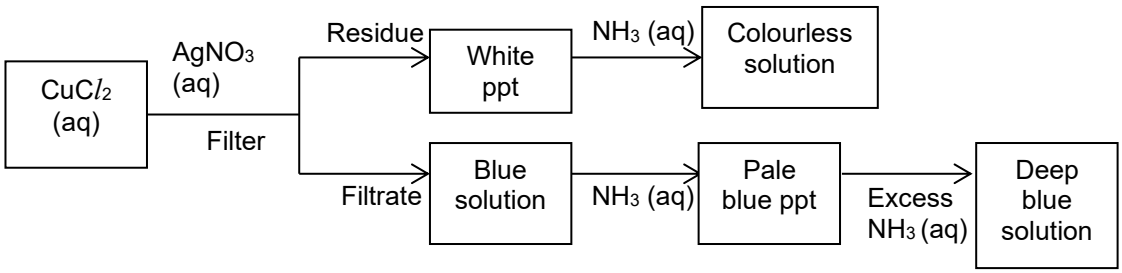


(i) Give the formula of the chromium-containing species in ***P, Q, R, S, T*** and ***U***.

(ii) When barium nitrate is added to the aqueous solution of salt ***P***, a white precipitate is seen which is insoluble upon the addition of dilute nitric acid.
Suggest the identity of the white precipitate.

(iii) Explain why the effervescence of a colourless and odourless gas is observed when zinc is added to a fresh sample of aqueous solution of ***Q***. Include relevant equations in your answer.

14 Aqueous copper(II) chloride, $CuCl_2$, is a green-blue solution which gives the following reactions.

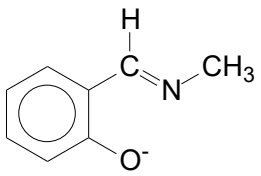


(i) Explain the observations above, include equations when necessary.

(ii) How would the observations be different if $CuCl_2$ is replaced by ZnI_2?

Application Questions

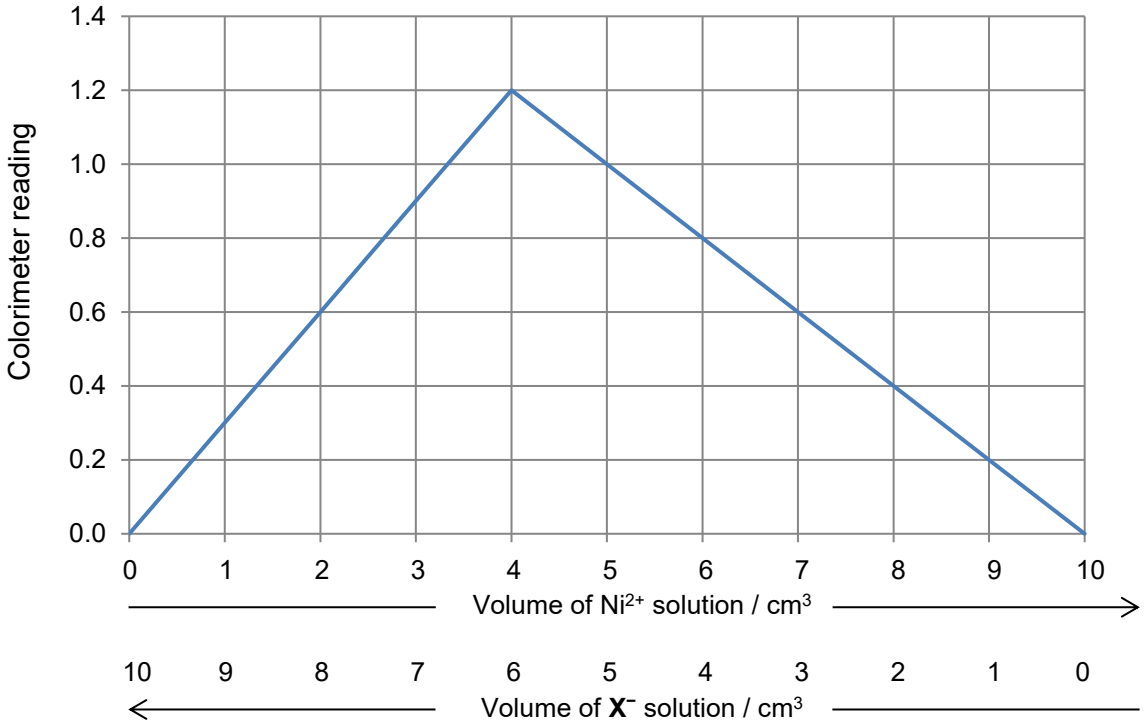
15 The complex of nickel with ligand $\mathbf{X}^-$ (shown below) is red at room temperature.



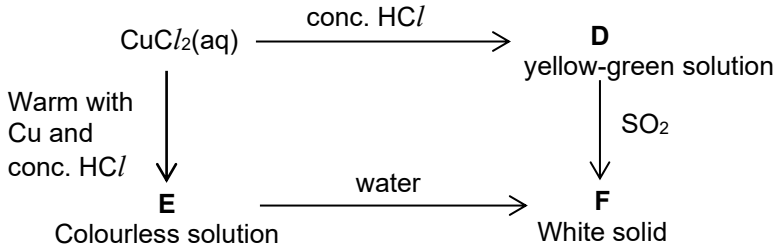
Ligand $\mathbf{X}^-$

The following graph was obtained when the colour intensities of various mixtures of 4×10^{-3} mol dm^{-3} solution of $\mathbf{X}^-$ and 3×10^{-3} mol dm^{-3} solution of nickel(II) chloride were measured using a colorimeter at room temperature.

Determine the formula of the complex.



16 (a) ***[N2008/II/4 modified]*** Aqueous $CuCl_2$ undergoes the following reaction.



D and **E** contain complex ions of copper and chlorine. **F** is a compound of copper and chlorine only.

When $CuCl_2$(aq) is converted to **D** and into **E**, one mole of $CuCl_2$ reacts exactly with two moles of HCl. In each case no other compound is formed.

The oxidation number of copper in **E** is the same as **F**.

(i) Write balanced equations for the formations of **D** and **E** from $CuCl_2$ respectively.

(ii) Suggest the formula of the complex ions present in **D** and of the complex ion present in **E**.

(iii) What type of reaction occurs when **D** is formed from $CuCl_2$(aq)?

(iv) Suggest the shape of the complex ion present in **D**.

(v) What is the oxidation number of copper in the complex ion in **E**?

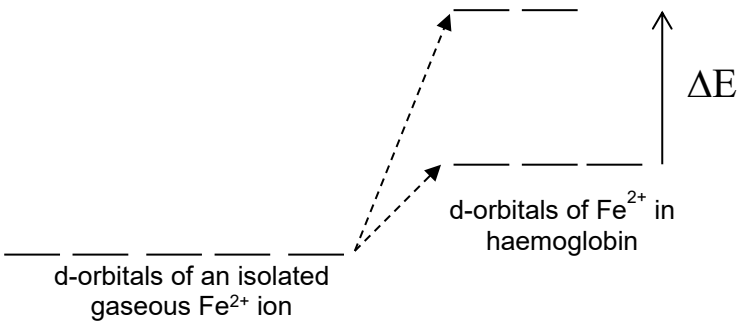
(vi) What type of reaction occurs when **D** is converted to **F**?
Suggest a formula for compound **F**.

(vii) Explain why **E** and **F** are both colourless.

(b) When a sample of copper(I) sulfate is added to water, a pink solid ***Y*** and a pale blue solution ***Z*** are obtained.
Identify ***Y*** and ***Z***. Explain the above observation, using relevant data from the *Data Booklet.*

17 ***[N2011/III/4(c)]*** The iron atom in haemoglobin has an oxidation state of +2 and is surrounded by five nitrogen-containing ligands, and one oxygen-containing ligand, which is H_2O in deoxyhaemoglobin and O_2 in oxyhaemoglobin.

In the absence of the ligands, the d-orbitals in free gaseous Fe^{2+} are degenerate (same energy). However, in an octahedral environment, the d-orbitals are split as in the diagram below.



(i) Use this diagram to outline the origin of the red colour of haemoglobin.

When H_2O in haemoglobin is changed to O_2, the Fe^{2+} ion changes its electronic configuration from a "high spin" state to a "low spin" state.

In a "high spin" state, the electrons occupy all the d-orbitals singly, before starting to pair up in the lower energy d-orbitals.

In a "low spin" state, the lower energy d-orbitals are filled up first, by pairing up if necessary, before the higher energy d-orbitals are used.

(ii) Use diagrams like the one above to show the electronic distribution of a Fe^{2+} ion in a high spin state, and in a low spin state.

(iii) Suggest why electrons usually prefer to occupy orbitals singly, rather than in pairs.

(iv) Use this explanation, together with the information given above concerning the spin states of deoxyhaemoglobin and oxyhaemoglobin, state and explain which of the two haemoglobins will contain the larger energy gap, E, between its d-orbitals.

Answers to Discussion Questions MCQ:

6	7	10
B	C	D

Integrated Questions

18 ***N2021/II/5***

Iron is essential to health, but if excessive amounts are consumed it can be harmful. The pharmaceutical industry tests medicines to ensure they do not contain any iron that might have been accidentally added during the manufacturing process.

A 'limit test' for iron can be used to check that a medicine does not contain too much iron.

Method for the limit test for iron.

A standard solution of iron of known concentration is prepared. A sample solution of the medicine to be tested is also prepared.

To both solutions;
Step 1. Add an excess of thioglycolic acid followed by a solution of ammonia.
Step 2. Mix and leave for 5 minutes.
Step 3. Compare the colour of the two solutions. If the sample solution is darker than the standard solution, it contains an unacceptably large concentration of iron ions.

Thioglycolic acid carries two functions in this process; to convert any Fe^{3+} to Fe^{2+} and then to complex with the Fe^{2+} ions.

Equation 5.1 describes the reaction of thioglycolic acid with any iron(III) ions present in the sample.

Equation 5.1 $2\ HSCH_2CO_2H + 2Fe^{3+} \longrightarrow 2\ Fe^{2+} + {}^{-}O_2CCH_2{-}S{-}S{-}CH_2CO_2^{-} + 4\ H^+$

When thioglycolic acid reacts with the iron(II) ions, ligand exchange occurs and a colourless complex, **L**, is formed, $Fe(SCH_2CO_2H)_2$.

In basic conditions, **L** forms a pink-coloured complex **M**, $[Fe(SCH_2CO_2)_2]^{2-}$. The depth of the colour of the complex formed depends on the concentration of iron(II) ions and ranges from pale to deep red/purple as the concentration of iron(II) ions increases. Each ligand forms two bonds with the central iron(II) ion.

(a) Identify the role of thioglycolic acid when it reacts with the iron(III) ions. Explain your answer.

(b) Draw a diagram of the structure of complex **M**, showing the 3-dimensional arrangement around the central iron ion. Indicate the overall charge on this complex.

(c) Suggest why ammonia is added to the solutions in step 1.

(d) Construct an equation to show the reaction occurring when **L** reacts with ammonia to form **M** in step 1.

(e) When $NH_3(aq)$ is added directly to a standard sample of $[Fe(H_2O)_6]^{2+}$, a small amount of green precipitate is initially observed; this turns brown on standing in air.

(i) Complete the equation which describes the formation of the green precipitate from 1 mole of $[Fe(H_2O)_6]^{2+}$. Include state symbols.

$[Fe(H_2O)_6]^{2+}(aq) + \ldots\ NH_3(aq) \rightarrow$ ……

(ii) Suggest why the green precipitate turns brown.

(f) The standard solution of iron(II) is prepared by making a standard solution of $Fe(NH_4)_2(SO_4)_2.6H_2O$.

A sample of x g of $Fe(NH_4)_2(SO_4)_2.6H_2O$ is weighted and transferred to a 250.0 cm^3 volumetric flask. It is dissolved in sulfuric acid and made up to the required volume using deionised water. 10.00 cm^3 of this solution is taken and transferred to a volumetric flask. Deionised water is added to make a total volume of 100.0 cm^3 of diluted solution.
This diluted solution contains 10.0 ppm of iron ions.
(1 ppm of iron(II) ions = 1 mg of iron(II) ions in 1000 cm^3 of solvent.)

[M_r $Fe(NH_4)_2(SO_4)_2.6H_2O$ = 392.0]

Calculate the value of x in g. Show your working.

(g) When the human body absorbs too much iron, it is stored in organs such as the heart and liver and can cause health problems.

Drugs can be used to remove the excess iron by forming soluble complexes with the stored iron which can then be removed.

The table below describes two of these iron-removing drugs, **Y** and **Z**.

Drug	Molecular formula	M_r
Y	$C_7H_9NO_2$	139.0
Z	$C_{25}H_{48}N_6O_8$	560.0

The soluble complexes made when either **Y** or **Z** combine with iron
- Only contain iron and either **Y** or **Z**
- Contain one iron atom in an octahedral complex.

1 g of **Y** reacts with 2.40×10^{-3} mol of stored iron.
1 g of **Z** reacts with 1.78×10^{-3} mol of stored iron.

Calculate the number of bonds formed by each ligand, **Y** or **Z**, when each one combines with one central iron ion to form the complex.

19 **(a)** Aqueous solutions of chlorine and iodine are added separately to two test-tubes each containing Fe^{2+} ions. Aqueous sodium hydroxide is then added to each test-tube. Results are given in the table below.

	Cl_2(aq) added	I_2(aq) added
Fe^{2+}(aq)	Green solution turns yellow	No observable change
After addition of NaOH (aq)	Brown precipitate	Green precipitate

(i) What does the colour change when Cl_2(aq) is added to Fe^{2+}(aq) indicate? Use $E^{\ominus}$ values from the *Data Booklet* to explain your answer.

(ii) Explain why there is no change when I_2(aq) is added to Fe^{2+}(aq).

(b) When I^-(aq) are added to Fe^{3+}(aq), a brown solution is obtained. However, when the same process is repeated in the presence of excess CN^- ions, no brown solution is observed.

Using the *Data Booklet*, explain the difference in the observations of the two experiments.

(c) In an experiment, a student added aqueous potassium fluoride to a sample of yellow iron(III) chloride solution. It was noted that the solution decolourised, forming $[FeF_5(H_2O)]^{2-}$.

(i) What type of reaction has occurred?

(ii) Suggest a reason why $[FeF_5(H_2O)]^{2-}$ is colourless.

(d) **(i)** The pH of a 0.150 mol dm^{-3} solution of iron(III) chloride was found to be pH 1.52.

Calculate the acid dissociation constant, K_a, of $[Fe(H_2O)_6]^{3+}$.

(ii) Explain why the pH of a solution of iron(II) chloride is higher than that of a solution of iron(III)chloride of the same concentration.

(e) Iron metal catalyses the reaction between nitrogen and hydrogen in the Haber Process.

(i) What type of catalysis does this illustrate?

(ii) Explain how iron catalyses this reaction.