Raffles Institution
Year 6 Chemistry 2023
Lecture Notes 23 – An Introduction to the Chemistry of Transition Elements

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Learning Outcomes

Candidates should be able to:

(a) explain what is meant by a transition element, in terms of d-block elements forming one or more stable ions with partially filled d subshells
(b) state the electronic configuration of a first row transition element and of its ions
(c) explain why atomic radii and first ionisation energies of the transition elements 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
(h) predict, using $E^\ominus$ values, the likelihood of redox reactions (see Electrochemistry I)
(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 metals and/or their compounds can act as catalysts (see Reaction Kinetics)

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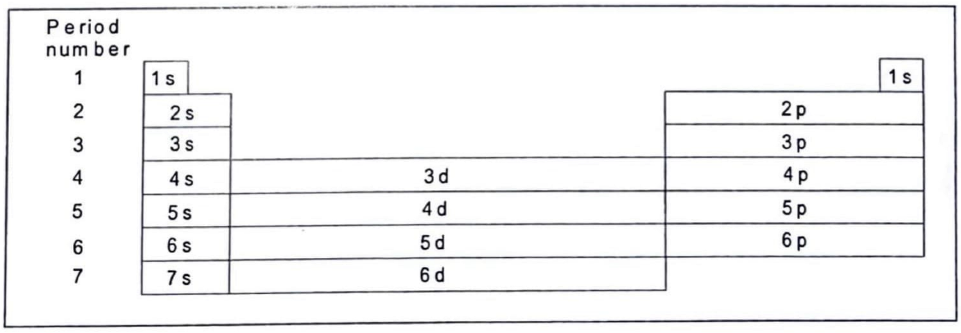
1. INTRODUCTION

1.1 The d-block elements

- These elements have atoms in which either the **inner 3d, 4d, 5d** or **6d subshells** are being filled up. Their atoms are characterised by 'inner building' of d subshells.



- We will focus on the **first row** of the **d-block elements**.

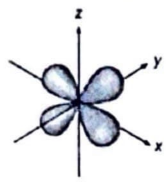
21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4

- The 3d row contains **ten elements**, because the **3d subshell** contains **five orbitals**, each able to accommodate up to two electrons. These elements involve the filling of the 3d orbitals.

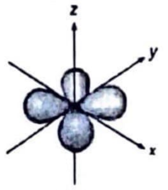
- They are all metals and tend to be hard metals compared with the s-block metals.

1.2 Shapes of the 3d orbitals

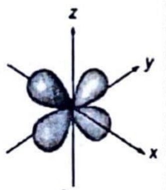
- There are **five d orbitals** (i.e. d_{xz}, d_{xy}, d_{yz}, $d_{x^2-y^2}$ and d_{z^2}) in a d subshell.



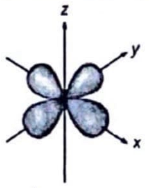
d_{xz}



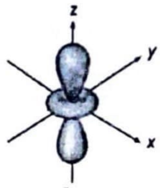
d_{xy}



d_{yz}



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



d_{z^2}

- These three orbitals have a similar 4–lobed shape.
- These orbitals have their lobes **pointing between the axes.**

- This orbital also has a 4–lobed shape but it has its lobes **aligned along the x and y axes.**

- This orbital consists of a dumb–bell surrounded by a small doughnut shaped ring at its waist
- This orbital is **aligned along the z axis.**

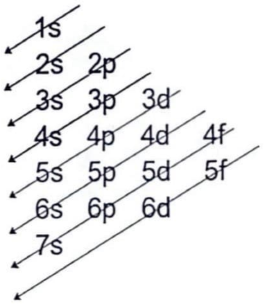
1.3 Electronic Configurations of the Elements

- The principles that govern the distribution of electrons in the orbitals are:

The Aufbau (building-up) Principle
- Electrons fill orbitals from the lowest energy orbital upwards.

The Pauli Exclusion Principle
- No more than two electrons may occupy a single orbital and, if two electrons do occupy a single orbital, their spins must be opposite.

Hund's Rule
- Orbitals of a sub-shell (degenerate) must be occupied singly and with parallel spins before they can be occupied in pairs (with opposite spins).



- Recall from Atomic Structure:
  - Electrons occupy the 4s subshell before the 3d subshell.
  - When filled, the 4s subshell has a higher energy than the 3d subshell

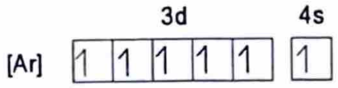
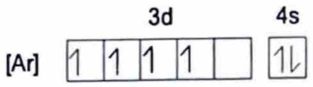
- Electronic configuration of the first-row d-block elements

Element	'Electrons-in-boxes' diagram							Electronic configuration
		3d					4s	
$_{21}$Sc	[Ar]	↑					↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ **$3d^1$ $4s^2$**
$_{22}$Ti	[Ar]	↑	↑				↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ **$3d^2$ $4s^2$**
$_{23}$V	[Ar]	↑	↑	↑			↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ **$3d^3$ $4s^2$**
$_{24}$Cr	[Ar]	↑	↑	↑	↑	↑	↑	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ **$3d^5$ $4s^1$**
$_{25}$Mn	[Ar]	↑	↑	↑	↑	↑	↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ **$3d^5$ $4s^2$**
$_{26}$Fe	[Ar]	↑↓	↑	↑	↑	↑	↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ **$3d^6$ $4s^2$**
$_{27}$Co	[Ar]	↑↓	↑↓	↑	↑	↑	↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ **$3d^7$ $4s^2$**
$_{28}$Ni	[Ar]	↑↓	↑↓	↑↓	↑	↑	↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ **$3d^8$ $4s^2$**
$_{29}$Cu	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ **$3d^{10}$ $4s^1$**
$_{30}$Zn	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ **$3d^{10}$ $4s^2$**

Two exceptions:

1. Electronic configuration of chromium: **$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$**

   For Cr, the configuration [Ar] $3d^5\ 4s^1$ is **more stable** than [Ar] $3d^4\ 4s^2$.

 The electrons occupy the 3d and 4s orbitals singly so that interelectronic repulsion is minimised.	 There is a repulsion between the two 4s electrons within the same orbital.

2. Electronic configuration of copper: **$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$**

   For Cu, the configuration [Ar] $3d^{10}\ 4s^1$ is **more stable** than [Ar] $3d^9\ 4s^2$.

1.4 Electronic Configurations of the Ions

- In the formation of cations, the 4s electrons, which are at a higher energy level than the 3d electrons, are removed first.
- To write the electronic configuration of ions,

  Step 1: Write out the electronic configuration of **element**, filling the **4s orbital first** before the 3d orbitals.

  Step 2: Remove the **4s electrons first before the 3d electrons.**

Example:

	Electronic configuration
Cr	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$
Cr^+	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$
Cr^{2+}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^4$
Cr^{3+}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$

	Electronic configuration
Fe	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$
Fe^+	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^1$
Fe^{2+}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$
Fe^{3+}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$

Exercise 1

For which transition element does its ground state atom have an unpaired electron in its s orbital?

A chromium
B cobalt
C iron
D manganese

A

Exercise 2

Which one of the following represents the electronic configuration of the +1 ion of an element with atomic number 29?

A $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9\ 4s^2$
B $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9\ 4s^1$
C $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$
D $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$

D

1.5 The Transition Elements

A **transition element** is a d-block element which can form one or more stable ions with a partially filled d subshell.

- Based on the above definition, which first row d-block elements are **not** transition elements?

Scandium and zinc are not transition elements since they do not form any stable ions with a partially filled d subshell. They ONLY form Sc^{3+} and Zn^{2+} ions respectively that do not have partially filled d subshell.

Sc	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$	Zn	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$
Sc^{3+}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$	Zn^{2+}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$

- The element copper forms Cu^+ ion (electronic configuration: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$) which has a fully filled d subshell. Is copper a transition element?

Copper is still regarded as a transition element because it can form Cu^{2+} ion with a partially filled d subshell.

Cu $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$ Cu^{2+} $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$

transition elements

21	22	23	24	25	26	27	28	29	30
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
scandium	titanium	vanadium	chromium	manganese	iron	cobalt	nickel	copper	zinc
45.0	47.9	50.9	52.0	54.9	55.8	58.9	58.7	63.5	65.4

d-block elements

2. GENERAL PHYSICAL PROPERTIES

- The first-row transition elements are all metals and all elements are remarkably **similar** in their physical properties.
  - they are hard and have high densities
  - they have high melting and boiling points
  - they are good conductors of heat and electricity

2.1 Atomic Radius

The atomic radii of the first-row transition elements (in particular, from V to Cu) in Period 4 are **almost constant / relatively invariant.**

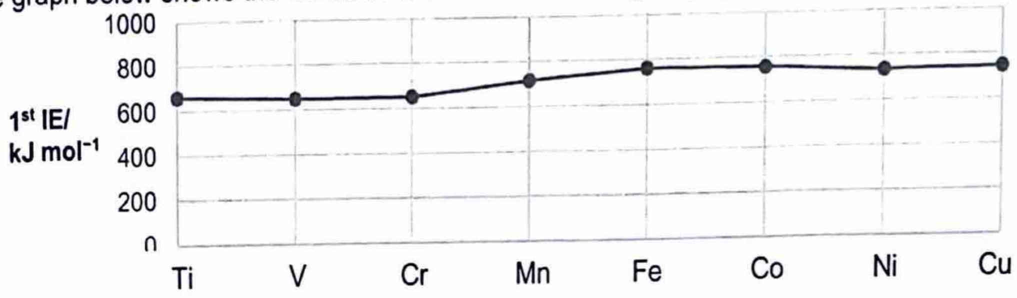
Element	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Atomic radius/nm	0.146	0.135	0.129	0.132	0.126	0.125	0.124	0.128

- In traversing the first-row transition elements, the **number of protons increases**, and hence, the **nuclear charge increases**.
- As electrons are added to the 3d subshell, the **increase in the number of inner 3d electrons provide more shielding** between the nucleus and the outer 4s electrons.
- This **increase in shielding effect offsets the increase in nuclear charge** considerably.
- Hence, there is only a **small increase in the effective nuclear charge**, and the force of attraction between the nucleus and outer electrons only increases slightly.
- The atomic radii are **relatively constant / relatively invariant**.
- Some of the first-row transition elements readily form alloys with each other partly because they have similar atomic radii.

2.2 Ionisation Energies

The **first ionisation energies** of the transition elements from Ti to Cu is **almost constant / relatively invariant.**

The graph below shows the variation of 1st ionisation energies (IE) from Ti to Cu.



First IE of transition elements is almost constant / relatively invariant. This is because

- The electron being removed comes from the 4s orbital.
- Across a period, **proton number increases** and thus **nuclear charge increases.**
- As electrons are added to the 3d subshell, the increase in the number of **inner 3d electrons provide more shielding** between the nucleus and the outer 4s electrons.
- This **increase in shielding effect offsets the increase in nuclear charge** considerably.
- Thus, energy required to remove the first electron is **almost constant / relatively invariant.**

2.3 Melting Points and Boiling Points

Comparing s-block and transition elements, the melting point of transition elements are generally **higher** than the s-block elements in the same period.

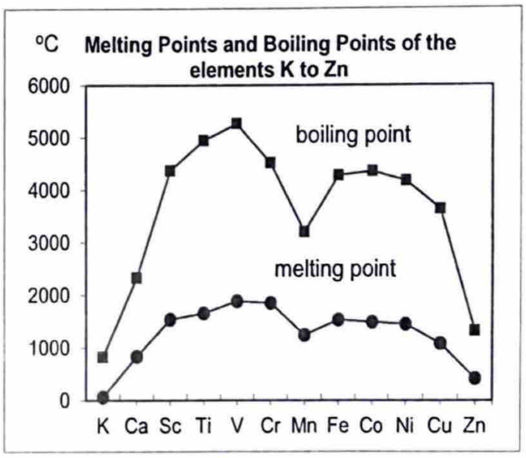
s-block elements

transition elements

Element	**K**	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
Melting point / °C	64	839	1541	1660	1890	1857	1244	1535	1495	1455	1083	420
Boiling point / °C	760	1494	2831	3287	3380	2670	1962	2750	2870	2730	2567	907

Reason:

- The valence 3d and 4s electrons are close in energy (see Atomic Structure notes).
- Thus, both **3d and 4s electrons are available for delocalisation** into the sea of electrons.
- With a greater number of delocalised electrons and higher charge density of the cations, the metallic bonding is stronger in the transition elements.



Explain why the melting point of Ti is higher than that of Ca.

Both Ti and Ca are metals. Ti is a transition element and both its 3d and 4s electrons are available for delocalisation into the sea of electrons since the 3d and 4s electrons are close in energy. With a greater number of delocalised electrons and higher charge density of the titanium cations, Ti has stronger metallic bonding than Ca, which requires more energy to overcome.

2.4 Density

Element	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Density /g cm^{-3}	1.54	2.99	4.50	5.96	7.20	7.20	7.86	8.90	8.90	8.92

Comparing s-block and transition elements, the transition elements are generally **much denser** than the s-block elements in the same period.

Transition elements have

- smaller atomic size/radius (see *Data Booklet*) and thus have more atoms per unit volume.
- larger atomic mass

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

Comparing transition elements from Ti to Cu, there is a gradual increase in density.

- The almost constant atomic radius, coupled with increasing relative atomic mass, accounts for most of this trend.

3. CHARACTERISTIC CHEMICAL PROPERTIES

- Some important characteristic chemical properties of transition elements are listed below and contrasted against those of s-block elements.

1. **The transition elements form compounds in which the transition element shows a variety of oxidation states.**

   Examples:

   $\overset{+2}{FeCl_2}$ $\overset{+3}{FeCl_3}$ $\overset{+6}{K_2FeO_4}$

1. **The s-block elements form compounds in which they exist in a fixed oxidation state.**

   Examples:

   $\overset{+1}{KCl}$ $\overset{+1}{K_2SO_4}$

2. **The transition elements form coloured compounds and ions.**

   Examples:

$[CuCl_4]^{2-}$(aq)	yellow
$[Cu(NH_3)_4]^{2+}$ (aq)	dark blue
$[Cr(H_2O)_6]^{3+}$(aq)	green
$[Cr(OH)_6]^{3-}$ (aq)	dark green
$[Cu(H_2O)_6]^{2+}$(aq)	blue
$[Fe(SCN)(H_2O)_5]^{2+}$(aq)	blood-red

2. **The s-block elements form compounds that are usually white in the solid state and colourless in aqueous solution.**

   Examples:

$CaSO_4$(s)	white
$CaCl_2$(aq)	colourless

3. **The transition elements and their compounds often show catalytic activity.**

   Examples: Fe/Fe_2O_3

   $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

3. **The s-block elements and their compounds show little or no catalytic activity.**

4. **The transition elements show a great tendency to form stable complexes.**

   Examples:

   $[Fe(CN)_6]^{3-}$(aq), $[Cr(OH)_6]^{3-}$(aq), $[CuCl_4]^{2-}$(aq), $[Fe(SCN)(H_2O)_5]^{2+}$(aq)

4. **The s-block elements show much less tendency to form stable complexes.**

   Examples:

   $[Be(OH)_4]^{2-}$(aq), $[Ca(edta)]^{2-}$(aq)

4. VARIABLE OXIDATION STATES

4.1 Transition elements and variable oxidation states

Compound	$CrSO_4$	$CrCl_3$	K_2CrO_4
Oxidation state of Cr	+2	+3	+6

- **Why are transition elements able to show variable oxidation states in their compounds?**
  - ➢ This is primarily due to the **close similarity in energy of the 3d and the 4s electrons**, that both the 3d and the 4s electrons are available for bond formation (ionic or covalent).

- **Lower oxidation states**
  - o The lower oxidation states are usually found in **ionic** compounds.
  - o Compare the successive ionisation energies of chromium (a typical transition element) and calcium (a typical s-block element).

IE / kJ mol^{-1}	1st	2nd	3rd	4th
Cr	653	1590	2990	4770
Ca	590	1150	4940	6480

  - ➢ The successive IEs of chromium increase gradually (due to similarity in energy of the 3d and 4s electrons). Hence, Cr ([Ar]$3d^5 4s^1$) can form cations of variable oxidation states by losing two electrons to form Cr^{2+} ([Ar]$3d^4$) or three electrons to form Cr^{3+} ([Ar]$3d^3$).
  - ➢ This is in contrast to calcium which has a large increase between the 2nd and 3rd IE. The third electron of calcium is from an inner shell and experiences much stronger attraction, requiring more energy to be removed. Hence, calcium forms only one cation, Ca^{2+} with a fixed oxidation state of +2.

- **Higher oxidation states**
  - o The higher oxidation states are usually found in species where the transition element is covalently bonded to other more electronegative atoms.
  - o For example, chromium can exist in a high oxidation state of +6 in CrO_4^{2-} where it utilises all its 3d electrons and 4s electrons (a total of six electrons) in covalent bond formation. This is possible due to the close similarity in the energies of the 3d and 4s electrons.

4.2 Common Oxidation Numbers

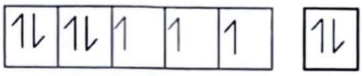
- The table below summarises the known oxidation numbers of the elements K to Zn.

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

- **Highest possible oxidation state**
  An observation can be made that **in general,**

  highest possible oxidation state = No. of <u>unpaired</u> d-electrons + 4s electrons

  Example: Co: [Ar]



  No. of unpaired d-electrons = 3, No. of 4s electrons = 2
  Maximum oxidation state of Co = 3 + 2 = +5

Some generalisations

(a) From Sc to Mn, the number of available oxidation states for the element increases. The value of the highest oxidation number for Sc to Mn suggests that in each element all the available 3d and 4s electrons may be used for bonding.

(b) From Mn to Zn, there is a decrease in the number of oxidation states exhibited by the elements.

(c) The common oxidation states for each element include +2 or +3 or both.

(d) Oxides of elements in low oxidation states tend to be basic as they are ionic while oxides of elements in high oxidation states tend to be acidic as they are covalent. Using compounds of manganese as an example,

MnO	+2	basic	($MnO + H_2SO_4 \longrightarrow MnSO_4 + H_2O$)
Mn_2O_3	+3	basic	
MnO_2	+4	amphoteric	
MnO_3	+6	acidic	
Mn_2O_7	+7	acidic	($Mn_2O_7 + 2NaOH \longrightarrow 2NaMnO_4 + H_2O$)

Exercise 3

N92/4/20 and J99/3/18
Titanium has the electronic structure $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$.
Which titanium compound is **unlikely** to exist?

[✓ **A**] K_2TiO_4 **B** K_3TiF_6 **C** $TiCl_3$ **D** TiO

4.3 Redox systems involving transition metal ions

(a) The relative stabilities of different oxidation states are best understood in terms of standard electrode potentials.

$$M^{3+} + e^- \rightleftharpoons M^{2+} \qquad E^\ominus(M^{3+}/M^{2+})$$

A more positive $E^\ominus$ value ⇒ position of equilibrium position lies more to the right, i.e. the +2 oxidation state is favoured over the +3 oxidation state.

$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$ $E^\ominus = -0.41$ V

$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$ $E^\ominus = +1.54$ V

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^\ominus = +0.77$ V

$Co^{3+} + e^- \rightleftharpoons Co^{2+}$ $E^\ominus = +1.82$ V

	Electronic configurations	
	M^{3+}	M^{2+}
Cr	[Ar] $3d^3$	[Ar] $3d^4$
Mn	**[Ar] $3d^4$**	**[Ar] $3d^5$**
Fe	**[Ar] $3d^5$**	**[Ar] $3d^6$**
Co	[Ar] $3d^6$	[Ar] $3d^7$

(i) Going across the transition elements, there is a **general** increase in $E^\ominus$ value.

(ii) There is a decrease in $E^\ominus$ from Mn^{3+}/Mn^{2+} to Fe^{3+}/Fe^{2+}.

  - ➢ Addition of an electron to Fe^{3+} results in a $3d^6$ configuration, where there is inter-electronic repulsion between the paired electrons in the same 3d orbital. Thus, reduction of Fe^{3+} to Fe^{2+} is less favoured.

(b) Aqueous $KMnO_4$ acidified with dilute H_2SO_4 and aqueous $K_2Cr_2O_7$ acidified with dilute H_2SO_4 are common oxidising agents used in laboratories.

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O \qquad E^\ominus = +1.52\text{ V}$$

purple → very light pink / colourless

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O \qquad E^\ominus = +1.33\text{ V}$$

orange → green

5. CATALYTIC ACTIVITY

- Transition elements, both in the elemental form and in their compounds, are effective and important catalysts.
- **What is a catalyst?**

A catalyst is a substance which increases the rate of a reaction without itself undergoing any permanent change.

- **How does a catalyst increase the rate of a reaction?**

A catalyst increases the rate of a reaction by providing an alternative pathway for the reaction, one with a lower activation energy than that of the uncatalysed reaction. Consequently more reactant particles have energy greater than or equal to the activation energy, leading to a higher effective collision frequency and hence a faster reaction rate. A lower activation energy also results in a larger rate constant, k, and hence a faster reaction.

- **What are the two types of catalysis?**

1. heterogeneous catalysis – catalyst and the reactants are in <u>different physical phases</u>
2. homogeneous catalysis – catalyst and the reactants are in the <u>same phase</u>

- Transition elements and their compounds are useful in both heterogeneous catalysis and homogeneous catalysis.

Transition element or their compounds used as catalyst.	Reaction catalysed		Type of catalysis
V_2O_5	$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$	Contact process	Heterogeneous
MnO_2	$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$	--	Heterogeneous
Fe/Fe_2O_3	$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$	Haber process	Heterogeneous
Ni	$RCH{=}CH_2 + H_2 \longrightarrow RCH_2CH_3$	Hardening of vegetable oils (e.g. manufacture of margarine)	Heterogeneous
$FeCl_3$	$C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl$	Electrophilic substitution of benzene	Homogeneous
Mn^{2+}	$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$	An example of autocatalysis	Homogeneous

5.1 Heterogeneous Catalysis

- In heterogeneous catalysis, the **catalyst and the reactants are in different phases.**
  - ➢ The catalyst is usually in the solid phase and it provides **active sites** at which the reaction can take place and the reactants are usually liquids or gases.

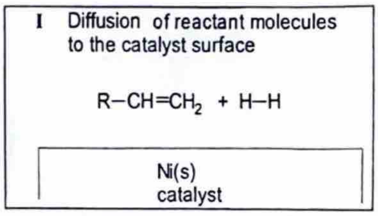
- For heterogeneous catalysis to occur, the reactant molecules need to be readily adsorbed onto the catalyst surface. Such type of catalysis is a surface effect which involves the formation of weak attractive forces between reactant molecules and the atoms of the surface of the catalyst.

- **What are the important features of first row transition elements (and their compounds) that enable them to function effectively as heterogeneous catalysts?**

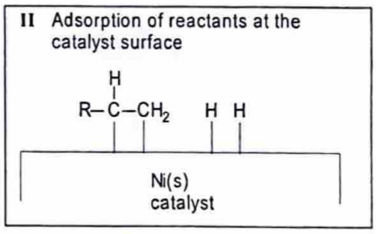
The availability of **a partially filled 3d subshell** allows for ready exchange of electrons to and from reactant molecules, facilitating the formation of weak bonds with the reactant molecules.

- This is due to the availability of 3d electrons for bond formation with reactant molecules or the availability of low-lying vacant orbitals which can accept electron pairs from the reactant molecules.

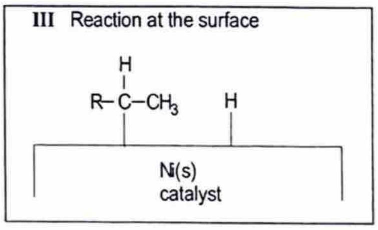
1. **Diffusion**
   Reactant molecules diffuse towards catalyst surface.


I Diffusion of reactant molecules to the catalyst surface

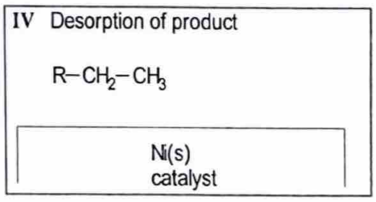
2. **Adsorption**
   Reactant molecules become **adsorbed** onto the **active sites** of the catalyst surface through attractive forces. This adsorption leads to an **increase in reaction rate** since
   - the **bonds** within the reactant molecules are weakened, thereby **reducing the activation energy**
   - the reactant molecules are brought into **close contact** with **correct orientation** for reaction


II Adsorption of reactants at the catalyst surface

3. **Chemical Reaction**
   This reaction has lower activation energy than the uncatalysed reaction


III Reaction at the surface

4. **Desorption**
   This is the reverse of adsorption. The product molecule eventually breaks free from the catalyst surface.


IV Desorption of product

5. **Diffusion**
   The product molecule diffuses away from the surface. The vacant active sites are now available for adsorbing other reactant molecules.

5.2 Homogeneous Catalysis

- In homogeneous catalysis, the **catalyst and the reactants are in the same phase**, either liquid, aqueous or gaseous.

- Consider a reaction $A + B \longrightarrow D$ catalysed by Ct

Uncatalysed reaction: $A + B \longrightarrow D$

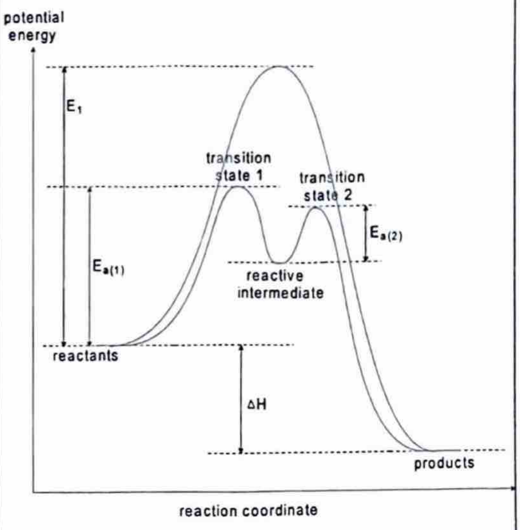
Catalysed reaction: *Step 1* $A + Ct \longrightarrow Ct'$
Step 2 $Ct' + B \longrightarrow D + Ct$

Overall reaction $A + B \longrightarrow D$

- Typical features of homogeneous catalysis:

1. The catalyst (Ct) takes part in the reaction by being **converted into an intermediate** compound (Ct').
2. The intermediate compound subsequently undergoes reaction to yield the product(s) and the **catalyst is regenerated.**
3. The larger activation energy for the uncatalysed reaction is, in this case, replaced by two smaller activation energies for the catalysed reaction.

Energy Profiles for a Catalysed and an Uncatalysed Reaction



$E1$ = activation energy of uncatalysed reaction
$E_{a(1)}$ = activation energy of first step of catalysed reaction
$E_{a(2)}$ = activation energy of second step of catalysed reaction

- **What are the important features of transition elements which enable them to function effectively as homogeneous catalysts?**

1. Their ability to exist in different oxidation states, and
2. The relative ease of conversion from one oxidation state to another.

These features facilitate the formation of, and decomposition of, the intermediate formed from the transition metal ion catalyst and the reactants.

- **Example of homogeneous catalysis**

The reaction between peroxodisulfate ions and iodide ions **catalysed by Fe^{2+} or Fe^{3+}.**

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

Do not confuse the reaction (on the left) with the reaction between iodine and thiosulfate.
$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$

Relevant $E^\ominus$ values:
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ $E^\ominus = +2.01$ V
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^\ominus = +0.77$ V
$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\ominus = +0.54$ V

(i) Uncatalysed reaction

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

- Since $E^\ominus_{cell} = 2.01 - 0.54 = +1.47\ V > 0\ V$, the uncatalysed reaction is spontaneous (thermodynamically feasible) under standard conditions.
- However, the uncatalysed reaction involves the collision between negatively charged ions. The electrostatic repulsion between these negatively charged ions causes the reaction to have a **high activation energy** and hence proceeds slowly.

(ii) Reaction catalysed by Fe^{3+} or Fe^{2+}

Exercise 4

Q1 – Write equations to show how the reaction is catalysed by **Fe^{3+} ion**.

Step 1: $2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(aq)$

$E^{\ominus}_{cell} = 0.77 - 0.54 = +0.23\ V > 0$

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

$E^{\ominus}_{cell} = 2.01 - 0.77 = +1.24\ V > 0$

- The catalysed reaction proceeds via two steps. For each step, $E^{\ominus}_{cell} > 0$ V indicating that each step is spontaneous (thermodynamically feasible) under standard conditions.
- Each step involves a reaction between oppositely charged ions which have a natural tendency to attract each other. This lowers the activation energy and enhances the reaction rate.

Q2 – Write equations to show how the reaction is catalysed by **Fe^{2+} ion**.

Step 1: $2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \longrightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$

$E^{\ominus}_{cell} = 2.01 - 0.77 = +1.24\ V > 0$

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

$E^{\ominus}_{cell} = 0.77 - 0.54 = +0.23\ V > 0$

In the above given example, it is expected that other couples involving transition metal cations would also act as catalysts, as long as their $E^{\ominus}$ values are between 0.54 V and 2.01 V.

6. COMPLEXES

6.1 Introduction

One of the most important chemical properties of transition elements is their ability to form complexes.

This ability is **not** confined to the transition elements e.g. A*l* forms the complex ion $[Al(OH)_4]^-$, I forms the tri-iodide complex ion I_3^- and Pb forms the complex $[PbCl_4]^{2-}$.

- What is a **complex**?

A **complex** contains a **central metal atom or ion** linked to one or more surrounding ions or molecules (called ligands) by **co-ordinate bond (or dative covalent bond)**. If the species carries an overall charge, it is called a **complex ion**.

- What is a **ligand**?

A **ligand** is an ion or a molecule which contains at least one atom bearing a **lone pair of electrons** which can be donated into a **low-lying vacant orbital of a central metal atom or ion** forming a **co-ordinate bond (or dative covalent bond)**, resulting in the formation of a complex.

Examples of ligand: Cl^-, OH^- CN^-, H_2O, NH_3, CO, $H_2N\text{–}CH_2CH_2\text{–}NH_2$

Based on the definition, ligands act as Lewis bases and the central metal atom or ion they bond to is a Lewis acid.

- For complexes, the number of bonds formed with the metal ion exceeds the oxidation state of the metal ion. For example,

  $CuCl_2$ is not a complex. Oxidation state of Cu is +2 and there are 2 bonds.
  $[CuCl_2]^-$ is a complex. Oxidation state of Cu is +1 and there are 2 bonds.

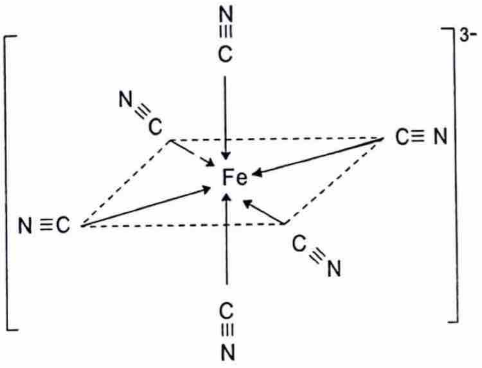
- A complex species may be neutral, cationic or anionic.

	Examples	**Central atom/ion**	**Co-ordination number**
neutral complexes	$Ni(CO)_4$ $Fe(CO)_5$	Ni Fe	4 5
cationic complexes	$[Fe(H_2O)_6]^{2+}$ $[Ag(NH_3)_2]^+$	Fe^{2+} Ag^+	6 2
anionic complexes	$[Fe(CN)_6]^{4-}$ $[CuCl_4]^{2-}$	Fe^{2+} Cu^{2+}	6 4

  - ➢ The **co-ordination number** of the central metal ion (or atom) is the **total number of co-ordinate bonds** that the central metal ion (or atom) forms with ligands.
  - ➢ The net charge on the complex ion is the algebraic sum of the charge on the central metal ion and the total charge carried by the ligands. For example,

$[Ag(NH_3)_2]^+$	overall charge of complex ion = (1)(1+) + (2)(0) = 1+
$[CuCl_4]^{2-}$	overall charge of complex ion = (1)(2+) + (4)(1–) = 2–
$[Fe(CN)_6]^{4-}$	overall charge of complex ion = (1)(2+) +(6)(1–) = 4–
$[Fe(SCN)(H_2O)_5]^{2+}$	overall charge of complex ion = (1)(3+)+(1)(1–) + 5(0) = 2+

- Summary of terms applied to the $[Fe(CN)_6]^{3-}$ complex



Name of complex ion	hexacyanoferrate(III) ion
Central metal ion	Fe^{3+}
Ligand	CN^-
Type of bond between Fe^{3+} and CN^-	Co-ordinate bond
Co-ordination number of Fe^{3+} in the complex ion	6
Co-ordination geometry	Octahedral

- Salts containing complex ions are known as complex salts (co-ordination compounds).

Complex salt	*constituent cation*	*constituent anion*
$[CoCl(NH_3)_5]Cl_2$ pentaamminechlorocobalt(III) chloride	$[CoCl(NH_3)_5]^{2+}$ a complex cation	Cl^- a simple anion
$K_4[Fe(CN)_6]$ potassium hexacyanoferrate(II)	K^+ a simple cation	$[Fe(CN)_6]^{4-}$ a complex anion

Q1 – Determine the oxidation number of the metal in each of the following complexes/ complex ions:

(a) $[Fe(OH)_2(H_2O)_4]$

+2

(b) $K[Cu(CN)_2]$

+1

(c) $[CoCl_4]^-$

+3

Q2 –Determine the overall charge of the following ions:

(a) $[Fe(SCN)(H_2O)_5]^{2+}$

Fe(III)

$+3 \; -1 \; +0 = +2$

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

Ni(II)

$+2 \; +0 = +2$

(c) $[VO_3(OH)]^{2-}$

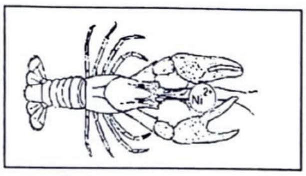
V(V)

$+5 \; -6 \; -1 = -2$

6.2 Types of Ligands

- Ligands are classified according to the **number of co-ordinate bonds** that the ligand forms with the central metal atom or ion.

Type of ligand	*Number of co-ordinate bonds which the ligand forms with the central metal ion*	1. The word "dens" means tooth in Latin. 2. A polydentate ligand is one which can form more than one co-ordinate bonds with the central metal ion. It has "many teeth". 3. The complex ions which are formed between polydentate ligands and cations are known as chelates or chelated compounds from a Greek work "chelos" meaning "a crab's claw", since the ligand forms a clawing pincer-like grip on the metal ion.
monodentate ligand	1	
polydentate ligand	> 1	
1. bidentate ligand	2	
2. tridentate ligand	3	
3. hexadentate ligand	6	



Polydentate ligands are also called **chelating agents.** The term chelate comes from the Greek word *chela*, meaning "crab's claw."

(a) Monodentate ligands

- A monodentate (or unidentate) ligand is one which can form **only one co-ordinate bond** with a central metal ion (or atom).

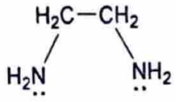
Examples of monodentate ligands: Cl^-, OH^- CN^-, H_2O, NH_3, $C{\equiv}O$

Examples of complexes with monodentate ligands: $[Fe(SCN)(H_2O)_5]^{2+}$, $[CoCl_4]^{2-}$

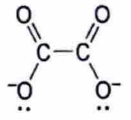
(b) Bidentate ligands

- A bidentate ligand is one which can **form two co-ordinate bonds** simultaneously with the central metal ion (or atom).

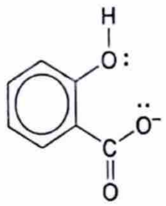
Examples of bidentate ligands:



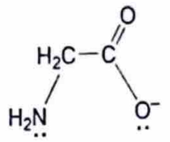
ethane-1,2-diamine
(or 1,2-diaminoethane
or ethylenediamine)
commonly abbrievated as "en"



ethanedioate ion
(or oxalate ion)



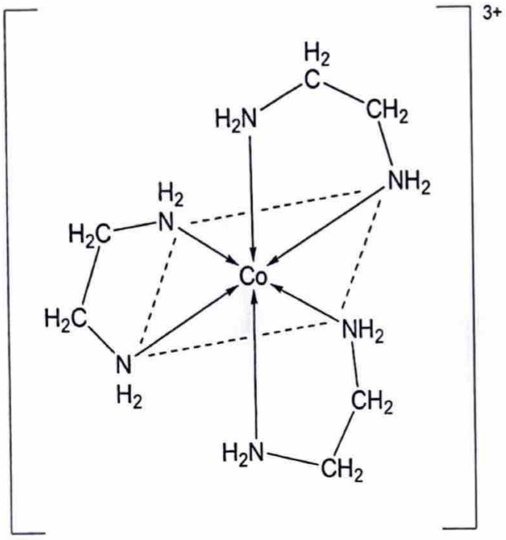
2-hydroxybenzoate ion



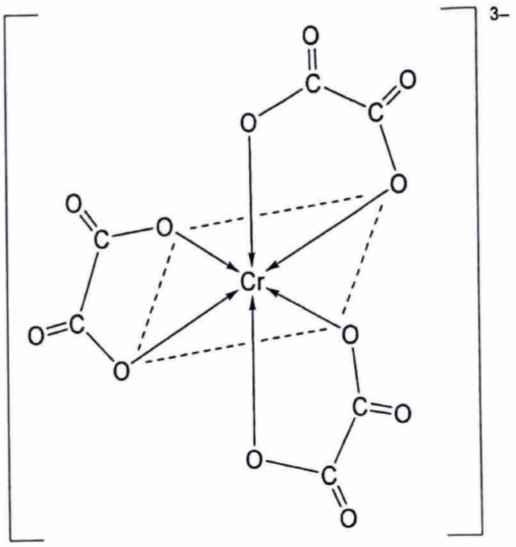
aminoethanoate ion
(or glycinate ion)

Examples of complexes with bidentate ligands:

$[Co(H_2NCH_2CH_2NH_2)_3]^{3+}$



$[Cr(C_2O_4)_3]^{3-}$



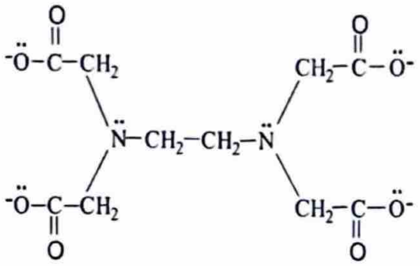
(c) Hexadentate ligands

- A hexadentate ligand is one which can form **<u>six</u> co-ordinate bonds** simultaneously with the central metal ion (or atom).

<u>Example of a hexadentate ligand:</u>

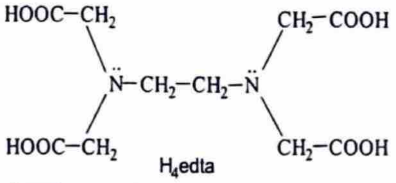
ethylenediaminetetraacetate ion

- edta^{4-} ion or EDTA^{4-} ion
- or sometimes just represented by edta or EDTA



Note:

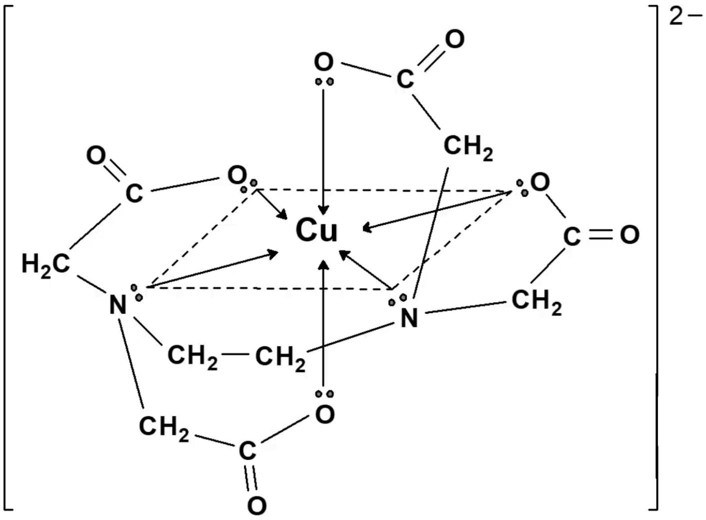
1. The edta^{4-} ion is formed from ethylenediaminetetraacetic acid, which may be written as H_4edta.



H_4edta

2. Edta is a useful ligand. It is used in many situations to 'mop up' metal ions. For example, it is
   - added in trace amounts in some foods to prevent metal ions catalysing the reaction that makes fat rancid.
   - added to cosmetics to keep minerals and other trace elements from binding with other ingredients in a cosmetic formulation to prevent deterioration and skin deposition.
   - added to shampoos, bath foams and other cleansing products to help soften the water

Examples of complexes with edta ligand: $[Cu(edta)]^{2-}$, $[Fe(edta)]^-$



$[Cu(edta)]^{2-}$

6.3 Transition Metal Ions and Complex Formation

- Complex formation

$$\underset{\substack{\text{metal ion}\\ \text{Lewis acid}\\ \text{(electron pair acceptor)}}}{Ni^{2+}} \;+\; \underset{\substack{\text{ligand}\\ \text{Lewis base}\\ \text{(electron pair donor)}}}{6\,H_2\ddot{O}} \;\rightleftharpoons\; \underset{\text{complex ion}}{[Ni(H_2O)_6]^{2+}}$$

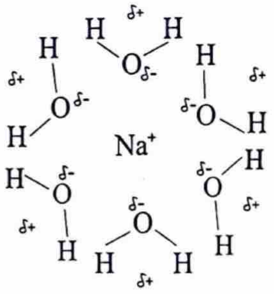
- **What are the conditions required for complex formation?**

1. the presence of ligands (i.e. species with at least one atom having a lone pair of electrons) to donate electron pairs to form co-ordinate bonds
2. the presence of a central metal ion (or atom) capable of
   (a) attracting the lone pair of electrons from the ligand, and
   (b) accommodating the lone pair of electrons in its low-lying vacant orbitals to form a co-ordinate bond

- **Why do transition metal ions show a high tendency to form complexes?**

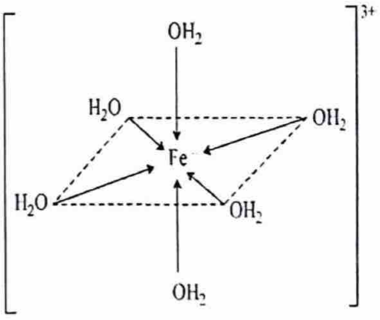
1. The transition metal ions **have low-lying vacant orbitals** (e.g. 3d, 4s and 4p orbitals) to accommodate the lone pairs of electrons from the ligands to form co-ordinate bonds.
2. The transition metal ions are relatively small and highly charged. Consequently, they have relatively high charge to size ratio (charge density) and are able to attract the lone pair of electrons from the ligands. Their high charge density and hence polarising power, produces a strong tendency towards covalent bond formation with ligands.

6.4 Aqua Complexes



- In aqueous solution, the cations of Group 1 elements are surrounded by water molecules, with the negative ends of dipoles of these water molecules directed towards the cations. The cations are said to be **hydrated**.

- The type of interaction between the cations and the water molecules is that of **ion-dipole interaction**, i.e. electrostatic attraction between the positive ion and the negative ends of the dipoles.



- Due to their high charge density, transition metal ions exist as aqua complexes in aqueous solution. Each oxygen atom of a water molecule donates a lone pair of electrons into a low-lying vacant orbital of the transition metal ion and forms a coordinate bond. In general, aqua complexes are of the form $[M(H_2O)_6]^{n+}$, where n = 2 or 3. (Note: Other cations with high charge density, e.g. Mg^{2+} and Al^{3+}, also form aqua complexes.)

Solution	Cation	Complex ions
$NaCl(aq)$	$Na^+(aq)$	-
$MgSO_4(aq)$	$Mg^{2+}(aq)$	$[Mg(H_2O)_6]^{2+}(aq)$
$AlCl_3(aq)$	$Al^{3+}(aq)$	$[Al(H_2O)_6]^{3+}(aq)$
$Cr(NO_3)_3(aq)$	$Cr^{3+}(aq)$	$[Cr(H_2O)_6]^{3+}(aq)$
$FeCl_3(aq)$	$Fe^{3+}(aq)$	$[Fe(H_2O)_6]^{3+}(aq)$

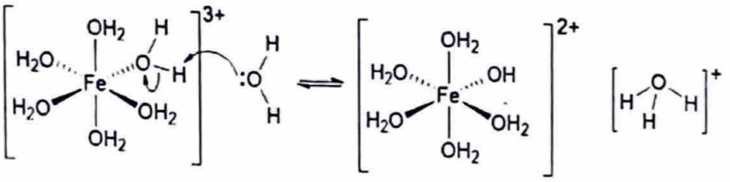
6.5 Acidity of Aqua Complexes

- **Why is an aqueous solution of $FeCl_3$ acidic?**

In aqueous $FeCl_3$ solution, the Fe^{3+} ion exists as an aqua complex ion, $[Fe(H_2O)_6]^{3+}$.

Due to its high charge and small size, the Fe^{3+} ion has **high charge density** and is hence **strongly polarising**. It **distorts the electron cloud** of the H_2O molecules bonded to it, **weakening the O–H bonds** and enabling these H_2O molecules bonded to it to become proton donors. The free water molecules in the solution act as bases and the following equilibrium is established:

$$[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Fe(OH)(H_2O)_5]^{2+}(aq) + H_3O^+(aq)$$



The Fe^{3+} ion is consequently said to undergo **appreciable hydrolysis** in aqueous solution. The slight excess of H_3O^+ ions in the solution causes the solution to be **acidic**.

- The aqueous solutions of most transition metal compounds such as $CrCl_3(aq)$, $FeCl_3(aq)$, $CuSO_4(aq)$ and $Co(NO_3)_2(aq)$ are acidic.

- An aqueous solution containing either **Cr^{3+} or Fe^{3+}** ions is **acidic** enough to react with sodium carbonate to produce carbon dioxide gas together with the formation of a hydroxide precipitate.

- **What happens when Na_2CO_3 is added to an aqueous solution containing Fe^{3+} ions?**

The following three equilibria are relevant to the Fe^{3+} ion in aqueous solution:

$$[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Fe(OH)(H_2O)_5]^{2+}(aq) + H_3O^+(aq) \quad \text{..........(1)}$$

$$[Fe(OH)(H_2O)_5]^{2+}(aq) + H_2O(l) \rightleftharpoons [Fe(OH)_2(H_2O)_4]^{+}(aq) + H_3O^+(aq) \quad \text{.........(2)}$$

$$[Fe(OH)_2(H_2O)_4]^{+}(aq) + H_2O(l) \rightleftharpoons [Fe(OH)_3(H_2O)_3](s) + H_3O^+(aq) \quad \text{...........(3)}$$

Upon addition of sodium carbonate, effervescence is observed as the following reaction occurs:

$$CO_3^{2-}(aq) + 2H_3O^+(aq) \longrightarrow CO_2(g) + 3H_2O(l)$$

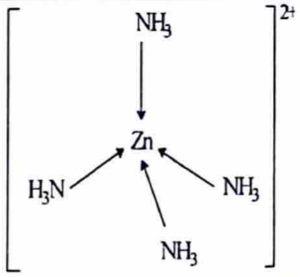
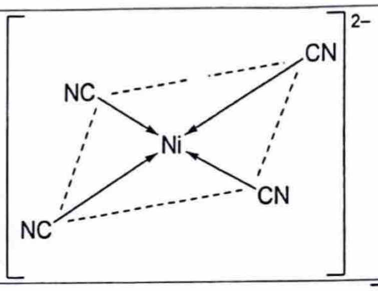
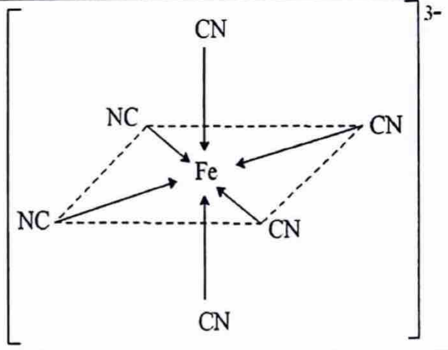
The consumption of H_3O^+ ions causes the equilibrium position of reaction (1) to shift to the right. With more CO_3^{2-} ions added, and hence more H_3O^+ ions removed, the equilibrium position of reaction (2) and then subsequently that of reaction (3) are also forced to shift to the right. Consequently, **a red-brown precipitate** of $[Fe(OH)_3(H_2O)_3]$ (usually written simply as **$Fe(OH)_3$**) is obtained ***together*** with the evolution of CO_2.

Overall: $2[Fe(H_2O)_6]^{3+}(aq) + 3CO_3^{2-}(aq) \longrightarrow 2[Fe(OH)_3(H_2O)_3](s) + 3CO_2 + 3H_2O$
This reaction also occurs for $[Al(H_2O_6)]^{3+}$ and $[Cr(H_2O_6)]^{3+}$.

7. STEREOCHEMISTRY OF COMPLEXES

7.1 Shapes of complexes

The shape of the complex ion depends on the coordination number and nature of the metal ion.

Co-ordination number	Shape	Examples	
2	linear	$[Ag(NH_3)_2]^+$ $[Ag(CN)_2]^-$ $[CuCl_2]^-$	$[H_3N \longrightarrow Ag \longleftarrow NH_3]^+$ $[Cl \longrightarrow Cu \longleftarrow Cl]^-$
4	tetrahedral	$Ni(CO)_4$ $[Zn(NH_3)_4]^{2+}$ $[CoCl_4]^{2-}$ $[Cu(CN)_4]^{3-}$ $[CuCl_4]^{2-}$	
	square planar	$[Ni(CN)_4]^{2-}$ $[Cu(NH_3)_4]^{2+}$	
6	octahedral	$[Fe(CN)_6]^{3-}$ $[Fe(CN)_6]^{4-}$ $[Ni(NH_3)_6]^{2+}$	

Note:

$[Cu(NH_3)_4(H_2O)_2]^{2+}$ vs $[Cu(NH_3)_4]^{2+}$: both are commonly used and accepted. However, the shape about Cu^{2+} in $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is octahedral instead of square planar.

7.2 Isomerism in compounds of transition elements

Compounds of transition elements can undergo isomerism. For example, when green crystals of chromium(III) chloride, $[Cr(H_2O)_4Cl_2]Cl\cdot 2H_2O$, are dissolved in water, the following changes occur.

$$\underset{\text{green}}{[Cr(H_2O)_4Cl_2]Cl\bullet 2H_2O} \longrightarrow \underset{\text{blue-green}}{[Cr(H_2O)_5Cl]Cl_2\bullet H_2O} \longrightarrow \underset{\text{violet}}{[Cr(H_2O)_6]Cl_3}$$

The compounds produce different amounts of free chloride ions and hence can be distinguished by precipitation of the free chloride ion using aqueous silver nitrate.

The complex cations $[Cr(H_2O)_4Cl_2]^+$, $[Cr(H_2O)_5Cl]^{2+}$, $[Cr(H_2O)_6]^{3+}$ are different even though they originate from the same ionic compound: chromium(III) chloride.

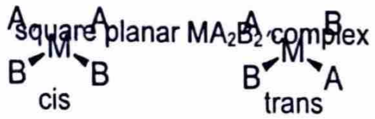
7.3 Stereoisomerism in Complexes of Transition Elements

Similar to organic compounds, some complexes of transition elements may exhibit stereoisomerism such as cis-trans isomerism or enantiomerism due to their structures.

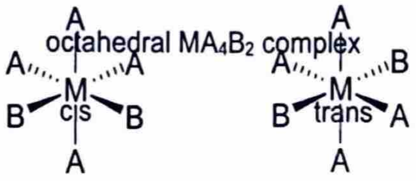
(a) Cis-Trans Isomerism

- Some transition metal complexes with square planar or octahedral geometry exhibit cis-trans isomerism as shown below.

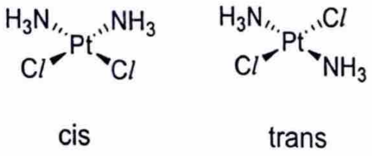
square planar MA$_2$B$_2$ complex



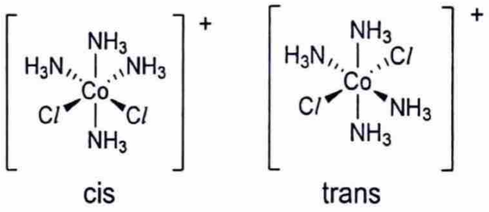
octahedral MA$_4$B$_2$ complex



e.g. PtCl_2(NH$_3$)$_2$



e.g. [CoCl_2(NH$_3$)$_4$]$^+$

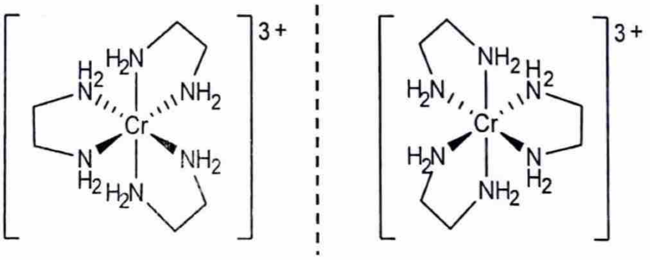


- In the **cis-isomer**, the pair of identical ligands **occupies positions adjacent to each other**. In the **trans-isomer**, the pair of identical ligands **occupies positions diagonally opposite each other**.
- Cis- and trans- isomers usually have different dipole moments and colours.

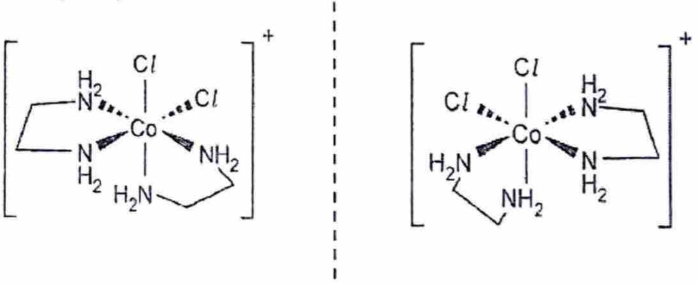
(b) Enantiomerism

- Complexes of transition metals which lack a plane of symmetry in their structures exhibit enantiomerism, as shown by the two complexes below.

  .(i) [Cr(H$_2$NCH$_2$CH$_2$NH$_2$)$_3$]$^{3+}$ (an example of the general form ML$_3$ where L is a bidentate ligand)



  .(ii) [CoCl_2(H$_2$NCH$_2$CH$_2$NH$_2$)$_2$]$^+$ (an example of the general form *cis*-[MA$_2$L$_2$] where L is a bidentate ligand)



Exercise 6

Q1 – N02/17

The anti-cancer drug, *cisplatin* has the formula $PtCl_2(NH_3)_2$. In the human body, one of the chloride ions of *cisplatin* is replaced by one water molecule.

+2 +2

$$PtCl_2(NH_3)_2 + H_2O \longrightarrow [PtCl(NH_3)_2(H_2O)]^+ + Cl^-$$

What is the oxidation number of platinum in *cisplatin* and in the aqua complex?

Q2 – N05/1

Like other transition elements, platinum(IV) chloride combines with ammonia to form compounds. The co-ordination number of platinum in these compounds is 6. A formula unit of one of the compounds contains a cation and only two chloride ions.

What is the formula of this compound?

A $Pt(NH_3)_3Cl_4$

[✓ **B**] $Pt(NH_3)_4Cl_4$

C $Pt(NH_3)_6Cl_2$

D $Pt(NH_3)_6Cl_4$

Q3

Chromium(III) chloride combines with ammonia to form compound **X** in which the co-ordination number of chromium is 6. When solution **X** is treated with an excess of aqueous silver nitrate, only two thirds of the total chloride present is precipitated as AgCl.

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

A $Cr(NH_3)_3Cl_3$

B $Cr(NH_3)_4Cl_3$

[✓ **C**] $Cr(NH_3)_5Cl_3$

D $Cr(NH_3)_6Cl_3$

8. COLOUR OF COMPLEXES

Transition metal compounds are frequently coloured, both in the solid state and in solution.

- Typical colours for common ions (i.e. with H_2O as the ligand) are summarised below.

Aqua complex ion	Electronic configuration of the cation	Colour
$[Sc(H_2O)_6]^{3+}$	[Ar] $3d^0$	colourless
$[Ti(H_2O)_6]^{3+}$	[Ar] $3d^1$	violet
$[V(H_2O)_6]^{3+}$	[Ar] $3d^2$	green
$[V(H_2O)_6]^{2+}$	[Ar] $3d^3$	violet
$[Cr(H_2O)_6]^{3+}$	**[Ar] $3d^3$**	**violet / green**
$[Cr(H_2O)_6]^{2+}$	[Ar] $3d^4$	blue
$[Mn(H_2O)_6]^{3+}$	[Ar] $3d^4$	violet
$[Mn(H_2O)_6]^{2+}$	**[Ar] $3d^5$**	**faint pink**
$[Fe(H_2O)_6]^{3+}$	**[Ar] $3d^5$**	**pale violet (lilac) / yellow**
$[Fe(H_2O)_6]^{2+}$	**[Ar] $3d^6$**	**pale green**
$[Co(H_2O)_6]^{2+}$	[Ar] $3d^7$	pink
$[Ni(H_2O)_6]^{3+}$	[Ar] $3d^8$	green
$[Cu(H_2O)_6]^{2+}$	**[Ar] $3d^9$**	**blue**
$[Zn(H_2O)_6]^{2+}$	**[Ar] $3d^{10}$**	**colourless**

Note:

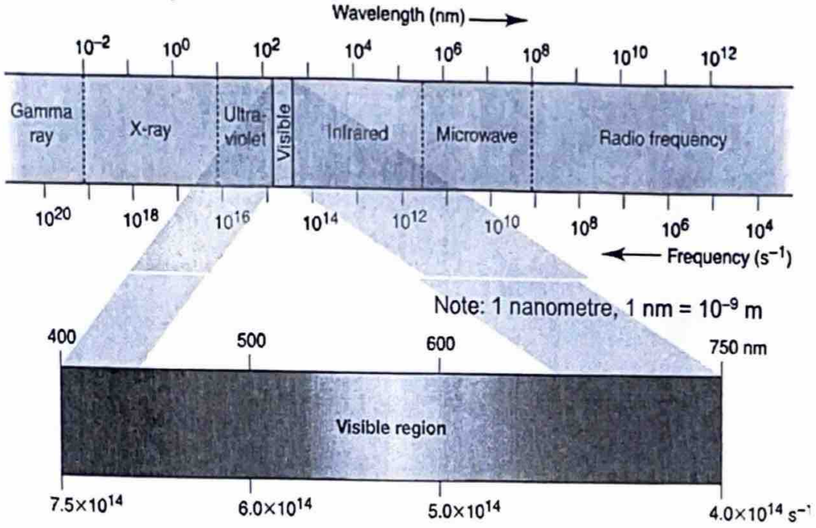
1. **Vacant or fully filled d sub-shell is associated with a lack of colour.**

2. **Aqueous solutions of Cr^{3+}**
   - $[Cr(H_2O)_6]^{3+}$ is violet in cold aqueous solution.
   - The observed green colour of its solutions is due to the partial replacement of water ligands by other ligands, e.g. Cl^- or SO_4^{2-}.
   - For simplicity, the green solution is still commonly written as $[Cr(H_2O)_6]^{3+}$.

3. **Aqueous solutions of Fe^{3+}**
   - $[Fe(H_2O)_6]^{3+}$ is pale violet.
   - The observed yellow colour of its solutions is due to the partial loss of H^+ by a water ligand to form $[Fe(OH)(H_2O)_5]^{2+}$, which is yellow.
   - For simplicity, the yellow solution is still commonly written as $[Fe(H_2O)_6]^{3+}$.

8.1 Occurrence of colour

(a) The electromagnetic spectrum



- White light (e.g. sunlight) contains **all** the wavelengths of light in the visible region of the electromagnetic spectrum. It can be dispersed into a spectrum of colours, each of which has a characteristic range of wavelengths.

(b) Coloured objects

- If selected wavelengths of the incident white light are absorbed and other wavelengths are reflected/transmitted, then the object will appear **'coloured'**. In general, an object appears coloured because it preferentially absorbs some wavelengths of light in the visible spectrum and transmits or reflects light that is richer in the remaining wavelengths of the visible spectrum.

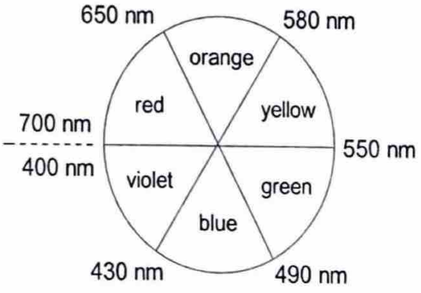
- **What determines the observed colour of a coloured object?**

  The observed colour is the colour due to the combination of wavelengths of visible light reflected (for opaque objects) or transmitted (for transparent objects).

- The observed colour is usually estimated using the idea of complementary colours.

(c) Complementary colours

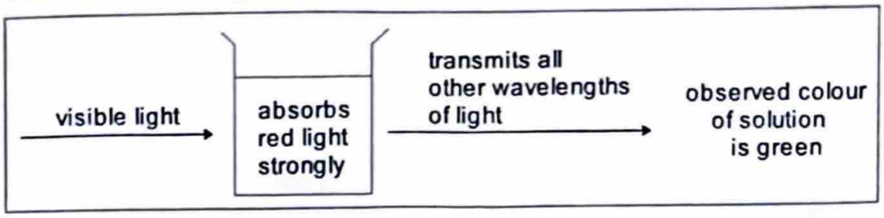
Wavelength range (nm)	Colour	Complementary colour
400 – 430	violet	yellow
430 – 490	blue	orange
490 – 550	green	red
550 – 580	yellow	violet
580 – 650	orange	blue
650 – 700	red	green



Each colour has a **complementary colour** as shown in the table above. A **colour wheel** can be used to help predict the colour that will be seen when absorption occurs in part of the visible spectrum. Colours directly opposite each other on the colour wheel are called **complementary colours.**

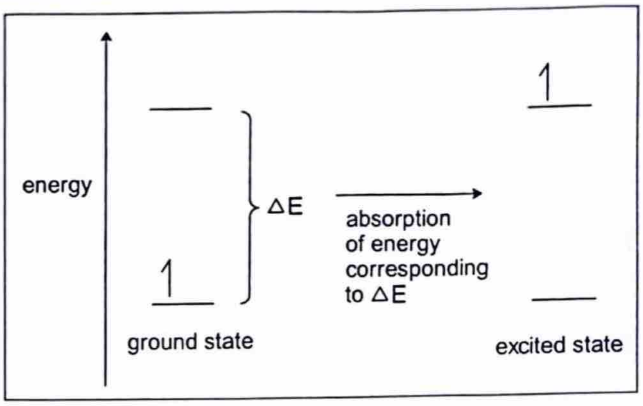
- **Example: A green object**

  When white light (containing a broad spectrum of all visible wavelengths) passes through a substance that absorbs red light, the colour observed is green; green is the complement of red.



- The observed colour is said to be **complementary** to the colour of light absorbed. Hence if a compound absorbs light of one colour, we see the complement of that colour.

8.2 Absorption of Light Energy and Electronic Transition



- When light energy is absorbed by a substance, an electron in the atom or ion of that substance is promoted from an orbital of lower energy to one of higher energy.
- The atom or ion absorbing the radiation changes from what is described as its **ground state** to an **excited state**.
- There can be more than one electronic transition. The different electronic transitions involve the absorption of radiation of different wavelengths (or different frequencies) and **if the absorbed wavelengths are in the visible region of the spectrum, then the substance appears coloured.**

8.3 Sodium chloride solution

Why is an aqueous solution of sodium chloride colourless?

- Consider the ground state and the excited state of the Na^+ ion.

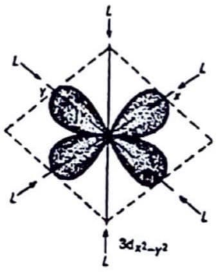
$$\begin{array}{c} Na^+ \\ \text{(ground state)} \\ 1s^2\ 2s^2\ 2p^6 \end{array} \longrightarrow \begin{array}{c} Na^+ \\ \text{(excited state)} \\ 1s^2\ 2s^2\ 2p^5\ 3s^1 \end{array}$$

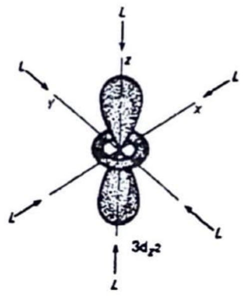
- The excitation of an electron from the lower energy 2p orbital to the higher energy 3s orbital requires wavelength of light well beyond the range of visible spectrum. Radiation from the visible spectrum does not provide sufficient energy to promote electrons in Na^+ ions to even the lowest of their possible excited electronic states.

8.4 Occurrence of Colour in Octahedral Complexes

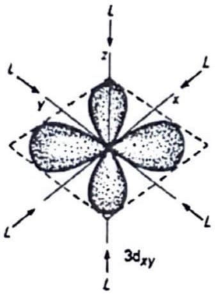
(a) Crystal Field Theory

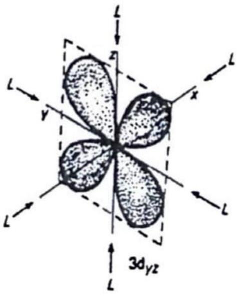
- **Crystal Field Theory** provides a way of determining, by simple electrostatic considerations, how the energies of the metal ion orbitals will be affected by the set of surrounding ligands.
- In an isolated metal ion in the gaseous phase, the five 3d orbitals all have the same energy and are said to be **degenerate**.
- In an octahedral complex, six ligands L approach the central metal ion M **along the x, y and z axes.** This results in electrostatic repulsion between the electrons in the 3d orbitals and the lone pairs on the ligands, and thus an increase in potential energy. Hence the energy of an electron in either of the 3d orbitals in a complex of M is higher than in an isolated M atom.
- **$3d_{x^2-y^2}$ and $3d_{z^2}$**: These orbitals have their greatest electron density **along** the co-ordinate axes on which the ligands are situated. Hence electrons in these orbitals are pointing towards the lone pairs of ligands, and will be **repelled** by them.

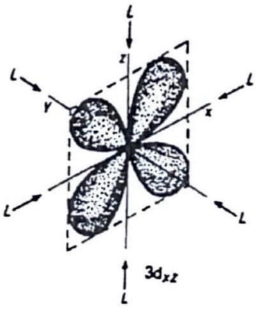




- **$3d_{xy}$, $3d_{yz}$, $3d_{xz}$** : These orbitals have their greatest electron density in **between** the co-ordinate axes. Hence the repulsion between electrons in these orbitals and those of the approaching ligands will be **less** compared to electrons in $3d_{x^2-y^2}$ or $3d_{z^2}$ orbitals.



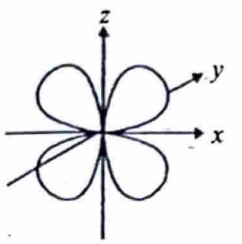




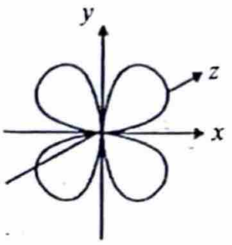
- Thus, **the five 3d orbitals are affected differently by the approach of the ligands**. The $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals experience greater repulsion, causing their orbitals to have a higher energy level than that of the $3d_{xy}$, $3d_{yz}$ and $3d_{xz}$ orbitals. Hence, the orbitals are split into two energy levels with an energy gap between them, and the degeneracy of the five 3d orbitals is destroyed in complexes.

Worked Example 1

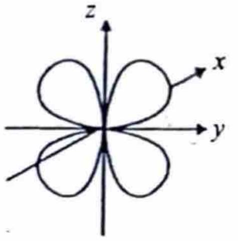
Using the Cartesian axes, draw and label diagrams to show the d orbitals that the electrons in a transition metal ion might occupy.



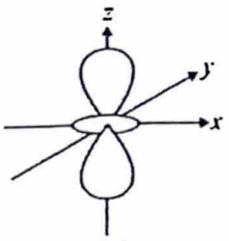
d_{xz}
(in between *x* and *z* axes)



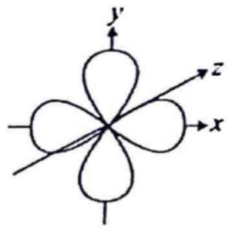
d_{xy}
(in between *x* and *y* axes)



d_{yz}
(in between *y* and *z* axes)



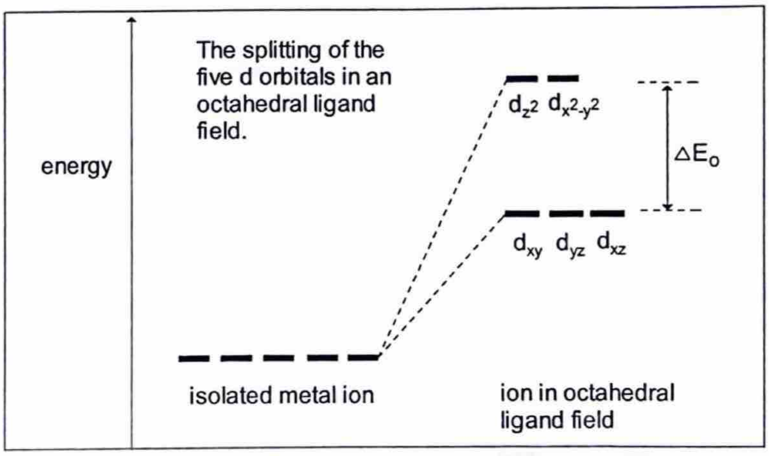
d_{z^2}
(along *z* axis)



$d_{x^2-y^2}$
(along *x* and *y* axes)

(b) The splitting of the five d-orbitals in octahedral complexes

- In the presence of the ligands, the five 3d orbitals of the central metal ion are split into two energy levels as illustrated.



- The resulting **small energy gap (i.e. ΔE_o)** between the two sets of d-orbitals turns out to correspond to energies of electromagnetic radiation in the **visible region of the spectrum**.

- Transition metal compounds are therefore coloured because radiation in the visible region of the spectrum is of the right quantity of energy to promote electrons from d-orbitals of lower energy to one of higher energy (i.e. **d-d transitions**). The colour observed is the **complement** of the colour absorbed.

- **Why is an aqueous solution of $NiCl_2$ coloured?**

In aqueous solution, Ni^{2+} exists as an octahedral complex $[Ni(H_2O)_6]^{2+}$.
The presence of the H_2O ligands causes the splitting of the five originally degenerate 3d orbitals in the Ni^{2+} ion into two sets of slightly different energy levels.
Since the 3d subshell is partially filled (Ni^{2+}: [Ar] $3d^8$), the electrons from the lower energy d orbitals can absorb energy corresponding to certain wavelengths from the visible spectrum and get promoted to the higher energy d orbitals.
Such d-d transitions are responsible for the colour observed in $NiCl_2(aq)$. The colour observed is the complement of the colour absorbed.

L	• presence of **ligands** causes the
S	• **splitting** of the five 3d orbitals into two sets of slightly different energy levels.
P	• Since these 3d subshell is **partially filled**,
E	• **electrons** from the lower-energy d orbitals can absorb energy corresponding to certain wavelengths from the visible spectrum and get promoted to the higher-energy d orbitals. (d-d transitions)
C	• The **colour observed** is the complement of the colour absorbed.

8.5 Factors affecting the Colour of Transition Metal Complexes

- The colour of a transition metal complex is dependent on the energy gap (ΔE) between the two groups of d orbitals. This in turn depends on the following factors.

1. **The identity of the metal and its oxidation state (which depends on the number of d electrons present).**

$[Cr(H_2O)_6]^{2+}(aq)$	$[Cr(H_2O)_6]^{3+}(aq)$	$[Fe(H_2O)_6]^{2+}(aq)$	$[Fe(H_2O)_6]^{3+}(aq)$
[Ar] $3d^4$	[Ar] $3d^3$	[Ar] $3d^6$	[Ar] $3d^5$
blue	violet	pale green	lilac

- Compounds of the same element in different oxidation states show different colours.
- $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ have different no. of d-electrons and repel the electrons of the ligands to different extent, thus the energy gap between the split d-orbitals are different.

2. **The nature of the ligands bonded to the central metal ion/atom.**

$[Ni(H_2O)_6]^{2+}(aq)$	green	$[Cu(H_2O)_6]^{2+}(aq)$	blue
$[Ni(NH_3)_6]^{2+}(aq)$	blue	$[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$	dark blue

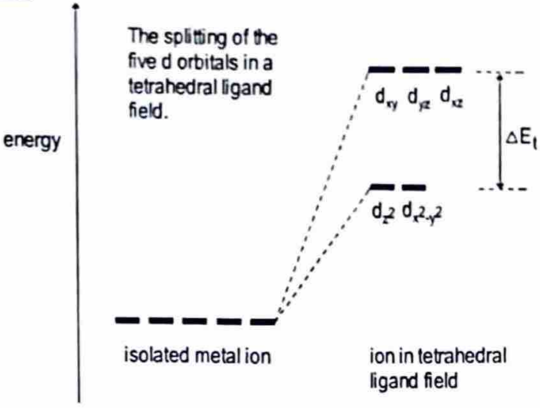
- Different ligands split the d orbitals of the metal ion into two sets of slightly different energy levels to **different extents**. Hence different transition metal complexes **absorb different wavelengths of light** from the visible spectrum for d-d transitions (i.e. the promotion of electrons from the lower energy d orbitals to the higher energy d orbitals).

- Consequently, different colours, corresponding to the complements of the different colours absorbed, are observed for different complexes.

8.6 Splitting of d-orbitals in Tetrahedral Complexes

- In tetrahedral complexes, the situation is the reverse of that in octahedral complexes. The four ligands in tetrahedral complexes approach the central metal ion **in between** the x, y and z axes.

- Electrons in the $3d_{xy}$, $3d_{yz}$ and $3d_{xz}$ orbitals now experience the greatest electrostatic repulsion from the ligand lone pairs, so have a higher energy than electrons in the $3d_{x^2-y^2}$ and the $3d_{z^2}$ orbitals.



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9. LIGAND EXCHANGE

9.1 Stability constant

- An aqueous solution of nickel(II) sulfate contains $[Ni(H_2O)_6]^{2+}$ ions. When **excess** aqueous ammonia is added to this solution, there is a noticeable change of colour because some of the $[Ni(H_2O)_6]^{2+}$ ions are converted into $[Ni(NH_3)_6]^{2+}$ ions.

- A **ligand exchange reaction** occurs and the following equilibrium is established:

$$\underset{\text{green}}{[Ni(H_2O)_6]^{2+}(aq)} + 6NH_3(aq) \rightleftharpoons \underset{\text{blue}}{[Ni(NH_3)_6]^{2+}(aq)} + 6H_2O(l)$$

- The equilibrium constant, K_{stab}, of the above reaction, <u>taking the concentration of water as being constant</u>, is

$$K_{stab} = \frac{[\,Ni(NH_3)_6{}^{2+}\,]}{[\,Ni(H_2O)_6{}^{2+}\,]\;[\,NH_3\,]^6} = 4.8 \times 10^7 \text{ mol}^{-6}\text{ dm}^{18}$$

- K_{stab} is known as the **stability constant** for the $[Ni(NH_3)_6]^{2+}$ ion. It is a measure of how stable the $[Ni(NH_3)_6]^{2+}$ ion is as compared to the $[Ni(H_2O)_6]^{2+}$ ion.

- Definition of K_{stab}

The stability constant, K_{stab}, of a complex ion may be defined as the **equilibrium constant for its formation.** The greater the value of K_{stab}, the more stable the complex ion is relative to the aqua complex containing the same metal ion.

- The large value of K_{stab} means that:

  - The equilibrium position for the above reaction lies very much to the right.
  - The $[Ni(NH_3)_6]^{2+}$ ion is **relatively more stable** than the $[Ni(H_2O)_6]^{2+}$ ion.
  - NH_3 is a **stronger ligand** than H_2O.
  - NH_3 forms a **stronger dative covalent bond** with the Ni^{2+} ion.
  - There will be **replacement of the H_2O ligands by the NH_3 ligands** when excess NH_3 is added to $NiSO_4(aq)$ (i.e. a ligand exchange reaction can occur).

9.2 Ligand exchange in terms of stability constants

The formation of a complex ion can be regarded as a competition between two ligands for the metal ion. In general, the ligands forming the complex of higher stability constant will replace those forming the complex of lower stability constant.

(a) Complexes of copper(II) with water and ammonia

K_{stab} of complexes of copper(II)

complex	$[CuCl_4]^{2-}$	$[Cu(NH_3)_4(H_2O)_2]^{2+}$	$[Cu(edta)]^{2-}$
log K_{stab}	5.6	13.1	18.8
colour	yellow	dark blue	light blue

Worked Example 2 (N93/2/1a)

(i) Describe and explain what happens when dilute aqueous ammonia is gradually added to an aqueous solution containing $Cu^{2+}(aq)$.

$$\underset{\text{blue solution}}{[Cu(H_2O)_6]^{2+}(aq)} \xrightarrow{NH_3(aq)} \underset{\text{light blue precipitate}}{Cu(OH)_2(s)} \xrightarrow{\overset{\text{excess}}{NH_3(aq)}} \underset{\text{deep blue solution}}{[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)}$$

Aqueous NH_3 is a weak base which ionises in water to form OH^- ions.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

An aqueous solution containing Cu^{2+} ions is blue due to the presence of $[Cu(H_2O)_6]^{2+}$ ions. When dilute $NH_3(aq)$ is gradually added, a pale blue precipitate of $Cu(OH)_2$ is first formed since ionic product of $Cu(OH)_2$ exceeds the K_{sp} of $Cu(OH)_2$.

$$\underset{\text{blue solution}}{[Cu(H_2O)_6]^{2+}(aq)} + 2OH^-(aq) \rightleftharpoons \underset{\text{pale blue precipitate}}{[Cu(OH)_2(H_2O)_4](s)} + 2H_2O(l) \quad \text{..................(1)}$$

or $\quad Cu^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s)$

When excess NH_3 is added, a **ligand exchange reaction** occurs and the following equilibrium is established.

$$\underset{\text{blue solution}}{[Cu(H_2O)_6]^{2+}(aq)} + 4NH_3(aq) \rightleftharpoons \underset{\text{dark blue solution}}{[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)} + 4H_2O(l) \quad \text{..........(2)}$$

The equilibrium position of reaction (2) lies very much to the right as the formation of the more stable $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion is favourable.

The formation of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ions results in a decrease in the concentration of $[Cu(H_2O)_6]^{2+}$ and hence decreases the ionic product of $Cu(OH)_2$ to below its K_{sp} value. Hence the pale blue precipitate of $Cu(OH)_2$ dissolves to give a dark blue solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

Note:

1. In this case, there exist two **competing equilibria**, (1) and (2). Both NH_3 and OH^- compete to combine with $Cu^{2+}(aq)$. With a large excess of NH_3 (i.e. higher $[NH_3]$), the formation of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is more favourable.

2. The following equation is sometimes used to represent the dissolution of the pale blue precipitate upon the addition of excess aqueous NH_3.

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

(ii) Describe and explain what happens when an aqueous solution of edta is added to the solution in **(i)**.

When aqueous edta is added to a dark blue solution containing the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ions, the colour of the solution lightens considerably as a ligand exchange reaction occurs. The hexadentate edta ligand replaces the NH_3 and H_2O ligands to form the more stable $[Cu(edta)]^{2-}$ ions leading to the formation of a light blue solution. The following equilibrium is established and the equilibrium position lies more to the right.

$$[Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + edta^{4-}(aq) \rightleftharpoons [Cu(edta)]^{2-}(aq) + 4NH_3(aq) + 2H_2O(l)$$

Worked Example 3

J91/4/1bii Describe and explain what is seen when concentrated hydrochloric acid is added to a solution of Cu^{2+} ions in water.

A solution of Cu^{2+} ions in water is blue in colour due to the presence of $[Cu(H_2O)_6]^{2+}$ ions. A ligand exchange reaction occurs where the Cl^- ligands replace the water ligands in the $[Cu(H_2O)_6]^{2+}$ ions to form the more stable $[CuCl_4]^{2-}$ ions. The following equilibrium is established:

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

The presence of both the blue $[Cu(H_2O)_6]^{2+}$ ions and yellow $[CuCl_4]^{2-}$ ions results in a green solution.

Addition of more concentrated HCl to the green solution increases the Cl^- concentration, causing the equilibrium position of the above reaction to shift further right. The green solution turns yellow as more yellow $[CuCl_4]^{2-}$ ions are formed.

(b) Complexes of Ag(I):

- One of the fascinating and intriguing demonstrations of different ligands for a particular cation is outlined in the sequence reactions involving Ag^+ shown below.

	Ligand	Colour and state of complex
$[Ag(H_2O)_2]^+(aq)$	H_2O	Colourless solution
↓ add NaCl(aq)		
$AgCl(s)$	Cl^-	White precipitate
↓ add NH_3 (aq)		
$[Ag(NH_3)_2]^+(aq)$	NH_3	Colourless solution
↓ add KBr(aq)		
$AgBr(s)$	Br^-	Cream precipitate
↓ add $Na_2S_2O_3$(aq)		
$[Ag(S_2O_3)_2]^{3-}(aq)$	$S_2O_3^{2-}$	Colourless solution
↓ add KI(aq)		
$AgI(s)$	I^-	Yellow precipitate
↓ add KCN(aq)		
$[Ag(CN)_2]^-(aq)$	CN^-	Colourless solution
↓ add Na_2S(aq)		
$Ag_2S(s)$	S^{2-}	Black precipitate
↓ add Na_2edta(aq)		
$[Ag(edta)]^-(aq)$	$edta^{2-}$	Colourless solution

Note:
Some of the reactions in the sequence result in the precipitation of insoluble solids. Being uncharged, they are less readily hydrated by polar water molecules than the charged complexes and so they are less likely to dissolve in water.

Going down the table, the ligands are increasing in strength and become stronger competitors for Ag^+: $H_2O < Cl^- < NH_3 < Br^- < S_2O_3^{2-} < I^- < CN^- < S^{2-} < edta^{2-}$

Exercise 7: (J96/IV/22)

The following table lists some stability constants for the following reaction.

$[M(H_2O)_6]^{m+} + nL^- \rightleftharpoons [M(H_2O)_{6-n}L_n]^{(m-n)+} + nH_2O$
(where *m* and *n* are whole numbers)

M^{m+}	L^-	*n*	K_{stab}
Fe^{3+}	SCN^-	1	9×10^2
Fe^{3+}	CN^-	6	1×10^{31}
Co^{3+}	CN^-	6	1×10^{64}

(i) Rewrite the above equation for the case of $M^{m+} = Fe^{3+}$ and $L^- = CN^-$. Write the expression for the equilibrium constant, K_{stab}, and state its units.

(ii) Use the data given in the table to predict what would be the predominant complex formed when

1: a solution containing equal concentrations of both SCN^- and CN^- ions was added to a solution containing $Fe^{3+}(aq)$ ions;

2: a solution containing equal concentrations fo $Fe^{3+}(aq)$ and $Co^{3+}(aq)$ ions was added to a solution containing CN^- ions.

[5]

(i) $[Fe(H_2O)_6]^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-} + 6H_2O$

$$K_{stab} = \frac{[\,Fe(CN)_6{}^{3-}\,]}{[\,Fe(H_2O)_6{}^{3+}\,]\,[\,CN^-\,]^6}$$

Units: $mol^{-6}\ dm^{18}$

(ii) 1: $[Fe(CN)_6]^{3-}$ formed as CN^- is a stronger ligand than SCN^- due to the larger K_{stab} value for the complex.

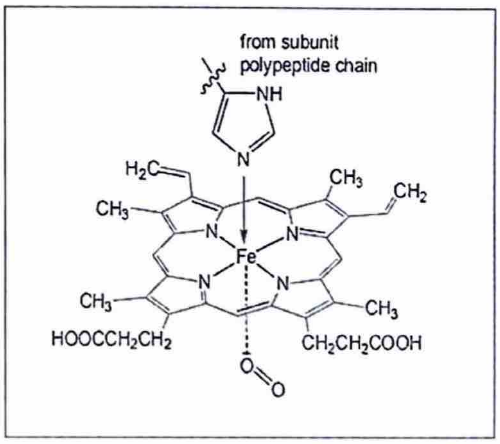
2: $[Co(CN)_6]^{3-}$ due to the larger K_{stab} value for the Co(III) complex.

9.3 Exchange of ligands in haemoglobin

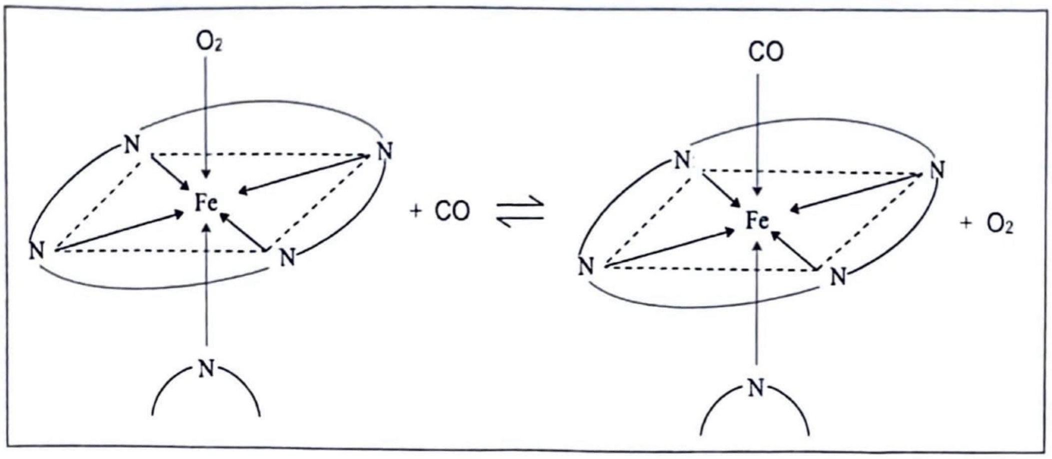
- The body of an adult contains about 4 g of iron, 75% of which is in the form of haemoglobin. This vital oxygen-carrying constituent of the blood contains iron(II).
- Haemoglobin – red pigment in red blood cells
  – acts as a transporter of oxygen in blood
  – contains iron(II) which has a co-ordination number of six

Structure:

- The iron(II) exhibits hexa co-ordination.
- Four of the co-ordination sites are taken up by nitrogen from a ring system called a porphyrin which acts as a tetradentate ligand. This complex is called 'haem'.
- Above the plane of this ring is a fifth nitrogen atom, acting as a ligand. This atom is part of a complex protein called globin.
- The oxygen molecule may become **reversibly** bonded at the sixth site allowing the haemoglobin to carry oxygen from one part of the body to another.



- Better ligands than oxygen can bond strongly (almost irreversibly) to the iron(II) and thus destroy the oxygen carrying capacity of haemoglobin. This accounts for the toxic nature of carbon monoxide and cyanide ions, both of which are very good ligands.



9.4 Effect of Ligand Exchange on $E^\ominus$ values

- Replacement of H_2O ligands in an aqua-complex by other ligands can cause large changes in electrode potential values.

(a) Effect of CN^- ligand on the relative stability of Fe(II) and Fe(III)

$[Fe(H_2O)_6]^{3+}(aq) + e^- \rightleftharpoons [Fe(H_2O)_6]^{2+}(aq)$ $E^\ominus = +0.77$ V
$[Fe(CN)_6]^{3-}(aq) + e^- \rightleftharpoons [Fe(CN)_6]^{4-}(aq)$ $E^\ominus = +0.36$ V

- Replacing the H_2O ligand by the CN^- ligand causes the $E^\ominus$ value for the Fe(III)/Fe(II) system to become less positive i.e. Fe(III) becomes less easily reduced and hence less oxidising.

- Hence there is stabilisation of the +3 oxidation state of iron relative to the +2 oxidation state of iron by the CN^- ligand.

- The positively charged $[Fe(H_2O)_6]^{3+}$ ion accepts an electron more readily since oppositely charged species attract each other naturally. The negatively charged $[Fe(CN)_6]^{3-}$ ion does not accept an electron readily since there is naturally repulsion between similarly charged species.

How can it be shown experimentally that $[Fe(CN)_6]^{3-}(aq)$ is a weaker oxidising agent than $[Fe(H_2O)_6]^{3+}(aq)$?

By reacting both species with KI(aq). Data: $\frac{1}{2}I_2(aq) + e^- \rightleftharpoons I^-(aq)$ $E^\ominus = +0.54$ V

$[Fe(H_2O)_6]^{3+}(aq) + I^-(aq) \longrightarrow [Fe(H_2O)_6]^{2+}(aq) + \frac{1}{2}I_2(aq)$ $E^\ominus_{cell} = +0.23 \text{ V} > 0 \text{ V}$
Since $E^\ominus_{cell} > 0$ V, the reaction is thermodynamically feasible under standard conditions.
Observation: Brown solution of $I_2(aq)$ formed.

$[Fe(CN)_6]^{3-}(aq) + I^-(aq) \longrightarrow [Fe(CN)_6]^{4-}(aq) + \frac{1}{2}I_2(aq)$ $E^\ominus_{cell} = -0.18 \text{ V} < 0 \text{ V}$
Since $E^\ominus_{cell} < 0$ V, the reaction is thermodynamically not feasible under standard conditions.
Observation: Brown solution of $I_2(aq)$ is not produced.

(b) Effect of NH_3 and CN^- ligands on the relative stability of Co(II) and Co(III)

$$[Co(H_2O)_6]^{3+}(aq) + e^- \rightleftharpoons [Co(H_2O)_6]^{2+}(aq) \qquad E^\ominus = +1.82\ V$$
$$[Co(NH_3)_6]^{3+}(aq) + e^- \rightleftharpoons [Co(NH_3)_6]^{2+}(aq) \qquad E^\ominus = +0.10\ V$$
$$[Co(CN)_6]^{3-}(aq) + e^- \rightleftharpoons [Co(CN)_6]^{4-}(aq) \qquad E^\ominus = -0.80\ V$$
$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O \qquad E^\ominus = +1.23\ V$$
$$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- \qquad E^\ominus = +0.40\ V$$

- The $E^\ominus$ values show that there is stabilisation of Co(III) with respect to Co(II) by the NH_3 and the CN^- ligands.
- $[Co(H_2O)_6]^{3+}$ ions are so strongly oxidising that they react with water to produce oxygen.
- $[Co(NH_3)_6]^{2+}(aq)$ and $[Co(CN)_6]^{4-}(aq)$ are so strongly reducing that they are oxidised by air.

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10. SUMMARY

10.1 Typical reactions undergone by transition metal ions

(a) Precipitation reactions

- Common reagents used: $NH_3(aq)$, $NaOH(aq)$
- See the QA Notes for details
- Explanation is usually couched in terms of ionic product exceeding K_{sp}

$$Cu^{2+}(aq) + 2OH^-(aq) \xrightarrow{NH_3(aq)} Cu(OH)_2(s)$$
blue solution — pale blue precipitate

(b) Ligand exchange reactions

- Prediction of whether such a reaction occurs is usually based on the given relative stability constants of the complex ions or the given observations (i.e. colour changes, dissolution of precipitate, etc.).
- Explanation is usually couched in terms of the relative stabilities of the complexes or the relative strengths of the ligands.

$$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \xrightarrow{\text{excess } NH_3(aq)} [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 2H_2O(l)$$
blue solution — dark blue solution

$$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \xrightarrow{\text{conc. } HCl} [CuCl_4]^{2-} + 6H_2O(l)$$
blue solution — yellow solution

$$[Fe(H_2O)_6]^{3+}(aq) + SCN^-(aq) \xrightarrow{KSCN(aq)} [Fe(SCN)(H_2O)_5]^{2+}(aq) + H_2O(l)$$
yellow solution — blood red solution

$$[Fe(H_2O)_6]^{3+}(aq) + 3C_2O_4^{2-}(aq) \xrightarrow{Na_2C_2O_4(aq)} [Fe(C_2O_4)_3]^{3-}(aq) + 6H_2O(l)$$
yellow solution — colourless solution

$$[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \xrightarrow{\text{conc. } HCl} [CoCl_4]^{2-}(aq) + 6H_2O(l)$$
pink solution — blue solution

(c) Redox reactions

- Justification of whether a redox reaction can occur is usually based on $E^\ominus$ values

$2Fe^{2+}(aq) + Cl_2(aq) \longrightarrow 2Fe^{3+}(aq) + 2Cl^-(aq)$
pale green solution — yellow solution

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

$2Cu^{2+}(aq) + 4I^-(aq) \longrightarrow 2CuI(s) + I_2(aq)$
cream ppt. brown solution

$Cu^{2+}(aq) + Zn(s) \longrightarrow Cu(s) + Zn^{2+}(aq)$
pink solid

(d) Hydrolysis of $[Fe(H_2O)_6]^{3+}$ and $[Cr(H_2O)_6]^{3+}$

An aqueous solution containing Fe^{3+} or Cr^{3+} is acidic due to hydrolysis.

$[M(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [M(OH)(H_2O)_5]^{2+}(aq) + H_3O^+(aq)$ where M = Fe or Cr

On addition of $Na_2CO_3(aq)$ separately to $Fe^{3+}(aq)$ or $Cr^{3+}(aq)$, CO_2 is evolved and the precipitate formed is $Fe(OH)_3$ and $Cr(OH)_3$ respectively.

APPENDIX

(I) Rules for Nomenclature of Complexes

The following rules apply to all complexes, whether or not they are derived from transition elements.

(a) Formulae of Complexes

1. The symbol for the central atom is written first, followed by anionic ligands and neutral ligands in that order. **Example: $[Fe(OH)(H_2O)_5]^{2+}$**
2. Within each ligand class, the order should be alphabetical in terms of the symbol for the donor atom of the ligand. **Example: $[Cu(NH_3)_4(H_2O)_2]^{2+}$**
   N is the donor atom in NH_3.
   O is the donor atom in H_2O.
3. Polyatomic ligands, but not monatomic ligands, are enclosed in curved brackets, and the formula of the whole complex is enclosed in square brackets. **Example: $[CrCl_2(NH_3)_4]^+$**

(b) Naming of Complexes

1. The cation is always named before the anion.
2. The names of the ligands precede the name of the central atom or ion.
3. The oxidation state of the central atom or ion is shown in Roman numerals in brackets immediately after its name.
4. Metals forming complex anions are given the word-ending *-ate*, whereas complex cations and neutral complexes are given their usual names.
5. Ligands are listed in alphabetical order, the multiplying prefix being ignored.
6. When a number prefix (e.g. di-, tri-) is already included in the name of the ligand, the name of the ligand is placed in a bracket with the prefix bis-, tris-, tetrakis- instead of di-, tri-, tetra- respectively.
7. Notice that the complex ion names are written as one word, with no spacing between the name and the oxidation state of the central atom.

(c) Steps to be taken

1. Identify the ligands (see **Box A**).

2. Identify the number of ligands (see **Box B**).

3. If several ligands are present, list them in alphabetical order. Note: prefixes do not alter order.

4. Name the central cation/atom and indicate its oxidation state using a Roman numeral in parentheses.

   For **complex cation**, use the name of the metal.

   For **complex anion**, modify the name of the metal to end in *–ate* (see **Box C**).

A

Monodentate ligands	
H_2O	aqua
NH_3	ammine
NO	nitrosyl
CO	carbonyl
Cl^-	chloro
CN^-	cyano
OH^-	hydroxo
NO_2^-	nitro
SCN^-	thiocyanato

Polydentate ligands	
en or $H_2NCH_2CH_2NH_2$	ethane-1,2-diamine
$C_2O_4^{2-}$	ethanedioato
edta	ethylenediaminetetraaceto

B

Prefixes used for monodentate ligands:

2 = di,
3 = tri,
4 = tetra,
5 = penta,
6 =hexa, etc.

Prefixes used for polydentate ligands:

2 = bis,
3 = tris,
4 = tetrakis

Names used for some metals in anionic complexes **C**

Element	Name in complex
Ti	titanate
V	vanadate
Cr	chromate
Mn	manganate
Fe	ferrate
Co	cobaltate
Ni	niccolate (ASE: nickelate)
Cu	cuprate
Zn	zincate
Ag	argentate
Au	aurate
Al	aluminate
Sn	stannate
Pb	plumbate

Raffles Institution
Year 6 H2 Chemistry 2023
23 An Introduction to the Chemistry of Transition Elements

Self-check questions

1 Define the following terms:
(a) *transition element*, **(b)** *complex ion*, **(c)** *ligand*, **(d)** *co-ordination number*

2 **(a)** Arrange the following species in order of increasing number of unpaired electrons:

(i) V, Cr, Fe, Ni and Cu **(ii)** V^{2+}, Ti^{2+}, Mn^{2+}, Co^{3+}, Zn^{2+}

(b) **(i)** An ion X^{2+} contains 22 electrons. What is the electronic configuration of X?

(ii) An ion Y^{2+} contains 40 protons. What is the electronic configuration of Y^{2+}?

(c) For each of the following species, state the oxidation state and electronic configuration of the metal cation/atom in the species.

(i) $TiCl_2$ **(ii)** $[V(H_2O)_6]^{3+}$ **(iii)** $[Cr(NH_3)_6]Cl_3$
(iv) $[Fe(SCN)(H_2O)_5]^{2+}$ **(v)** $[Fe(CN)_6]^{4-}$ **(vi)** $[Ni(CO)_4]$

3 **N2012/1/17**
The data below refers to a particular element.

density	10.5 g cm^{-3}
first ionisation energy	730 kJ mol^{-1}
second ionisation energy	2070 kJ mol^{-1}
third ionisation energy	3360 kJ mol^{-1}
melting point	1237 K

Where in the Periodic Table is this element likely to be found?

A Group 1 **B** Group 2 **C** Group 17 **D** the transition elements

4 **JJC/2008/P1/Q18**

A compound of chromium with the general formula $CrCl_3.6H_2O$ forms an aqueous solution. When this solution is treated with an excess of aqueous silver nitrate, only one third of the total chloride present is precipitated as AgCl.
What represents the structure of the chromium-containing ion present in the original compound?

A Cr^{3+} **B** $[Cr(H_2O)_6]^{3+}$ **C** $[Cr(H_2O)_5Cl]^{2+}$ **D** $[Cr(H_2O)_4Cl_2]^{+}$

5 **(a)** Suggest the function of haemoglobin in the body, and how it carries out this function.

(b) Explain why there is no change in the oxidation number of the iron(II) in the haem group when haemoglobin is converted into oxyhaemoglobin.

(c) Carbon monoxide acts as a poison through its interaction with haemoglobin. Describe this interaction and discuss why carbon monoxide is so much more poisonous than carbon dioxide.

(d) A patient suffering from carbon monoxide poisoning can be treated by being given pure oxygen to breathe. Suggest a reason why this treatment is effective.

(e) Name another poison that can affect haemoglobin, and describe how it reacts.

6 **[*Modified* N13/2/4]**

The table below gives some data about calcium, iron and copper:

Property	calcium	iron	copper
Relative atomic mass	40.1	55.6	63.5
Atomic radius (metallic)/ nm	0.197	0.126	0.128
Ionic radius (2+)/ nm	0.099	0.076	0.069
Melting point/ K	1112	1808	1358
Density/ g cm^{-3}	1.54	7.86	8.92
Electrical conductivity/ 10^6 S cm^{-1}	0.298	0.100	0.596

(a) **(i)** Explain why the atomic radii of iron and copper are similar.

(ii) Use relevant data from the table to explain why the densities of iron and copper are significantly greater than that of calcium (no calculations are required).

(iii) Explain why iron and copper have a tendency to vary in their oxidation states, whereas calcium does not.

(b) **(i)** Describe the structure and bonding in calcium with the aid of a labelled diagram.

(ii) Suggest why the melting point of iron is significantly higher than that of calcium.

(c) The high electrical conductivity of copper makes it a very useful element for making electrical components.

(i) Apart from high cost, suggest why copper is **not** usually used for overhead electrical cables.

(ii) The high conductivity of copper is a consequence of its electronic configuration. Complete the electronic configuration of:

Cu $1s^2 2s^2 2p^6$ ....; Cu^{2+} $1s^2 2s^2 2p^6$ ....

(iii) The copper used for electrical wiring must be very pure. Outline how impure copper is purified industrially.

7 The following table lists some of the cations found in the *Qualitative Analysis Notes* in the *Data Booklet*. Fill in the blanks.

			addition of excess NaOH(aq)		addition of excess NH_3(aq)	
cation	colour	formula of aqua complex ion	colour of complex ion formed	formula of complex ion formed	colour of complex ion formed	formula of complex ion formed
Al^{3+}(aq)					*ppt is insoluble is excess NH_3*	
Cr^{3+}(aq)					*ppt is insoluble is excess NH_3*	
Cu^{2+}(aq)			*ppt is insoluble is excess NaOH*			
Fe^{2+}(aq)			*ppt is insoluble is excess NaOH*		*ppt is insoluble is excess NH_3*	
Fe^{3+}(aq)			*ppt is insoluble is excess NaOH*		*ppt is insoluble is excess NH_3*	
Mn^{2+}(aq)			*ppt is insoluble is excess NaOH*		*ppt is insoluble is excess NH_3*	
Zn^{2+}(aq)						

Practice Questions

1 **[Modified N08/2/4]**

Copper is a typical transition element. It has more than one oxidation state and many of its compounds have colours in the blue-green-yellow part of the visible spectrum.

(a) Complete the electronic configuration of copper atoms and of copper(II) ions.

Cu $1s^2\ 2s^2\ 2p^6$ ____________________; Cu^{2+} $1s^2\ 2s^2\ 2p^6$ ________ ____________ **[2]**

(b) Aqueous copper(II) chloride, $CuCl_2$, is a green-blue solution which gives the following reactions. In each case the precipitate initially formed is separated before being treated with $NH_3(aq)$.

$$CuCl_2(aq) \xrightarrow{\text{Dilute } HNO_3,\ AgNO_3(aq)} \text{white ppt} \xrightarrow{NH_3(aq)} \textbf{B} \text{ (colourless solution)}$$

$$CuCl_2(aq) \xrightarrow{NH_3(aq)} \text{pale blue ppt} \xrightarrow{NH_3(aq) \text{ in excess}} \textbf{C} \text{ (deep blue solution)}$$

(i) State the formula of compound **B**.

(ii) What is the formula of the cation present in $CuCl_2(aq)$ and the cation present in **C**? **[3]**

(c) Aqueous $CuCl_2$ also undergoes the following reactions.

$$\begin{tikzcd} CuCl_2(aq) \arrow[r, "\text{conc. } HCl"] \arrow[d, "\text{warm with Cu and conc. } HCl"'] & \textbf{D} \text{ (yellow-green solution)} \arrow[d, "SO_2"] \\ \textbf{E} \text{ (colourless solution)} \arrow[r, "\text{water}"] & \textbf{F} \text{ (white solid)} \end{tikzcd}$$

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 into **D** and **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 in **F**.

(i) Suggest balanced equations for the formation of **D** from $CuCl_2$ and for the formation of **E** from $CuCl_2$.

(ii) Suggest the formulae of the complex ion 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**? **[7]**

(d) The oxidation number of copper in compound **F** is the same as that in complex ion **E**.

(i) What type of reaction occurs when **D** is converted into **F**?

(ii) Suggest a formula for the compound **F**. **[2]**

(e) Under suitable conditions, $CuCl_2$ can be converted into **G** which is pale green in colour. The composition of **G** by mass is Cu, 21.5 %; F, 38.7 %; K, 39.8 %.

(i) Use the data to calculate the empirical formula of **G**.

(ii) Suggest the oxidation state of copper in **G**. **[3]**

(f) **E** and **F** are both colourless. All other copper compounds mentioned are coloured.

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

(ii) With the aid of suitable diagram(s), explain why **G** is coloured. **[5]**

2 [*Modified* **N11/3/4(c)**]

The iron atoms in haemoglobin are in the oxidation state +2 and are in an octahedral environment. Each iron atom is surrounded by five nitrogen-containing ligands, and one oxygen-containing ligand, which is H_2O in deoxyhaemoglobin and O_2 in oxyhaemoglobin.

Fig. 1 shows how the d-orbitals are split in an octahedral environment.

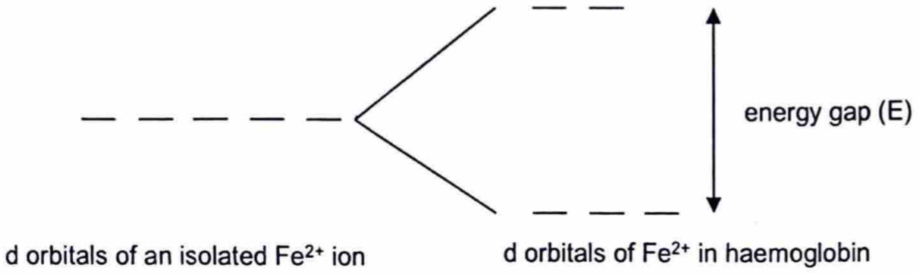

Fig. 1

(i) Using Cartesian axes, like those shown in Fig. 2, draw fully labelled diagrams of the following.

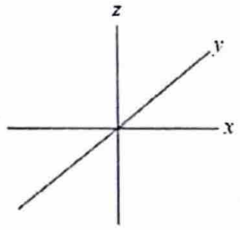

Fig. 2

- One of the d orbitals at the lower energy level in the octahedral environment. Label this diagram 'lower'.
- One of the d orbitals at the upper energy level in the octahedral environment. Label this diagram 'upper'.

(ii) Explain why splitting of the d-subshell occurs in the octahedral environment, using your d-orbital diagrams in **(i)**.

(iii) Use Fig. 1 to outline the origin of the red colour of haemoglobin.

When the H_2O ligand in haemoglobin is changed to an O_2 ligand 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 first, by pairing up if necessary before the higher energy d-orbitals are used.

(iv) Use diagrams like Fig. 1 to show the electronic distribution of a Fe^{2+} ion in a high spin state, and in a low spin state.

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

(vi) Using 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.

3 **[RI Prelim 2017/3/1(c) and (d)]**

An example of a complex of iron is the hexacyanoferrate(III) ion, $[Fe(CN)_6]^{3-}$. Its potassium salt $K_3[Fe(CN)_6]$ can be synthesised from the following steps.

Step 1 Pale green aqueous $FeSO_4$ is boiled with an excess of KCN, producing a yellow solution which contains $[Fe(CN)_6]^{4-}$ ions.

Step 2 The yellow solution is acidified, then chlorine is bubbled into the solution forming a red solution.

Step 3 The red solution is evaporated to give dark red crystals containing $[Fe(CN)_6]^{3-}$ ions.

(i) The complex ion $[Fe(H_2O)_6]^{2+}$ is responsible for the green colour of aqueous $FeSO_4$.

Write an appropriate equation to account for the colour change in **Step 1** and state the type of reaction that has occurred. [2]

(ii) Suggest why $[Fe(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$ have different colours. [1]

(iii) By using relevant data from the *Data Booklet*, predict whether iodine can be used instead of chlorine to carry out the reaction in **Step 2**. [1]

4 **[Modified N2021/2/5]**

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

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

equation 5.1 $2HSCH_2CO_2H + 2Fe^{3+} \rightarrow 2Fe^{2+} + {}^-O_2CCH_2\text{–}S\text{–}S\text{–}CH_2CO_2^- + 4H^+$

When thioglycolic acid reacts with the iron(II) ions formed, 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 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 iron(III) ions. Explain your answer. [1]

(b) Draw a diagram of complex **M** which shows how the bonds between the ligand and the central iron(II) ion are formed. Hence, state the shape about the central iron(II) ion. [2]

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

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

(e) When $NH_3(aq)$ is added directly to a standard sample of $[[Fe(H_2O)_6]^{2+}(aq)$, 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 $[Fe(H_2O)_6]^{2+}(aq)$. Include state symbols.

$[Fe(H_2O)_6]^{2+}(aq)$ + ...$NH_3(aq)$ → ______________________ [1]

(ii) Suggest why the green precipitate turns brown. [1]

5 [Modified N2017/4/1(c)]

The following table shows the observations in an experiment. **FA 1** is $H_2O_2(aq)$ and **FA 2** is $Fe(NO_3)_3(aq)$.

	Tests	Observations
1	Put about a 2 cm depth of **FA 2** into a test-tube. Add about a 2 cm depth of **FA 1** to the same test-tube and shake the mixture thoroughly. Observe the mixture until no further changes are seen.	**FA 2** is yellow in colour. Yellow solution turns brown. Effervescence is observed. Gas evolved relights a glowing splint. After some time, solution turns from brown back to yellow.
2	Test the **FA 2** solution using Universal Indicator paper.	Universal indicator paper turns orange (pH 3)

Steps **1** to **4** represent a possible mechanism for the catalysed decomposition of H_2O_2. In this mechanism, the O_2H ligand on one of the complex ions represents the H–O–O⁻ ion and the O represents the oxygen atom.

step 1 $[Fe(H_2O)_6]^{3+}(aq) + H_2O_2(aq) \rightleftharpoons [Fe(H_2O)_5O_2H]^{2+}(aq) + H_3O^+(aq)$

step 2 $[Fe(H_2O)_5O_2H]^{2+}(aq) \longrightarrow [Fe(H_2O)_5O]^{3+}(aq) + OH^-(aq)$

step 3 $[Fe(H_2O)_5O]^{3+}(aq) + H_2O_2(aq) \longrightarrow [Fe(H_2O)_6]^{3+}(aq) + O_2(g)$

step 4 $H_3O^+(aq) + OH^-(aq) \longrightarrow 2H_2O(l)$

(a) Explain fully how you can tell that the $[Fe(H_2O)_6]^{3+}$ ions are acting as a catalyst in this reaction, using evidence from the observations in test **1** and from the mechanism. [3]

(b) The crystals of hydrated iron(III) nitrate, $Fe(NO_3)_3.9H_2O$, used to prepare **FA 2** were pale violet in colour. The colour of the **FA 2** solution obtained by dissolving these crystals is due to $[Fe(H_2O)_6]^{3+}$ ion reacting with a water molecule.

Complete the equation below. Explain how you deduced the products of this reaction, using the observation from test **2**.

$[Fe(H_2O)_6]^{3+} + H_2O \longrightarrow$ .... + ... [2]

6 The rate of the reaction between iodide and peroxodisulfate(VI) ions, $S_2O_8^{2-}$, is increased by the presence of small concentrations of Fe^{2+}(aq) ions.

(a) Write an equation for the reaction between iodide and peroxodisulfate(VI) ions.

(b) Calculate the E°_{cell} for the reaction and suggest why the uncatalysed reaction is slow.

(c) Explain how Fe^{2+} ions can act as a **homogeneous catalyst** for this reaction. Use relevant data from the Data Booklet to show the spontaneity of the reactions involved.

(d) By considering relevant E° values from the *Data Booklet*, choose one other example of transition metal ions that would be predicted to act as catalysts for the above reaction.

7 **(a)** Explain the meaning of the term *heterogeneous catalysis*.

(b) Transition metals are often used as heterogeneous catalysts for industrial processes involving hydrogen. Give two examples of metals used in this way and write equations for the reactions they catalyse.

(c) Using one of the two examples in **(b)**, explain clearly how the transition metal catalyses the reaction.

8 Explain each of the following observations using relevant information from the *Data Booklet*.

(a) When treated with water, copper(I) sulfate reacts with water to give a blue solution and a pink-coloured solid.

(b) When aqueous iron(III) chloride is added to aqueous potassium iodide, a brown solution is formed, but aqueous potassium hexacyanoferrate(III) does not react with aqueous potassium iodide.

(c) Although acidic solutions of iron(II) salts are only slowly oxidised in air, the precipitate that is obtained on adding NaOH(aq) to a solution of iron(II) salt rapidly turns brown on the surface.