ANDERSON SERANGOON JUNIOR COLLEGE
2025 JC2 H2 Chemistry
AN INTRODUCTION TO THE CHEMISTRY OF TRANSITION ELEMENTS

Content

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

Learning Outcomes

Candidates should be able to:

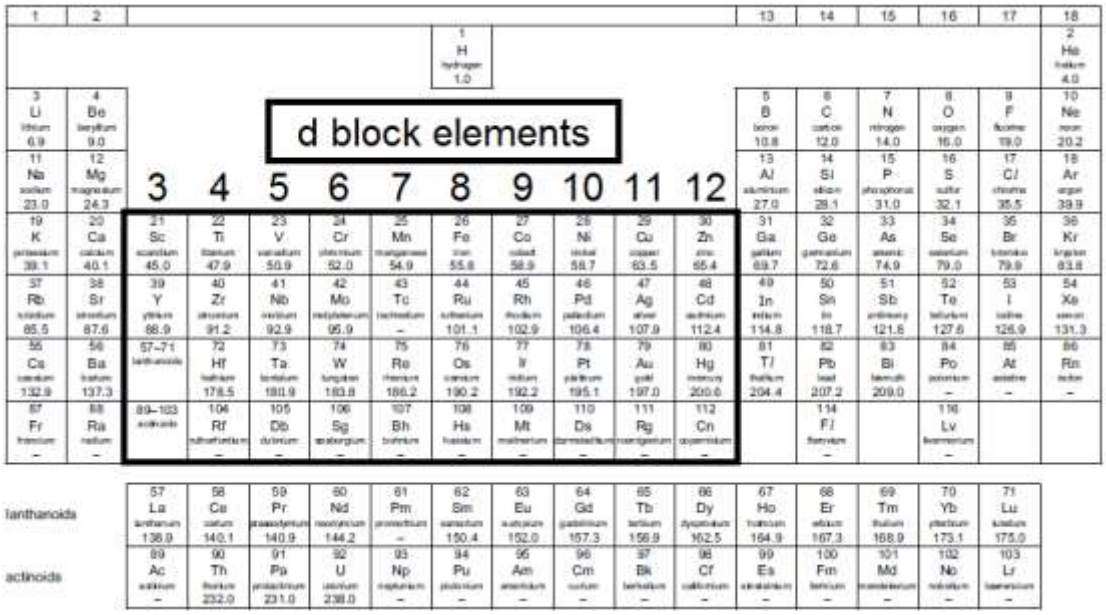
(a) explain what is meant by a transition element, in terms of d block elements forming one or more stable ions with partially filled d subshells
(b) state the electronic configuration of a first row transition element and its ions
(c) explain why atomic radii and first ionisation energies of the transition 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
(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 in haemoglobin
(k) describe, using the shape and orientation of the d orbitals, the splitting of degenerate d orbitals into two energy levels in octahedral complexes
(l) explain, in terms of d orbital splitting and d-d transition, why transition element complexes are usually coloured
[knowledge of the relative order of ligand field strength is **not** required]
(m) explain how some transition elements and/or their compounds can act as catalysts (see also 8(j))

References

1. Chemistry for Advanced Level, Peter Cann and Peter Hughes
2. Understanding Advanced Physical Inorganic Chemistry, The Learner's Approach, Jeanne Tan and Chan Kim Seng.

1. INTRODUCTION

In the Periodic Table, the d block elements are found in groups 3 to 12.



A transition element is a **d block element** that can form **one or more <u>stable</u> ions** with **_____ d subshells**.

The ten elements from scandium (Sc) to zinc (Zn) comprise the **<u>3d</u>** block of elements.

Based on the definition in our syllabus, we will focus on the following eight elements.

Ti	V	Cr	Mn	Fe	Co	Ni	Cu
titanium	vanadium	chromium	manganese	iron	cobalt	nickel	copper

Sc and Zn are not considered transition elements as they **do not form stable ions with <u>partially filled</u> d subshells**.

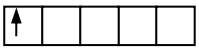
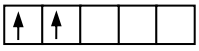
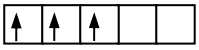
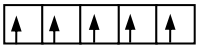
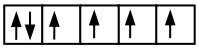
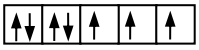
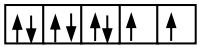
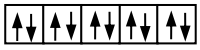
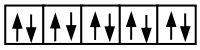
Sc	[Ar] $3d^1\,4s^2$	Zn	[Ar] $3d^{10}\,4s^2$
Sc^{3+}	[Ar]	Zn^{2+}	[Ar] $3d^{10}$

The common stable ion for Sc is Sc^{3+}, which has an **<u>empty</u>** d subshell.
As for Zn, its only stable ion Zn^{2+}, has a **<u>completely filled</u>** d subshell.

It is the presence of the <u>partially filled d subshell</u> that gives rise to the distinct properties of transition elements. Typical chemical properties of transition elements include the ability to **form coloured ions**, exist in **variable oxidation states**, **form complexes** and **act as catalysts**.

1.1 Electronic Configuration

Table 1 below shows the electronic configurations of the first row d block elements.

Symbol	Atomic (proton) Number	Electronic Configuration			
				3d	4s
Sc	21	[Ar] $3d^1\ 4s^2$	[Ar]		
Ti	22	[Ar] $3d^2\ 4s^2$	[Ar]		
V	23	[Ar] $3d^3\ 4s^2$	[Ar]		
Cr*	24	**[Ar] _____**	[Ar]		
Mn	25	[Ar] $3d^5\ 4s^2$	[Ar]		
Fe	26	[Ar] $3d^6\ 4s^2$	[Ar]		
Co	27	[Ar] $3d^7\ 4s^2$	[Ar]		
Ni	28	[Ar] $3d^8\ 4s^2$	[Ar]		
Cu*	29	**[Ar] _____**	[Ar]		
Zn	30	[Ar] $3d^{10}\ 4s^2$	[Ar]		

[Ar] represents electronic configuration ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$)
** anomalous electronic configurations*

Table 1: Electronic configurations of the first row d block elements

ATOMIC STRUCTURE

- The 4s orbital is filled with electrons first before the 3d orbitals. This is because the empty 4s orbital has a lower energy than the 3d orbitals.

- **Exceptions in Cr and Cu**: Electronic configurations with half–filled or completely filled d orbitals are unusually stable as both these configurations result in a **symmetrical charge distribution** around the nucleus. Hence, the electronic configuration of **Cr is [Ar]$3d^5 4s^1$** (instead of [Ar]$3d^4 4s^2$) and **Cu is [Ar]$3d^{10} 4s^1$** (instead of [Ar]$3d^9 4s^2$).

- When the 3d subshell is occupied by electrons, the 3d electrons repel the 4s electrons further away from the nucleus and cause the 4s electrons to be at a higher energy level. So when transition elements form ions, electrons are first removed from the 4s subshell before removing from the 3d subshell.

- Hence, when writing the electronic configuration of the cations, **write the electronic configuration of the neutral atom first** and then remove the electrons from the 4s subshell first before the 3d subshell.

Exercise 1

Write the electronic configuration of the following ions.

$_{24}Cr$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$	$_{24}Cr^{2+}$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^4$
$_{26}Fe$		$_{26}Fe^{2+}$	
$_{29}Cu$		$_{29}Cu^{+}$	

2. PHYSICAL PROPERTIES

2.1 Atomic radius and First Ionisation Energy

Atomic radii and first ionisation energies of transition elements are relatively invariant.

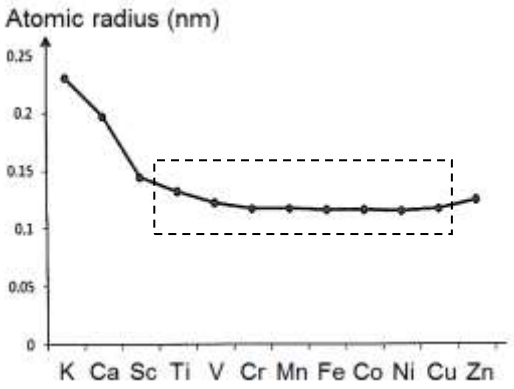


Figure 1: Trend of atomic radius

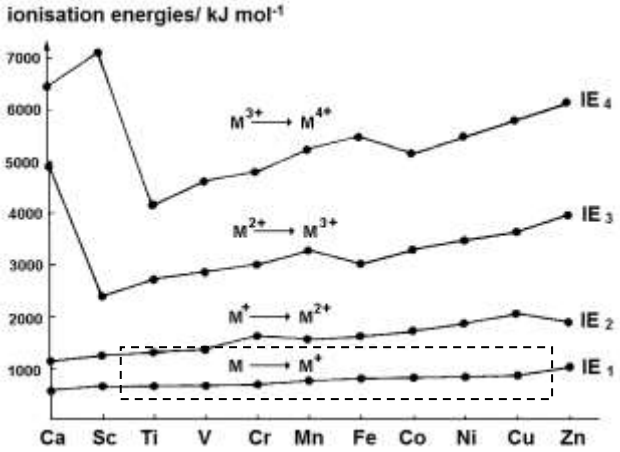


Figure 2: Trend of ionisation energies

Reason:

- The nuclear charge **increases** from Ti to Cu as the number of protons increases.
- **However, additional electrons are being added to the inner 3d orbitals which causes an increase in shielding effect**.
- As a result, the increase in shielding effect **nullifies / cancels out** the effect due to the increase in nuclear charge.
- Hence, the electrostatic attraction of the valence electrons from the nucleus **increases only slightly** or **remains fairly constant**.

• So, the atomic radii across the transition elements decreases very slightly or remains **fairly constant**.	• So, similar amount of energy is needed to remove the 4s valence electron from the elements, and • the first ionisation energies across the transition elements increases very slightly or remains **fairly constant**.

2.2 Melting point and density

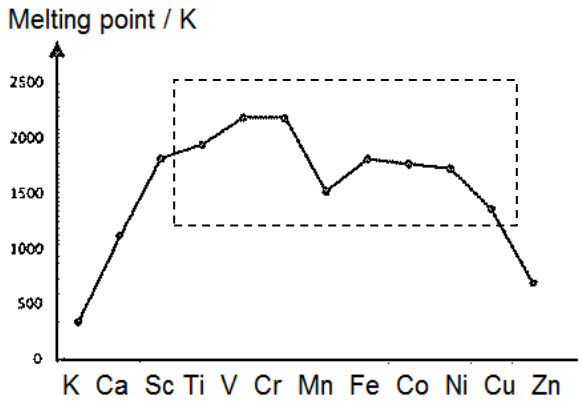


Figure 3:
Melting points of Ca and the d block elements

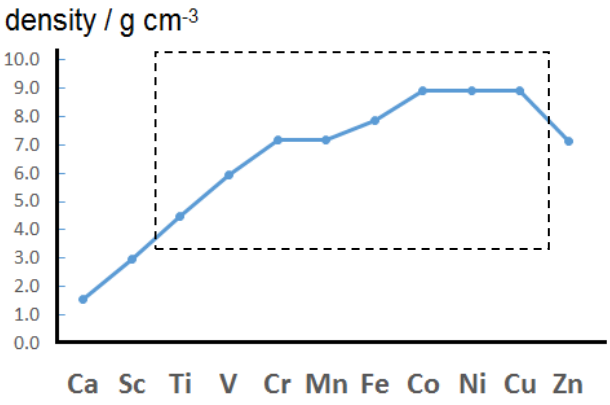


Figure 4:
Densities of Ca and the d block elements

Transition elements have higher melting points compared to s block elements, e.g. Ca

- Both *s* block elements and transition elements consist of a giant metallic lattice structure held together by strong metallic bonds.
- In transition elements, both the **3d and 4s electrons** are available for metallic bonds since the **energy level difference** between the 3d and 4s orbitals **is small**.
- In *s* block elements, only **one or two 4s electrons** is/are available for metallic bonding. (e.g. calcium metal contributes its two 4s electrons)
- The **greater** number of delocalised electrons available for metallic bonding in transition elements results in **stronger** electrostatic attraction between the positively charged ions and the 'sea' of delocalised electrons.
- **More energy** is required to overcome the **stronger** metallic bonds in transition elements as compared to the *s* block elements.
- **Exception: Manganese has a stable d^5 arrangement ($[Ar]3d^54s^2$) which results in the low availability of electrons for delocalisation and hence a relatively low melting point**.

Transition elements have higher densities compared to s block elements, e.g. Ca

- Transition elements have relatively **smaller atomic radii** and **higher atomic mass** compared to *s* block elements.
- Also, transition elements have **more closely packed structures** due to their stronger metallic bonding as compared to *s* block elements.
- Thus, transition elements are **denser** than *s* block elements.

For self-reading
Why do transition elements have smaller atomic radius than s block elements?
- *They have higher nuclear charge than s block elements, and*
- *d orbitals, being relatively diffused in nature, provide poor shielding from the attraction of the nucleus*
- *thus there is strong attraction of the nucleus for the valence electrons, resulting in smaller atomic radius.*

Exercise 2

Iron is a typical transition element and calcium is a typical s−block element. Data for four properties of these elements is given below.

Which one of the following is correct?

	Property	Iron	Calcium
A	Melting Point	1535 °C	850 °C
B	Atomic Radius	0.197 nm	0.126 nm
C	First Ionisation Energy	590 kJ mol^{-1}	762 kJ mol^{-1}
D	Density	1.54 g cm^{-3}	7.86 g cm^{-3}

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3. CHEMICAL PROPERTIES

Transition elements have the following unique chemical properties which are typically not shown by s block elements:

- display variable oxidation states
- exhibit catalytic properties
- form stable complexes
- form coloured compounds and ions

3.1 Variable Oxidation States

Transition elements display variable oxidation states in their compounds

Table 2 below shows the known oxidation states of the elements from Sc to Zn. The most common oxidation states are highlighted.

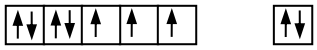
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+1	+1	+1	+1	+1	+1	+1	**+1**	
	+2	+2	+2	**+2**	**+2**	**+2**	**+2**	**+2**	**+2**
+3	**+3**	**+3**	**+3**	+3	**+3**	**+3**	+3	+3	
	+4	+4	+4	**+4**	+4	+4	+4		
		+5	+5	+5	+5	+5			
			+6	+6	+6				
				+7					

Table 2: Common oxidation states of d block elements.

Example of manganese compounds:

Compound	$MnCl_2$	$MnCl_3$	MnO_2	K_2MnO_4	$KMnO_4$
Oxidation state of Mn	+2	+3	+4	+6	+7

- Reason for existence of various oxidation states:
  - **electrons** in the **3d and 4s subshells** are **in energy** thus
  - different number of these electrons are available for use in bond formation, and
  - ions formed by using different number of electrons for bonding are of **similar stability**
- Generally, the **maximum** oxidation state of each element corresponds to the sum of the number of **4s and unpaired 3d electrons** (except Cu).

Example: Co 

Maximum oxidation state = three unpaired 3d electrons + two 4s electrons = +5

- In contrast, s block elements are limited to oxidation states of +1 (Group 1) and +2 (for Group 2).

Reason:
  - For the s block elements, once the valence s electrons are removed, further removal of inner shell p electrons would require too much energy.

Example:

Sharp increase between 2nd & 3rd I.E. for Ca → maximum 2 electrons lost
→ Ca only forms Ca^{2+}

Element	Electronic configuration	1st I.E. / kJ mol^{-1}	2nd I.E. / kJ mol^{-1}	3rd I.E. / kJ mol^{-1}	4th I.E. / kJ mol^{-1}
calcium	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$	590	1150	4940	6480
iron	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$	762	1560	2960	5400

Table 3: Successive I.E. of calcium and iron

Gradual increase in I.E. for Fe
→ Fe can form both Fe^{2+} and Fe^{3+}

Note

Variable oxidation state is **not** confined to transition elements (e.g. PCl_3 and PCl_5, $PbCl_2$ and $PbCl_4$).

Exercise 3

Vanadium has the electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$.
Which compound is likely to exist?

1 V_2O_5 **2** $VOCl$ **3** $K_2V_2O_7$

Answer: ( )

3.1.1 Oxidation states and type of bonding

- The elements exhibit **higher oxidation states** when they form **covalently bonded** oxo–anions or compounds with oxygen. The **3d and 4s** electrons are used in covalent bonding.

  Examples: $Cr_2O_7^{2-}$, VO_3^-, CrO_4^{2-}, TiO_2, V_2O_5, CrO_3

- The elements exhibit **lower oxidation states** when they **exist as free cations**.

  Example: Mn^{2+} exists but not Mn^{7+}.

Exercise 4

State one reason why the $Cr^{6+}(aq)$ ion does not exist but $CrO_4^{2-}(aq)$ ions are formed instead.

- Cr^{6+} ion has high charge density due to its **small size and high charge**.
- This leads to **high** _____ and will polarise the **O–H** bonds in the water molecules coordinated to it.
- The O–H bonds are **polarised and break off readily** to form $CrO_4^{2-}(aq)$ ions. Therefore, $Cr^{6+}(aq)$ does not exist.

3.1.2 Redox systems

Fe^{3+}/Fe^{2+}

Solutions of $Fe^{2+}(aq)$ are readily oxidised to $Fe^{3+}(aq)$ by many oxidising agents, including atmospheric oxygen and potassium dichromate(VI).

Example:

$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$ $\quad E^\ominus = +1.23$ V

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

$\frac{1}{2}O_2 + 2H^+ + 2Fe^{2+} \longrightarrow H_2O + 2Fe^{3+}$ $\quad$ **$E_{cell}^\ominus = +0.46$ V**

Example:

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

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

$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$ $\quad$ **$E_{cell}^\ominus = +0.56$ V**

$Cr_2O_7^{2-}/Cr^{3+}$

Dichromate(VI) $Cr_2O_7^{2-}$, is an oxidising agent.

Example:

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

$I_2 + 2e^- \rightleftharpoons 2I^-$ $\quad E^\ominus = +0.54$ V

$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$ $\quad$ **$E_{cell}^\ominus = +0.79$ V**

MnO_4^-/Mn^{2+}

Manganate(VII), MnO_4^- is a strong oxidising agent.

Example:

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

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

$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$ $\quad$ **$E_{cell}^\ominus = +0.75$ V**

This reaction is commonly used in a **redox titration** to determine the amount of iron in a solution. No indicator is required as the purple potassium manganate(VII) acts as its own indicator.

3.2 Catalytic property of transition elements & their compounds

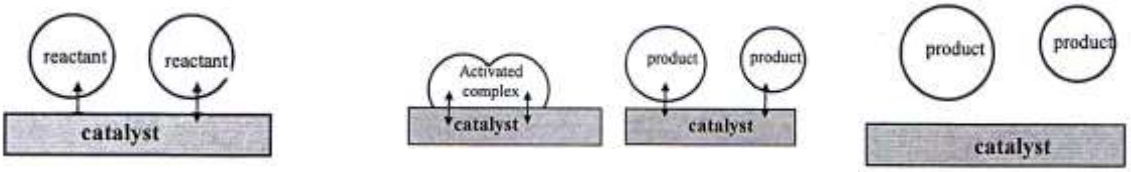
Transition element catalysts may be divided into two distinct groups:

- **homogeneous** catalysts whereby the catalysts are in the same phase as the reactants.
- **heterogeneous** catalysts whereby the catalysts are in a different phase from the reactants.

3.2.1 Heterogeneous catalysts

- In heterogeneous catalysis, the reactants are usually liquids or gases and the catalyst is a solid that provides active sites at which the reaction occurs.

- The mechanism of heterogeneous catalysis is summarised in Figure 5.



- Reactant molecules are *adsorbed* onto the catalyst surface by forming weak temporary bonds with the catalyst.
- Ready exchange of electrons to and from the reactant molecules takes place.
- *Desorption* of products from the catalyst surface.

Figure 5: Mechanism of heterogeneous catalysis

- Transition elements and their compounds are heterogeneous catalysts because they have **partially filled d subshells** which allow weak temporary bonds to be formed with the reactant molecules.

- *Examples of heterogeneous catalysts*:

catalyst	reactions catalysed	
Fe or Fe_2O_3	$N_2 + 3H_2 \rightleftharpoons 2NH_3$	(Haber process)
Ni	$RCH{=}CH_2 + H_2 \longrightarrow RCH_2CH_3$	(manufacture of margarine)
V_2O_5	$2SO_2 + O_2 \rightleftharpoons 2SO_3$	(Contact process)

How does a heterogeneous catalyst increase the reaction rate?

1. Reactant molecules form weak temporary bonds with the catalyst due to the presence of partially filled 3d subshells resulting in the weakening of existing bonds within the reactant molecules, thus lowering the activation energy of the reaction.

2. The reactant molecules are brought closer together at the active sites, thus resulting in higher concentration of reactants at the surface of the catalyst and increase in rate of reaction.

3.2.2 Homogeneous catalysts

Transition elements and their ions are homogeneous catalysts due to their **ability to exist in variable oxidation states.**

Interconversion of oxidation states enables the transition elements and their compounds to form intermediate compounds and then revert to the original state at the end of the catalysed reaction.

***Example*: Reaction of iodide ion, I^- and peroxodisulfate ion, $S_2O_8^{2-}$**

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

$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$	$E^\ominus = +0.54$ V
$S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq)$	$E^\ominus = +2.01$ V
$\mathbf{S_2O_8^{2-}(aq) + 2I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_2(aq)}$	$\mathbf{E_{cell}^\ominus = +1.47}$ V

- The reaction is *thermodynamically feasible* ($\mathbf{E_{cell}^\ominus > 0}$) but *kinetically slow* due to **electrostatic repulsion between two negatively charged ions** resulting in high activation energy.

- This reaction can be catalysed by either $Fe^{3+}(aq)$ or $Fe^{2+}(aq)$.

When the reaction is catalysed by ***Fe^{3+}*:**

Step 1: *Formation of intermediate* **(Fe^{3+} colliding with I^-)**

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

$\mathbf{2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(aq)}$ $\quad \mathbf{E_{cell}^\ominus = +0.23}$ V

Step 2: *Regeneration of catalyst* **(Fe^{2+} colliding with $S_2O_8^{2-}$)**

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

$\mathbf{2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \longrightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)}$ $\quad \mathbf{E_{cell}^\ominus = +1.24}$ V

- When the reaction is catalysed by Fe^{3+}, it proceeds via two steps that are thermodynamically feasible under standard conditions.
  ($\mathbf{E_{cell}^\ominus > 0}$ **for both steps)**
- These steps take place more readily since it involves collision between **two oppositely charged ions in both steps**.
- The activation energy for each step is lower than that of the uncatalysed reaction.
- Hence, reaction rate increases.
- The Fe^{3+} is regenerated at the end of the reaction.

When the reaction is catalysed by ***Fe^{2+}:***

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

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

$$\mathbf{2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \longrightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)} \quad \mathbf{E_{cell}^\ominus = +1.24\ V}$$

Step 2: *Regeneration of catalyst* **(Fe^{3+} colliding with I^-)**

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

$$\mathbf{2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(aq)} \quad \mathbf{E_{cell}^\ominus = +0.23\ V}$$

- Fe^{2+} is also an effective catalyst.
- The same two steps above will take place but in a reverse order and the overall reaction will still be the same.

Choice of catalyst

Is it true that any metal cation can act as a catalyst for the reaction?

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

$$\mathbf{2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(aq)} \quad \mathbf{E_{cell}^\ominus > 0.00\ V}$$

What should the $E^o_{Fe3+/Fe2+}$ be such that the E^o_{cell} for above overall reaction is > 0V?

- **Should be more than + 0.54V**

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

$$\mathbf{2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \longrightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)} \quad \mathbf{E_{cell}^\ominus = > 0.00\ V}$$

What should the $E^o_{Fe3+/Fe2+}$ be such that the E^o_{cell} for above overall reaction is > 0V?

- **Should be less than +2.01V**

- Other metal cations can also act as a catalyst for this reaction as long as their $E^\ominus$ values fall between **+0.54 V and +2.01 V**.

In general, the catalyst should have an $E^\ominus$ value between those of the reactants.

The energy profile below in Figure 6 compares the uncatalysed and catalysed reactions.

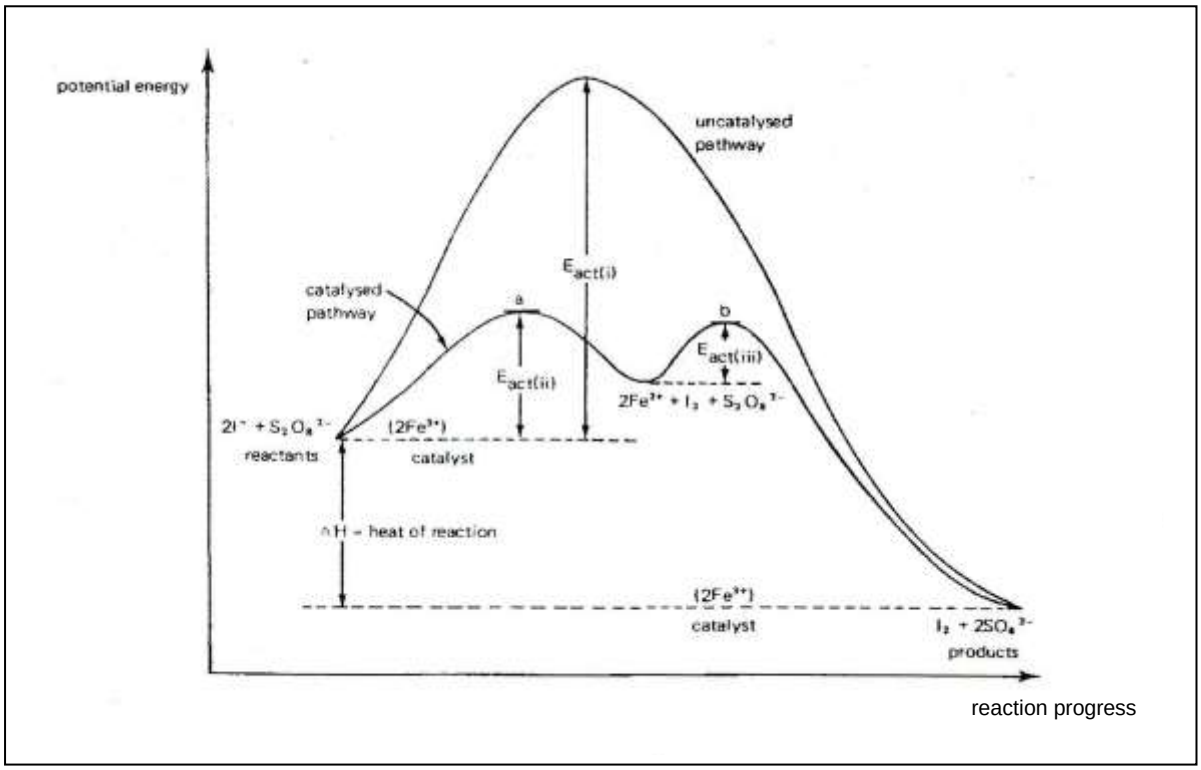


Figure 6: Reaction profile diagram of catalysed and uncatalysed reaction

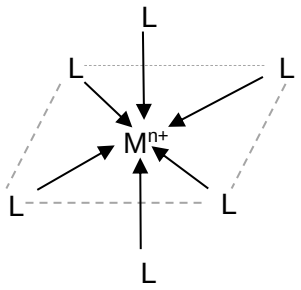
3.3 Formation of stable complexes

- A **complex** consists of **a central metal atom or ion** surrounded by **anions or molecules** called **ligands**.

- A **ligand** (L) is a **neutral molecule or an anion** that has at least one lone pair of electrons to be used in forming a **_____ bond** to the central metal atom or ion.

- All ligands are **Lewis bases** as they are lone pair donors.

Examples of ligands:
Cl^-, OH^-, CN^-, SCN^- (thiocyanate ion), H_2O, NH_3, CO (carbon monoxide)



- The **total number of dative bonds** that are attached to the central atom or ion is called the **co–ordination number** of the complex.

  Example: In $[Co(NH_3)_6]^{3+}$, the coordination number is 6.

- The co–ordination number around the central metal atom or ion is highly dependent on the nature of the metal atom or ion and the ligand involved.

- The difference in sizes of the ligands and the transition metal atoms or ions means that the number of ligands that can fit around the central metal atom or ion varies.

- The co–ordination number of **four** and **six** are the most common.

- A complex can be neutral (called neutral complex), or a cation or anion (called complex ions), depending on the overall charge.

  Example of neutral complex: $Ni(CO)_4$, $Cu(OH)_2(H_2O)_4$

  Example of complex ions: $[Fe(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{3-}$

- A complex ion does not exist on its own in a compound. An anionic complex ion forms ionic bonds with cations, while a cationic complex ion forms ionic bonds with anions.

  Examples:
  $K_4Fe(CN)_6$ contains four K^+ cations and one complex anion $[Fe(CN)_6]^{4-}$
  $K_3Fe(CN)_6$ contains three K^+ cations and **one** complex anion $[Fe(CN)_6]^{3-}$
  $[Cr(NH_3)_6]Cl_3$ contains **one** $[Cr(NH_3)_6]^{3+}$ complex cation and **three** Cl^- anions

In aqueous solution, Fe^{3+} ion exists as $[Fe(H_2O)_6]^{3+}(aq)$ and Cu^{2+} ion exists as $[Cu(H_2O)_6]^{2+}(aq)$.

Exercise 5

Complete the table below.

Complex	Co–ordination number	Oxidation number of central metal
$[Fe(CN)_6]^{3-}$		
$[Fe(SCN)(H_2O)_5]^{2+}$		
$[CuCl_4]^{2-}$		

Exercise 6a

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 ion present in the original compound?

A $Cr^{3+}(aq)$

B $[Cr(H_2O)_6]^{3+}$

C $[Cr(H_2O)_5Cl]^{2+}$

D $[Cr(H_2O)_4Cl_2]^{+}$

N95/IV/17

Working

Exercise 6b

Platinum(IV) chloride combines with ammonia to form compounds in which the co–ordination number of platinum is 6. A formula unit of one of the compounds contains a cation and only two chloride ions.

What is the formula of this complex ion?

A $[Pt(NH_3)_3Cl_3]^{+}$

B $[Pt(NH_3)_4Cl_2]^{2+}$

C $[Pt(NH_3)_5Cl]^{3+}$

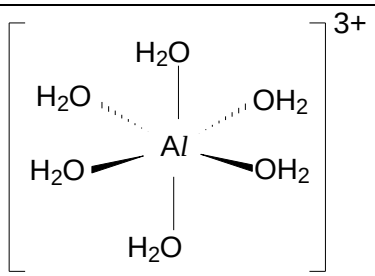
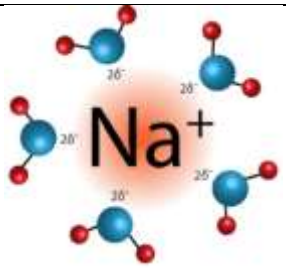
D $[Pt(NH_3)_6]^{4+}$

Answer: ( )

Working

Recall

Why does Al^{3+} or Mg^{2+} exist as $[Al(H_2O)_6]^{3+}$ or $[Mg(H_2O)_6]^{2+}$ respectively while Na^+ only form ion-dipole interactions with the water molecules?

	
Al^{3+} or Mg^{2+} being **high charge** density ions will form complexes with the water molecules.	Na^+ , being **low** charge density ions, form ion-dipole interactions with the water molecules.

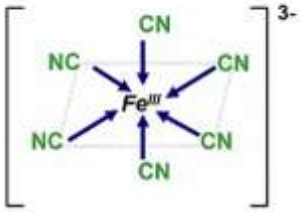
Important

Why do transition metal ions form complexes?

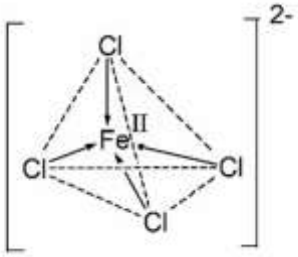
1. Transition metal ions have **small** ionic radius and hence **high** charge density, thus attracting ligands that contain lone pair of electrons.

2. (First row) transition metal ions have **vacant** 3d orbitals of low energy level that can accommodate lone pair of electrons from the ligands.

How to write the formulae of complexes?



How to determine overall charge of the complex ion?



3.3.1 Nature of ligands

- A ligand is classified according to the number of dative bonds it can form with the central transition metal atom or ion.

- Ligands that can form more than one dative covalent bond to the same central metal atom or ion are classified as **polydentate ligands**.

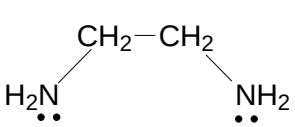
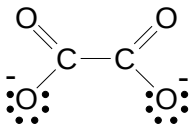
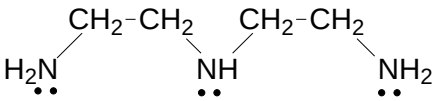
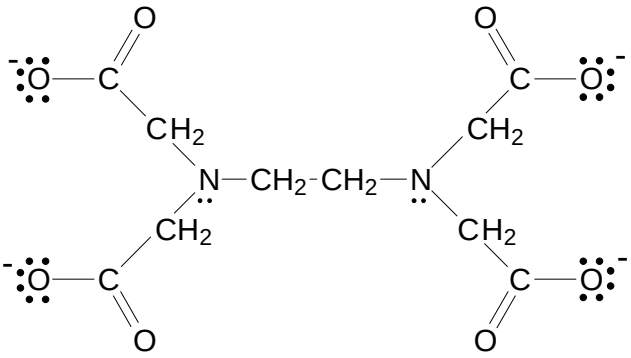
No. of dative bonds formed by ligand	Ligand type		Examples
1	**mono**dentate		NH_3, H_2O, Cl^-, CN^-, SCN^-
2	**poly**dentate	**bi**dentate	 Ethane-1,2-diamine  Ethanedioate
3		**tri**dentate	 Diethylenetriamine
6		**hexa**dentate	 Ethylene-diamine-tetraacetate ($EDTA^{4-}$)

Table 4: Some examples of ligands

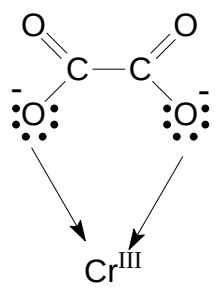
Exercise 7

Complete the table below.

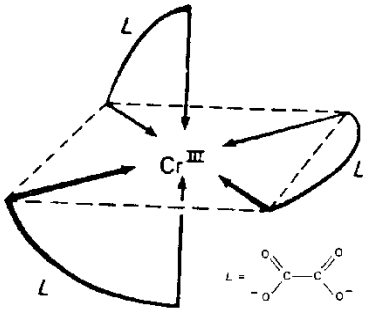
Complex	Co–ordination number	Oxidation number of central metal
$[Fe(EDTA)]^-$		
$[Co(en)_3]^{3+}$		

- Another term for polydentate ligand is **<u>chelating agent</u>** (derived from the Greek word for 'claw'). The resultant complex ion is called a *chelate* or *chelated* compound.

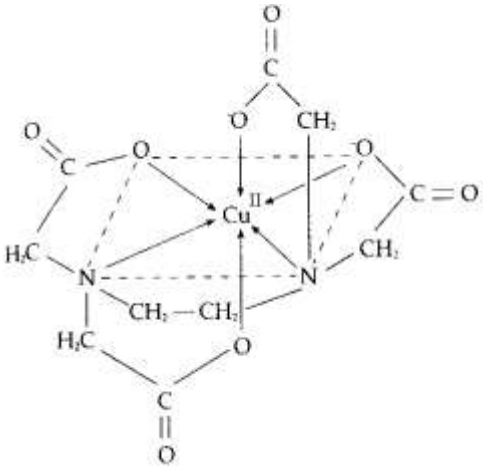
<u>Examples of chelates</u>:



One ethanedioate ligand ($C_2O_4^{2-}$) forms two dative bonds to the central Cr^{3+} ion, forming a ring structure



Each of the three ethanedioate ligands forms two dative bonds with the central metal ion in the complex ion, $[Cr(C_2O_4)_3]^{3-}$



$[Cu(EDTA)]^{2-}$ complex

- *Chelating agents* form **particularly stable complex ions** because

  ☞ They form **<u>multiple</u> dative covalent bonds** to the central metal atom or ion that are difficult to break.

  ☞ The formation of chelate complex is **accompanied by an <u>increase</u> in entropy**. (*Recall: increase in entropy favours spontaneity of reaction*).

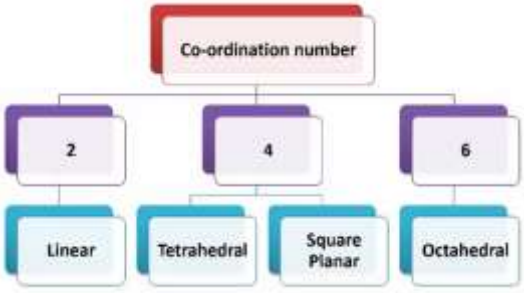
<u>Example</u>:

$$\underbrace{[Fe(H_2O)_6]^{3+} + 3C_2O_4^{2-}}_{\text{4 species}} \longrightarrow \underbrace{[Fe(C_2O_4)_3]^{3-} + 6H_2O}_{\text{7 species}}$$

(higher entropy when chelate forms)

- Many polydentate molecules occur naturally in biological systems. They include amino acids, proteins, fatty acids, saccharides etc.

3.3.2 Shapes of complexes



- Aqua complexes are generally octahedral in shape with co–ordination number of 6 as H_2O is a relatively small ligand, e.g. $[Cr(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{3+}$, $[Fe(H_2O)_6]^{3+}$ and $[Cu(H_2O)_6]^{2+}$.

- NH_3 and CN^- are also considered relatively small ligands, and complexes containing these ligands are generally **octahedral** in shape with the co–ordination number of **6** e.g. $[Ni(NH_3)_6]^{2+}$ and $[Fe(CN)_6]^{3-}$.

  However, there are *exceptions* such as $[Cu(CN)_4]^{3-}$, which is **tetrahedral** in shape with the co–ordination number of **4**.

- Cl^- is relatively larger and only four Cl^- ligands can fit around, for instance, cobalt and copper ions, e.g. $[CoCl_4]^{2-}$ and $[CuCl_4]^{2-}$ are tetrahedral.

- Ag^+ tends to form complexes with the co–ordination number of **2** and these are **linear** in shape, e.g. $[Ag(CN)_2]^-$ and $[Ag(NH_3)_2]^+$.

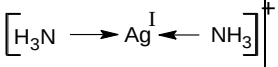
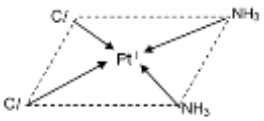
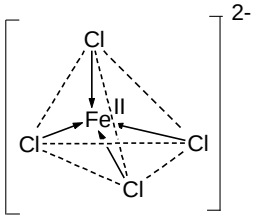
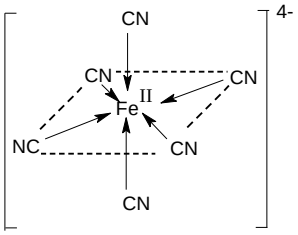
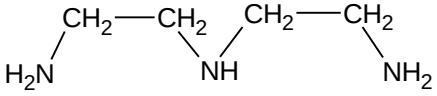
Coordination number	**2**	**4**	**4**	**6**
Shape	Linear	Square planar	Tetrahedral	Octahedral
Examples	$[Cu(CN)_2]^-$ **$[Ag(NH_3)_2]^+$** 	$[Ni(CN)_4]^{2-}$ $[PdCl_4]^{2-}$ $[PtCl_4]^{2-}$ **$[PtCl_2(NH_3)_2]$** 	$[Cu(CN)_4]^{3-}$ **$CuCl_4^{2-}$** **$CoCl_4^{2-}$** **$[Zn(NH_3)_4]^{2+}$** $Ni(CO)_4$ $FeCl_4^{2-}$ 	**$[Cu(H_2O)_6]^{2+}$** **$[Cu(NH_3)_4(H_2O)_2]^{2+}$** $[Cu(EDTA)]^{2-}$ **$[Cr(H_2O)_6]^{3+}$** **$[Fe(CN)_6]^{3-}$** **$[Fe(CN)_6]^{4-}$** 

Table 5: Some examples of complexes and their co–ordination number and shapes

3.3.3 Nomenclature of complexes

1. Identify and arrange the name of the ligands in alphabetical order (if there is more than one, ignore di–, tri– etc. in deciding the alphabetical order)

No. of ligands	1	2	3	4	5	6
Prefix	mono	di	tri	tetra	penta	hexa

Neutral ligands	**Name**	**Anionic ligands**	**Name**
H_2O	aqua (aquo)	F^-	fluoro
NH_3	ammine	Cl^-	chloro
CO	carbonyl	CN^-	cyano
	diethylenetriamine	OH^-	hydroxo
		NO_2^-	nitro

2. Name the central metal atom / ion. For net positive or neutral complexes, name the transition element. For net negative complexes, end the transition metal element with an 'ate'.

Name of transition element	
in net positive or neutral complexes	**in net negative complexes**
chromium	chrom**ate**
manganese	mangan**ate**
vanadium	vanad**ate**
iron	ferr**ate***
copper	cupr**ate***

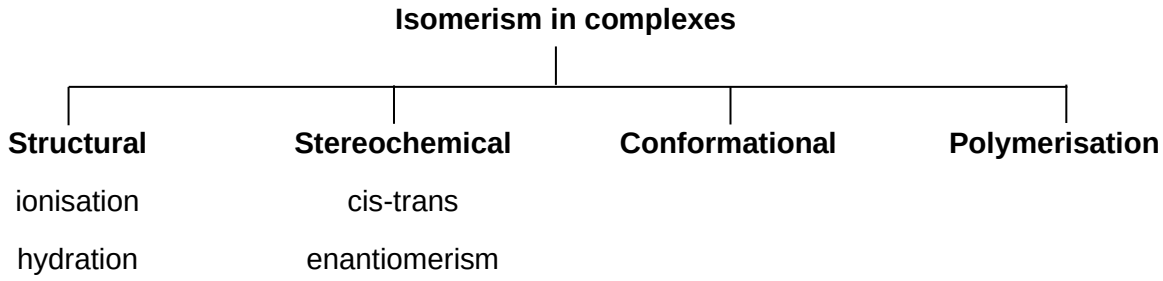
**For iron and copper, the Latin version of the metal name is used when the suffix '–ate' is used.*

3. The oxidation state of the central metal atom / ion is given in brackets at the end.
Examples:

Complex	**Name**	**Complex**	**Name**
$[Cr(H_2O)_6]^{3+}$	hexaaquachromium(III) ion (or simply, aqueous Cr(III) ion)	CrO_4^{2-}	chromate(VI) ion
$[Cu(H_2O)_6]^{2+}$	hexaaquacopper(II) ion	$[Fe(CN)_6]^{4-}$	hexacyanoferrate(II) ion
$[Cu(NH_3)_4(H_2O)_2]^{2+}$	tetraamminediaquacopper(II) ion	$[CoCl_4]^{2-}$	tetrachlorocobaltate(II) ion
$[CoCl_2(NH_3)_4]^+$	tetraamminedichlorocobalt(III) ion	$[Al(OH)_4]^-$	tetrahydroxoaluminate(III) ion
$Ni(CO)_4$	tetracarbonylnickel(0)		

3.3.4 Isomerism in complexes

Due to the different structural and/or stereochemical positions of the ligands with respect to the central metal ion/atom, isomerism can occur in complexes with co-ordination number 4 and 6. These are the different types of isomerism possible.



3.3.4.1 Structural isomerism

The isomers have the same molecular formula but different arrangement of atoms or groups of atoms.

In **ionisation** isomerism, the anionic ligands and counter ions can exchange positions.

e.g. 2 possible isomers with the molecular formula of $Cr(NH_3)_4Cl_2Br$ $[Cr(NH_3)_4Cl_2]^+Br^-$ and $[Cr(NH_3)_4ClBr]^+Cl^-$ exhibit ionisation isomerism.

In **hydration** isomerism, the water ligands and counter ions can exchange positions.

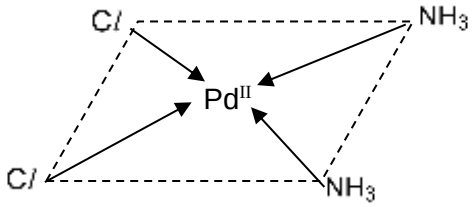
e.g. 2 possible isomers with the molecular formula of $Cr(H_2O)_6Cl_3$ $[Cr(H_2O)_6]^{3+}$ $3Cl^-$ and $[Cr(H_2O)_4Cl_2]^+Cl^-.2H_2O$ exhibit hydration isomerism. The isomers can be distinguished using aqueous silver nitrate solution. Each of them will form a different mass of AgCl due to the different number of (free) Cl^- counter ions. [*Recall Exercise 6*]

3.3.4.2 Stereochemical isomerism

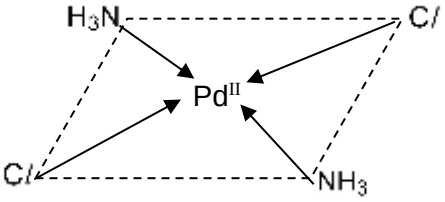
The isomers have the same molecular & structural formula but different spatial arrangement of atoms/groups with respect to the central ion/metal.

In **cis-trans** isomerism, it occurs mainly in square planar and octahedral complexes. Ligands may occur sites adjacent (cis) to each other or opposite (trans) of each other.

e.g. 2 possible isomers with the structural formula $Pd(NH_3)_2Cl_2$

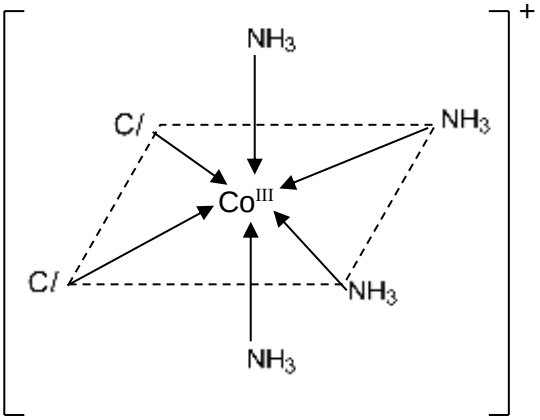


cis isomer

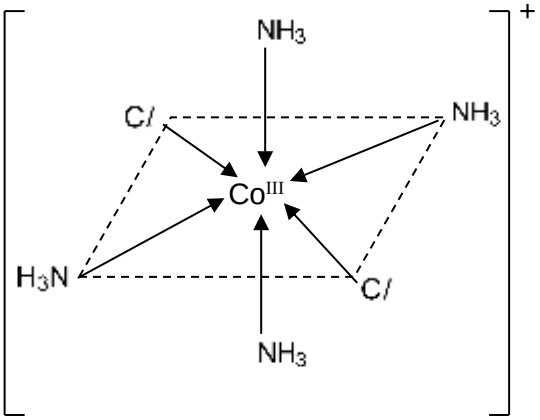


trans isomer

e.g. 2 possible isomers with the structural formula $[Co(NH_3)_4Cl_2]^+$



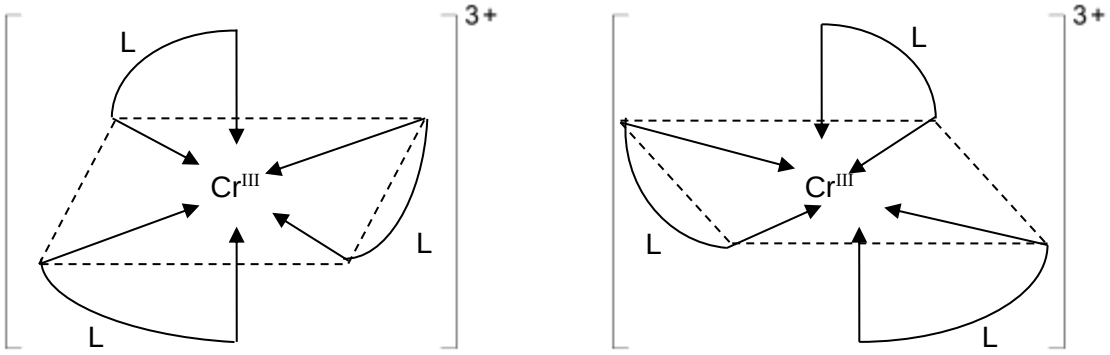
cis isomer



trans isomer

In **enantiomerism**, the isomers are non-superimposable mirror images of each other. There is no (internal) plane of symmetry nor centre of symmetry in the complex. It is usually exemplified in octahedral complexes containing at least two bidentate ligands.

e.g. 2 possible isomers with the molecular formula $[Cr(H_2NCH_2CH_2NH_2)_3^{3+}]$ (or $[Cr(en)_3]^{3+}$)

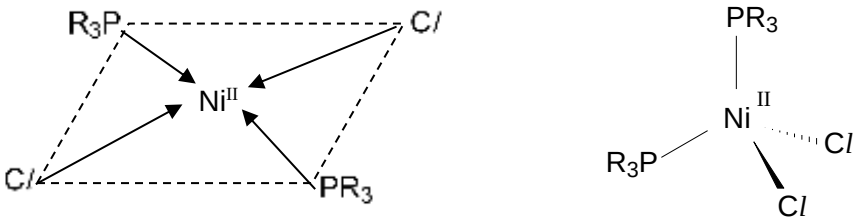


where L = en or $H_2NCH_2CH_2NH_2$ (a bidentate ligand)

3.3.4.3 Conformational isomerism [name is FYI]

The isomers have the same molecular & structural formula but the complexes can exist in two different geometries.

e.g. 2 possible isomers with the structural formula $NiCl_2(R_3P)_2$, where R is an alkyl group.



square planar **tetrahedral**

The isomers can be distinguished by their net dipole moment (if any).

3.3.4.4 Polymerisation isomerism [name is FYI]

It exists when the cation and anion of the compound are both complex ions. The cation-anion pair share the same empirical formula as a single complex but has twice the relative formula mass.

e.g. $[Pt(NH_3)_4]^{2+}$ $[PtCl_4]^{2-}$ has the same empirical formula as *cis*-platin (*cis*-$[PtCl_2(NH_3)_2]$ and *trans*-platin but its relative formula mass is twice that of either.

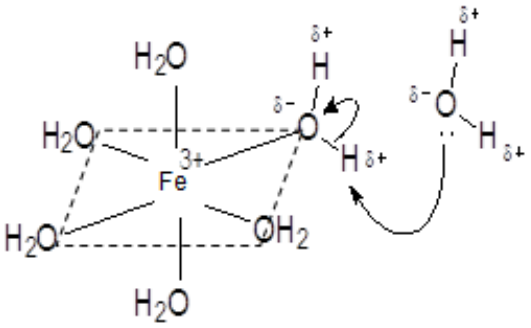
3.3.5 Acidity of transition metal ions in solution

- In aqueous solution, transition metal ions exist as aqua complexes with H_2O as the ligand e.g. $[Fe(H_2O)_6]^{3+}$. The aqua complex ions behave as **weak acids** in aqueous solution.

  Reason:
  - Transition metal ions have **high charge density** and thus, the O-H bonds in H_2O ligands are **polarised** and **break**. Thus, the aqua complex ions undergo **partial hydrolysis** to give H_3O^+.

Example: Aqueous solution of $[Fe(H_2O)_6]^{3+}$ is weakly acidic

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



- Highly charged (3+) transition metal ions such as $[Fe(H_2O)_6]^{3+}$ and $[Cr(H_2O)_6]^{3+}$ exhibit greater acidity. Reason: Ion has higher charge density, greater polarization of H_2O ligands.

Note: The **concept of hydrolysis** by a central metal ion with high charge density has already been covered in the topic of ***'The Periodic Table'***.

Exercise 8

The pH of a solution of iron(III) chloride is lower than the pH of a solution of iron(II) chloride of the same concentration. Explain.

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

Fe^{3+} has a _____ than Fe^{2+}. Thus Fe^{3+} polarises water to a _____ to give more H^+, causing the pH to be lower than a solution of Fe^{2+}.

Note: From the Data Booklet,
Ionic radius of Mg^{2+}, Fe^{2+} and Fe^{3+} respectively: 0.065nm, 0.061nm, 0.055nm.

3.3.6 Ligand exchange reaction

- Competition between ligands to form bonds with the central metal ion can lead to ligand exchange (or ligand displacement) reactions.

- Some ligands form a more stable complex than other ligands with a particular metal ion. These ligands are said to be **stronger** and tend to **displace** the weaker ones.
(*details on K_{stab} in Section 'Extra Reading'*)

Example:
When aqueous potassium cyanide is added to an aqueous iron(III) solution, the complex, $[Fe(CN)_6]^{3-}$, is formed.

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

The weaker water ligands have been displaced by the stronger CN^- ligands.

- The **concentration** of the ligands also affects whether displacement actually occurs.

Example: Adding $NH_3(aq)$ to $CuSO_4(aq)$

Blue precipitate of $Cu(OH)_2$ dissolves in excess $NH_3(aq)$ to give a deep blue solution.

In aqueous solution, the weak base NH_3 undergoes partial ionisation, producing OH^- ions.

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

When a small amount of $NH_3(aq)$ is added, the $OH^-(aq)$ undergoes acid-base reaction with $[Cu(H_2O)_6]^{2+}(aq)$ to produce a blue precipitate of $Cu(OH)_2$.

$$[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons \mathbf{[Cu(OH)_2](s)} + \mathbf{6H_2O(l)} \quad .....(1)$$
blue solution — blue ppt

When excess $NH_3(aq)$ is added, ligand exchange reaction occurs and the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion is formed.

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

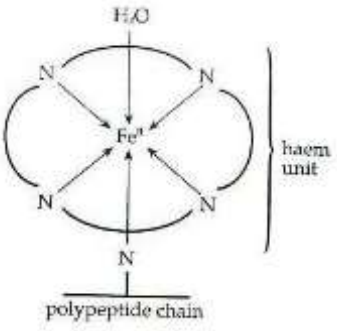
The increasing addition of $NH_3(aq)$ shifts the position of equilibrium (2) to the **right**, forming a deep blue solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$. As the concentration of $[Cu(H_2O)_6]^{2+}(aq)$ **decreases**, the position of equilibrium (1) shifts **left**, causing the blue precipitate of $Cu(OH)_2$ to **dissolve**.

$[Cu(OH)_2(H_2O)_4]$ can be simply written as $Cu(OH)_2$.

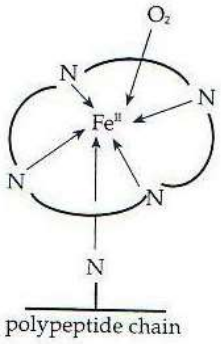
Effect of ligand exchange in haemoglobin

- Haemoglobin is a red pigment found in red blood cells. It is the biological molecule responsible for transporting oxygen molecules to other cells during respiration.

- Haemoglobin is a complex consisting of an **iron** metal centre.



Haemoglobin



Oxyhaemoglobin

Note

The iron in **haemoglobin**
(a) has an oxidation state of +2
(b) has a co–ordination number of 6.
(c) is attached to four nitrogen atoms of the haem unit and one nitrogen atom of the polypeptide chain.
(d) can be reversibly bonded to a water molecule at the 6th position.

- Competition between ligands takes place in the haemoglobin.

- When haemoglobin absorbs oxygen, it forms oxyhaemoglobin.

- Oxygen molecule displaces water molecule and forms a dative bond with the iron(II) central ion.

- Oxyhaemoglobin carries oxygen from one part of the body to another.

- In cells of lower oxygen concentration, the reverse reaction occurs. The water ligands displace the oxygen ligands, thus oxygen is released into the cells. Haemoglobin re-forms.

- Ligands such as **CO and CN^- ions** form **strong dative bonds** with the iron(II) central ion in haemoglobin.
  - ⇒ these bonds formed are **stronger** than the Fe–O_2 dative bonds
  - ⇒ thus, CO and CN^- are **irreversibly bonded** to haemoglobin
  - ⇒ these ligands act as acute poisons by inhibiting the oxygen–carrying ability of haemoglobin.

3.4 Formation of coloured complex ions

Most transition element complexes are **coloured**, unlike ions of non–transition elements (e.g. $[Mg(H_2O)_6]^{2+}$ is colourless).

Common examples:

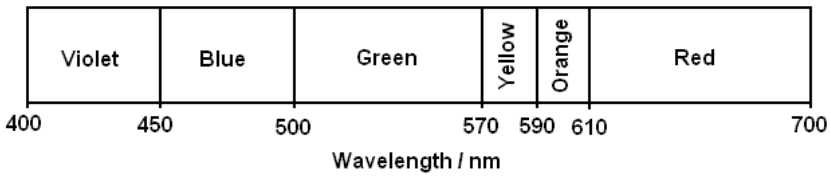
Complex	Colour	Complex	Colour
$[Cu(H_2O)_6]^{2+}$	blue	CrO_4^{2-}	yellow
$[Fe(H_2O)_6]^{2+}$	pale green	$Cr_2O_7^{2-}$	orange
$[Fe(H_2O)_6]^{3+}$	yellow	$[Cr(H_2O)_6]^{3+}$	green
$[Fe(SCN)(H_2O)_5]^{2+}$	blood–red	$[Cr(H_2O)_6]^{2+}$	blue
$[Co(H_2O)_6]^{2+}$	pink	MnO_4^-	purple
$[CoCl_4]^{2-}$	blue	$[Mn(H_2O)_6]^{2+}$	pale pink

Some background information on the appearance of colour:

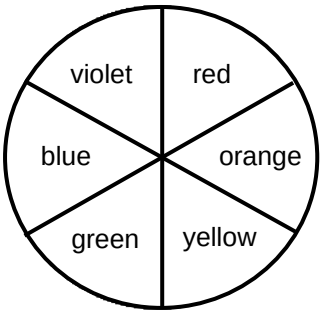
- White light is composed of various colours (i.e. with different wavelengths) that make up the visible region of the electromagnetic spectrum (refer to diagram below).
- When light falls on an opaque object, some or all the wavelengths of light may be absorbed.
- In general, the observed colour of an object is the reflected wavelengths that are not absorbed from the spectrum.

  The colour of the object is therefore the **complementary** colour of those colours that are absorbed.

  Example: If an object **absorbs** the **red** colour, it will **appear green** in colour, which is the complementary colour of red.



Visible region of the spectrum



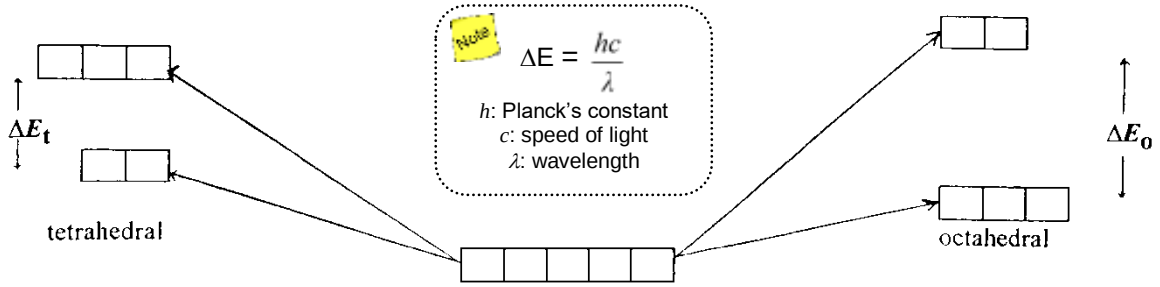
Colour wheel

Opposite colours in the wheel are complementary colours

Why are transition metal complexes coloured?

- In an isolated gaseous atom or ion of a transition metal, the five d orbitals are *degenerate* (i.e. have the same energy level).

- However, in the presence of **ligands** in transition metal complexes, the **d orbitals** are no longer degenerate but **split** into **two** sets of energy levels with an energy gap (ΔE) between them. This process is called **d orbital splitting.**



d orbitals split into two sets in a **tetrahedral** complex – three orbitals of higher energies and two of lower energies

degenerate d orbitals in an isolated gaseous atom

d orbitals split into two sets in an **octahedral** complex – two orbitals of higher energies and three of lower energies

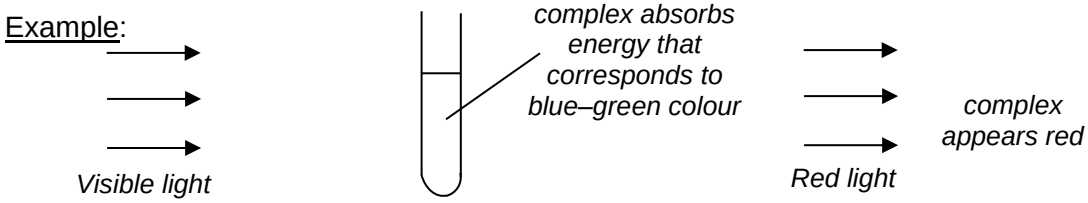
- The **energy gap, Δ*E*,** between the non–degenerate d orbitals is **small** and similar to the energies of the visible region of the spectrum.

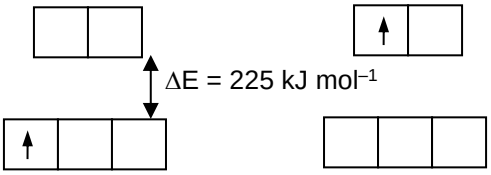
- When light passes through the transition metal complexes, energy **equal** to ΔE is absorbed from the visible spectrum.

- As the d orbitals are partially filled, the absorption of energy results in an **electron transition** from the **lower** energy level d orbital to a **higher** energy level d orbital. This process is called **d-d transition**.

- The colour of the complex ion is the **complementary** of the colours that are absorbed.

Example:





For d–d transition to occur, there must be presence of **at least one d electron** and an **empty d orbital** in the higher energy level.

- ***Why are compounds containing the ions Sc^{3+}, Ti^{4+}, Cu^{+} and Zn^{2+} colourless?***

  ⇒ Sc^{3+} and Ti^{4+} do not have electrons in the **d orbitals** for d–d transition to occur.
  ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^0}$)

  ⇒ Cu^{+} and Zn^{2+} do not have a **partially filled d orbital** in the higher energy level to allow for excitation of electron from the lower energy d orbitals.
  ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^{10}}$)

- For a s–block metal ion such as Na^{+} to undergo the electron transition (from $1s^2\ 2s^2\ \mathbf{2p^6}$ to $1s^2\ 2s^2\ \mathbf{2p^5\ 3s^1}$), the electron must absorb in the region of very high energy.
  ⇒ such 2p–3s transitions are out of the energy range of visible light
  ⇒ energy from visible light is not absorbed
  ⇒ solutions of Na^{+} are colourless

Exercise 9

Explain why an aqueous solution of Cr^{3+} is coloured.

In the presence of water _____, the partially filled 3d orbitals of Cr^{3+} are split into _____ with a small energy gap (d orbital splitting).
When energy is _____ from the visible light region, an electron is promoted from the d orbital of a _____ energy level to a d orbital of a _____ energy level (d–d transition).
The colour of $Cr^{3+}(aq)$ is _____ of the colour absorbed.

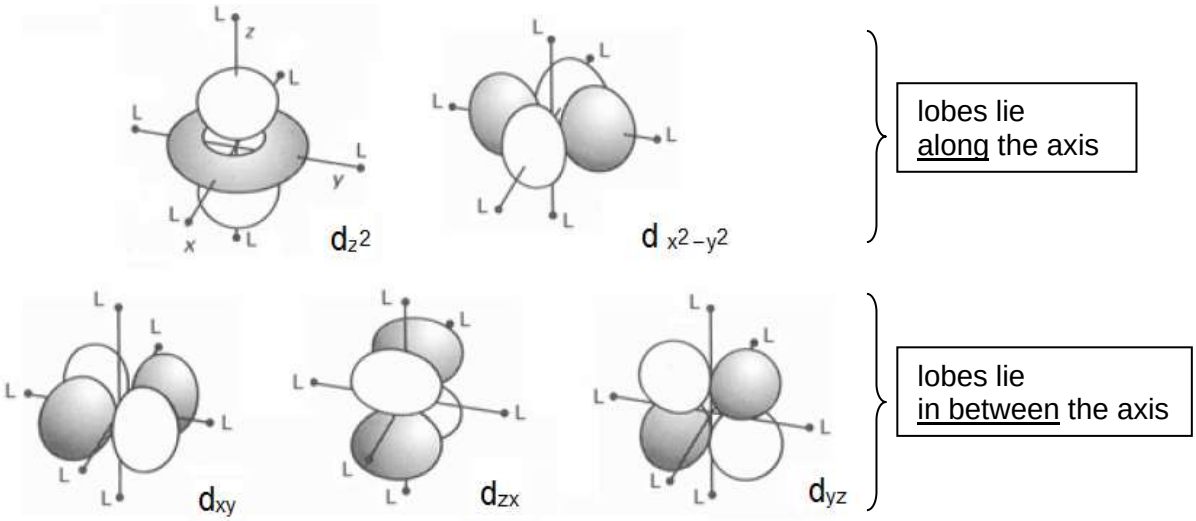
3.4.1 d orbital splitting

Why do the d orbitals split into two sets of energy levels in the presence of ligands?

- **Electrostatic repulsion** occurs between the lone pair of electrons on the donor atom of the approaching ligand and the electrons in the d orbitals of a transition metal.

- The strength of repulsion experienced by the five d orbitals is **not equal** because of the way they are arranged differently in space.

- Recall the shapes and orientation of the five d orbitals:



- For an **octahedral** complex,

  ☞ The six ligands approach the central metal cation along the x, y and z axes.

  ☞ Since the lobes of the $3d_{z2}$ and $3d_{x2-y2}$ orbitals lie along these axes, **greater** electrostatic repulsion occurs between the lone pairs of the ligands and electrons in these orbitals ⇒ these orbitals have **higher** energy level.

  ☞ **Smaller** electrostatic repulsion occurs between the lone pairs of the ligands and electrons in the $3d_{xy}$, $3d_{zx}$ and $3d_{yz}$ orbitals ⇒ these orbitals have **lower** energy level.

3.4.2 Factors affecting the colours of complex ions

- The extent of d orbital splitting in a complex, which is measured by the magnitude of the energy gap (ΔE), determines the colours absorbed, and therefore affects the observed colour of the complex.

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

where h: Planck's constant
c: speed of light
λ: wavelength

- The magnitude of d orbital splitting is affected by the following factors:

1. *Identity of the transition metal ion*
   e.g. $[Cr(H_2O)_6]^{2+}$ is blue and $[Fe(H_2O)_6]^{2+}$ is pale green.

2. *Electronic configuration of the transition metal ion*
   e.g. $[Fe(H_2O)_6]^{2+}$ is pale green and $[Fe(H_2O)_6]^{3+}$ is yellow.

3. *Type of ligands*
   e.g. $[Ni(H_2O)_6]^{2+}$ is green and $[Ni(NH_3)_6]^{2+}$ is blue.

Example: N17/5/2d
Crystals of hydrated iron(III) salts are violet. When dissolved in water, the solution is yellow or brown. Solid hydrated iron(II) are green.

	colour	**ion**
solid hydrated iron(III) ions	violet	$[Fe(H_2O)_6]^{3+}$
aqueous hydrated iron(III) ions	yellow or brown	$[Fe(H_2O)_5(OH)]^{2+}$
solid hydrated iron(II) ions	green	$[Fe(H_2O)_6]^{2+}$

The colour is due to the absorption of light at specific wavelengths. The colour observed is the complement of the colour absorbed.

Suggest why
- The solid containing hydrated iron(III) ions is a different colour from the aqueous solution of iron(III) ions,
- Solid iron(II) ions are a different colour from solid iron(III) ions.

ANSWER:
- **Type of ligands**

Solid hydrated iron(III) ions contain 6 water ligands, while aqueous hydrated iron(III) ions contain 5 water ligands and 1 OH^- ligand. The **different types of ligands** cause **magnitude** of the energy gap (ΔE) to be **different**.

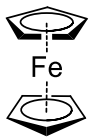
- **Electronic configuration of the transition metal ion**

Solid iron(II) ions and solid iron(III) ions have the same ligands. Solid iron(II) ions have an oxidation number of +2, with 6 electrons in the 3d subshell. Solid iron(III) ions have an oxidation number of +3, with 5 electrons in the 3d subshell. The **different electronic configurations** caused **magnitude** of the energy gap (ΔE) to be **different**.

When light passes through the complexes, energy equal to ΔE is absorbed from the visible light region of the spectrum. The absorption of energy results in an electron transition from the lower energy level d orbital to a higher energy level d orbital. Since the **ΔE is different** in the different complex ions, the **colours** of the complex ions are **different**.

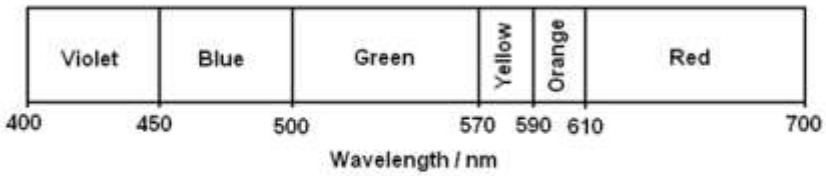
Exercise 10

Ferrocene, $Fe(C_5H_5)_2$, is an orange solid. In this complex, $C_5H_5^-$ is the ligand and it donates π electrons from the ring to the vacant 3d orbital of Fe. The structure of ferrocene is given below.

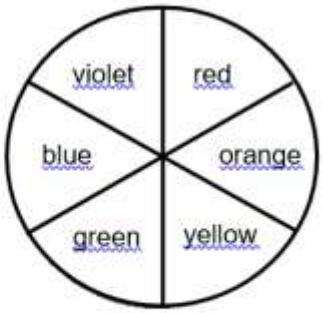


ferrocene

Example: The complementary colours are illustrated with the following colour wheel.



Visible region of the spectrum



Colour wheel

Opposite colours in the wheel are **complementary** colours

Aqueous Fe^{2+} ion is green in colour, suggest and explain if water causes a larger split between the two groups of 3d orbitals as compared to $C_5H_5^-$.

ANSWER:

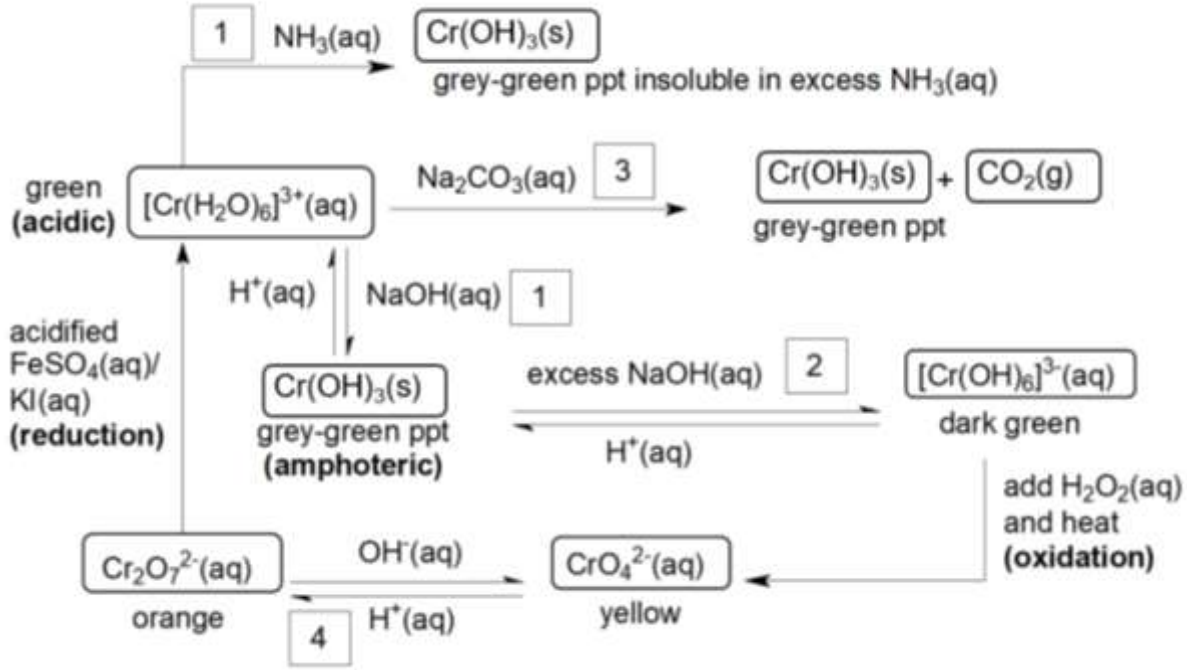
Since Fe^{2+} appears green, red light was absorbed. Since red light is of a longer wavelength, the energy gap is _____.

Since ferrocene appears orange, blue light was absorbed. Since blue light is of a shorter wavelength, the energy gap is _____.

Hence _____ causes a _____ in energy gap.

4. REACTIONS OF TRANSITION METALS AND THEIR COMPOUNDS

4.1 Some reactions of chromium and its compounds



(a) Acid–base reaction of $[Cr(H_2O)_6]^{3+}$

1

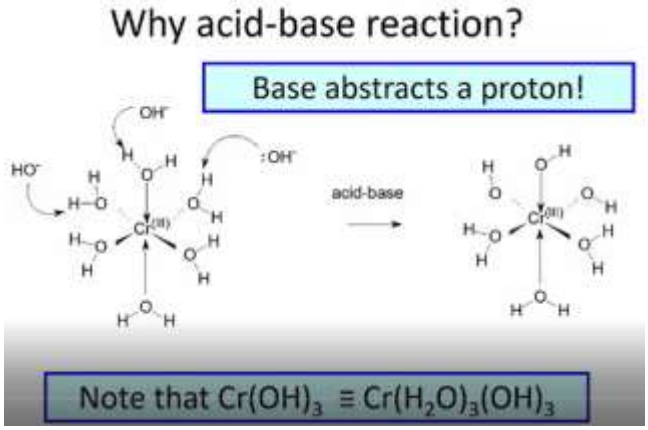
- When a limiting amount of aqueous NaOH or aqueous NH_3 is added to $[Cr(H_2O)_6]^{3+}$, an acid–base reaction takes place. The overall reaction is:

$$[Cr(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \longrightarrow \underset{\text{grey–green ppt}}{[Cr(OH)_3](s)} + 6H_2O(l)$$

- This applies to transition metal ions in the 3d block such as Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, and Mn^{2+}.
- This means that the formation of insoluble hydroxides from aqueous solutions of transition metal ions is NOT a simple precipitation reaction.

$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$
This is a simple precipitation reaction.

$Cr^{3+}(aq) + 3OH^-(aq) \longrightarrow Cr(OH)_3(s)$
This is NOT a simple precipitation reaction. This equation is just a simplified representation of the acid–base reaction.



2 • $Cr(OH)_3$ is soluble in excess NaOH as further acid–base reaction takes place.

$$\mathbf{Cr(H_2O)_3(OH)_3}(s) + 3OH^-(aq) \longrightarrow \underset{\text{dark green solution}}{\mathbf{[Cr(OH)_6]^{3-}(aq)}} + \mathbf{3H_2O(l)}$$

Note that $\mathbf{Cr(H_2O)_3(OH)_3 \equiv Cr(OH)_3}$ *(refer to page 33 for explanations)*

Note Metal hydroxides formed from **Zn^{2+}** and **Al^{3+}** can also dissolve in excess NaOH to form **$Zn(OH)_4^{2-}$** and **$Al(OH)_4^-$** respectively due to their amphoteric property.

3 • Cr^{3+} reacts with sodium carbonate (also a base) to give an insoluble hydroxide and carbon dioxide gas, also via an acid–base reaction.

$$2[Cr(H_2O)_6]^{3+}(aq) + 3CO_3^{2-}(aq) \longrightarrow 2Cr(OH)_3(s) + 3CO_2(g) + 9H_2O(l)$$

Note Other cations with **high charge density** (e.g. Al^{3+}, Fe^{3+}) also react with sodium carbonate to give insoluble hydroxides and carbon dioxide gas.

Note Cations with **low charge density** (e.g. Fe^{2+}, Cu^{2+}) react with sodium carbonate to give insoluble carbonates instead (e.g. $FeCO_3$, $CuCO_3$) as its aqua complex ions (e.g. $[Fe(H_2O)_6]^{2+}$, $[Cu(H_2O)_6]^{2+}$) are not acidic enough to react.

Important

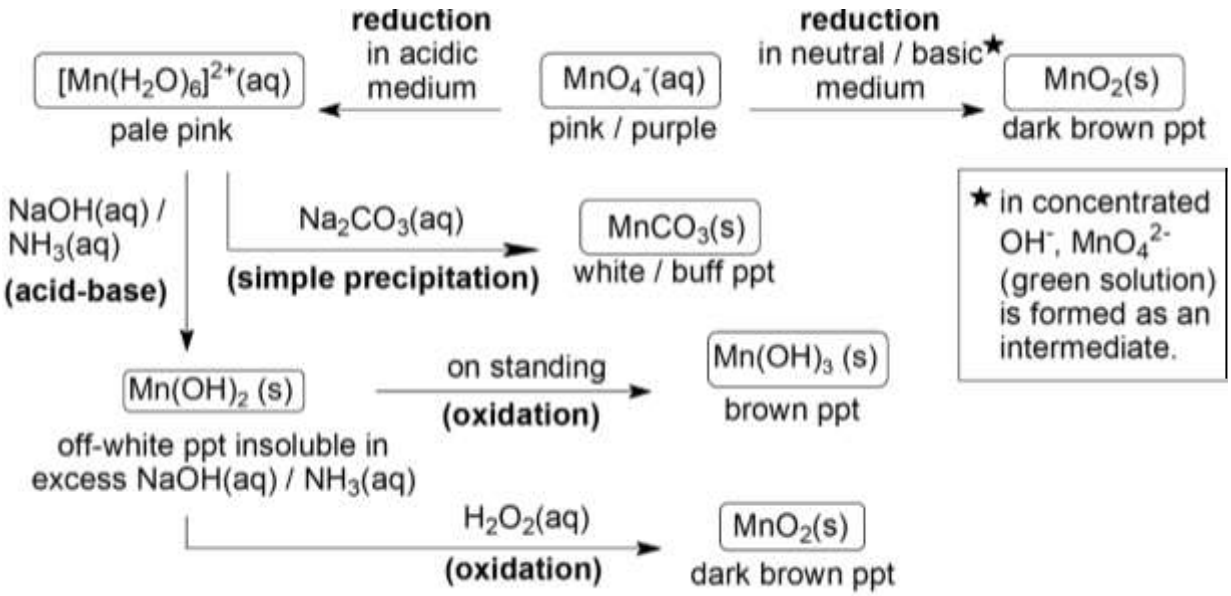
(b) Acid–base reaction of chromate(VI), CrO_4^{2-}

4

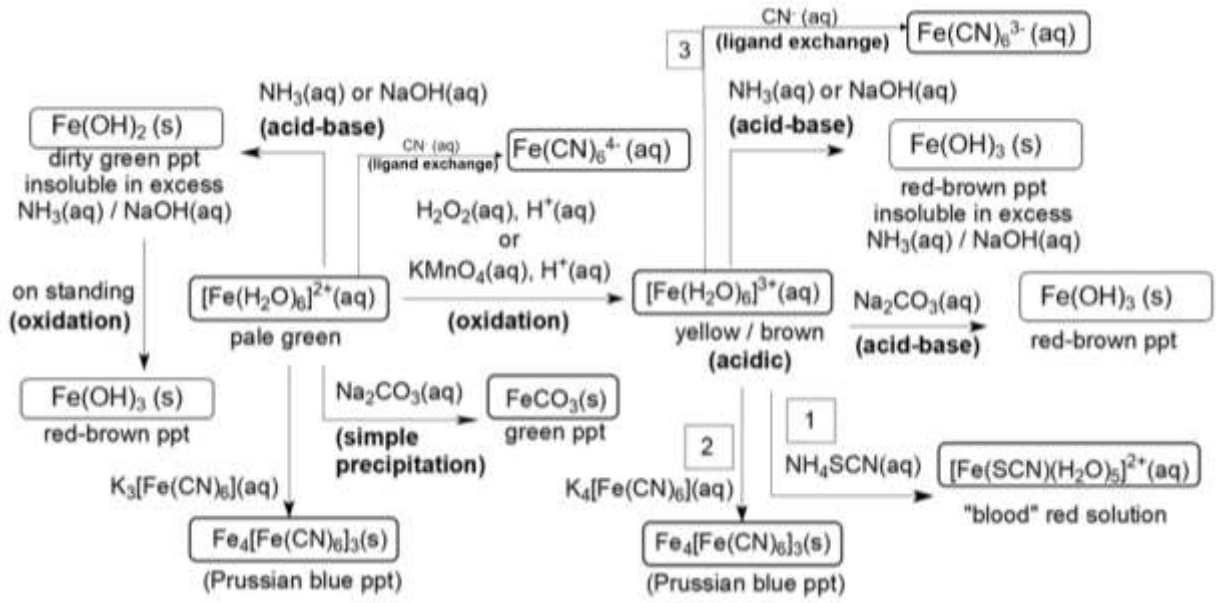
$$\underset{\text{yellow}}{2CrO_4^{2-}(aq)} + 2H^+(aq) \rightleftharpoons \underset{\text{orange}}{Cr_2O_7^{2-}(aq)} + H_2O(l)$$

This is NOT a redox reaction. (The oxidation state of chromium, oxygen and hydrogen remain unchanged.)

4.2 Some reactions of manganese and its compounds



4.3 Some reactions of iron and its compounds



Ligand exchange reaction

1

- $Fe^{3+}(aq)$ reacts with $SCN^-(aq)$ via a **ligand exchange reaction** to form $[Fe(SCN)(H_2O)_5]^{2+}$, a blood–red solution.

$$[Fe(H_2O)_6]^{3+}(aq) + SCN^-(aq) \rightleftharpoons \underset{\text{blood–red}}{\mathbf{[Fe(SCN)(H_2O)_5]^{2+}(aq)}} + H_2O(l)$$

2

- $Fe^{3+}(aq)$ reacts with $CN^-(aq)$ via ligand exchange to form $[Fe(CN)_6]^{3-}$. The stronger CN^- ligand has displaced the weaker H_2O ligand.

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

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3

- $Fe^{3+}(aq)$ reacts with $[Fe(CN)_6]^{4-}$ to give $Fe_4[Fe(CN)_6]_3$, a Prussian blue precipitate.

$$4Fe^{3+}(aq) + 3[Fe(CN)_6]^{4-}(aq) \longrightarrow Fe_4[Fe(CN)_6]_3(s)$$

- $Fe^{2+}(aq)$ also reacts with $[Fe(CN)_6]^{3-}$ to give the same Prussian blue precipitate.

$$Fe^{2+}(aq) + [Fe(CN)_6]^{3-}(aq) \longrightarrow [Fe(CN)_6]^{4-}(aq) + Fe^{3+}(aq)$$
$$4Fe^{3+}(aq) + 3[Fe(CN)_6]^{4-}(aq) \longrightarrow Fe_4[Fe(CN)_6]_3(s)$$

4.4 Reaction of $[Co(H_2O)_6]^{2+}$

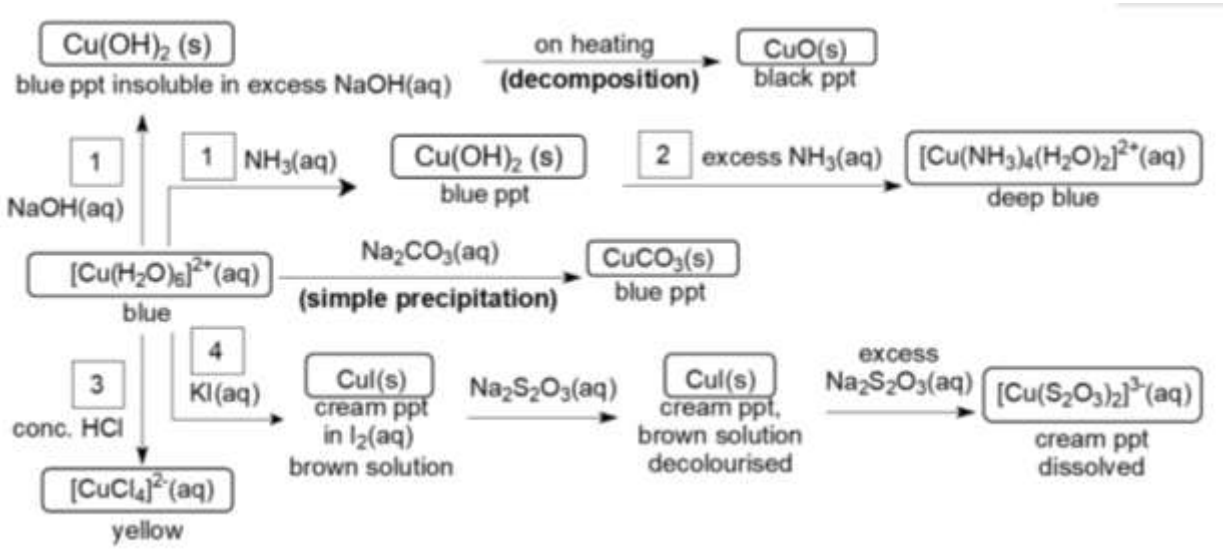
Ligand exchange reaction

- $Co^{2+}(aq)$ reacts with concentrated HC*l* via a **ligand exchange** reaction to form $[CoCl_4]^{2-}$, a blue solution. The stronger Cl^- ligand from concentrated HC*l* has displaced the weaker H_2O ligand.

$$[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CoCl_4]^{2-}(aq) + 6\,H_2O(l)$$
pink → blue

- When concentrated HC*l* is slowly added to $[Co(H_2O)_6]^{2+}$, the colour of the mixture changes from pink to purple to blue.
- The mixture appears purple due to the presence of both the pink $[Co(H_2O)_6]^{2+}$ and blue $[CoCl_4]^{2-}$ at equilibrium.
- When anhydrous blue cobalt(II) chloride paper is used to test for the presence of water, the reverse reaction occurs to produce $[Co(H_2O)_6]^{2+}$.

4.5 Some reactions of copper and its compounds



(a) Acid–base reaction of $[Cu(H_2O)_6]^{2+}$

1 • The OH^- reacts with $[Cu(H_2O)_6]^{2+}$ in an **acid–base** reaction to give a blue precipitate of $Cu(OH)_2$.

$$[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s) + 6H_2O(l)$$

2 • When **excess** $NH_3(aq)$ has been added, **ligand exchange** reaction occurs to give a deep blue solution. (refer to **Section 3.3.6**)

$$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$$

Note Metal hydroxides formed from Zn^{2+} and Ag^+ can also dissolve in excess NH_3 to form complexes $[Zn(NH_3)_4]^{2+}$ and $[Ag(NH_3)_2]^+$ respectively.

(b) Ligand exchange reaction

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

- The stronger Cl^- ligand from concentrated HC*l* has displaced the weaker H_2O ligand.
- The mixture is green in colour due to the presence of both the blue $[Cu(H_2O)_6]^{2+}$ and yellow $[CuCl_4]^{2-}$ in the reversible reaction.

(c) Redox reaction

4

- Cu^{2+} is reduced by excess KI to form CuI (copper(I) iodide) and I_2.

$$2Cu^{2+}(aq) + 5I^-(aq) \longrightarrow \underset{\text{cream ppt}}{2CuI(s)} + \underset{\text{brown solution}}{I_3^-(aq)}$$

- The brown solution of I_3^- will be decolourised when the reducing agent $Na_2S_2O_3$ is added.

$$I_3^-(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 3I^-(aq) + S_4O_6^{2-}(aq)$$

(d) Ligand exchange reaction

- When excess $Na_2S_2O_3$ is added, the cream ppt dissolves due to the formation of the soluble $[Cu(S_2O_3)_2]^{3-}$ complex ion.

$$CuI(s) + 2S_2O_3^{2-}(aq) \longrightarrow [Cu(S_2O_3)_2]^{3-}(aq) + I^-(aq)$$

General Summary of Reactions of Transition Metals and their Compounds

Type of reaction	Key concepts
Acid-base	Reaction with $OH^-(aq)$ • insoluble hydroxides formed • amphoteric hydroxides undergo further acid-base reaction to form soluble complexes
	Reaction with $CO_3^{2-}(aq)$ • Cation with high charge density – forms insoluble hydroxides and CO_2 is produced. • Cation with low charge density – forms insoluble carbonates. (This is a precipitation reaction, not an acid-base reaction)
	• dichromate(VI) - chromate(VI) interconversion
Ligand exchange	• Stronger ligand displaces weaker ligand • A weaker ligand can still displace the stronger ligand if a high concentration of the weaker ligand is used to shift the P.O.E. of the equilibrium reaction. • A colour change is often observed in the reaction. • No change in oxidation number of the species involved.
Redox	• There is a change in oxidation number of the species involved. • Reaction is feasible because $E^{\ominus}_{cell} > 0$ • A colour change is often observed in the reaction.

5. EXTRA READING

5.1 Stability constant of complexes

- **Complexation stability constant** describes the stability of the complex.

- The stability constant of a complex (K_{stab}) is the equilibrium constant K for its formation. **It is a measure of the relative stability of complex compared to its aqua complex.**

  For example, the K_{stab} for the $[Ni(NH_3)_6]^{2+}$ complex is given as:

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

  $$K_{stab} = \frac{[Ni(NH_3)_6^{2+}]}{[Ni(H_2O)_6^{2+}][NH_3]^6} mol^{-6}dm^{18}$$

  The concentration of water is taken to be a constant as the water molecules are present in large excess in aqueous medium.

  The calculated K_{stab} of $[Ni(NH_3)_6]^{2+}$ is 5×10^7 mol^{-6} dm^{18}.

  A large K_{stab} value indicates that:
  - the position of equilibrium lies to the right
  - $[Ni(NH_3)_6]^{2+}$ is a more stable complex ion than $[Ni(H_2O)_6]^{2+}$
  - NH_3 is a stronger ligand than H_2O
  - NH_3 forms a stronger dative covalent bond with the central metal ion than H_2O

- Thus, ligands that form a complex with higher stability constant will displace ligands that are only capable of forming a complex with lower stability constant.

The K_{stab} values for some common complexes are given below. Sometimes log K_{stab} is used for easier comparison, as big numbers can be dispensed with. The larger the K_{stab} value, the more stable the complex is.

Element	Complex Ion	K_{stab}	$\log K_{stab}$
Monodentate ligands			
Fe	$[Fe(CN)_6]^{4-}$	1×10^{24}	24
	$[Fe(CN)_6]^{3-}$	1×10^{31}	31
Ni	$[Ni(CN)_4]^{2-}$	1×10^{31}	31
	$[Ni(NH_3)_6]^{2+}$	5×10^{7}	7.7
Cu	$[Cu(CN)_4]^{3-}$	1×10^{27}	27
	$[Cu(NH_3)_4(H_2O)_2]^{2+}$	1.2×10^{13}	13.1
Bidentate ligands			
Ni	$[Ni(en)_3]^{2+}$	6×10^{18}	18.8
Cu	$[Cu(en)_2(H_2O)_2]^{2+}$	4×10^{19}	19.6
Hexadentate ligands			
Fe	$[Fe(edta)]^{2-}$	2×10^{14}	14.3
	$[Fe(edta)]^{-}$	1.3×10^{25}	25.1
Ni	$[Ni(edta)]^{2-}$	4×10^{18}	18.6
Cu	$[Cu(edta)]^{2-}$	6×10^{18}	18.8

The stability of the complexes involving polydentate ligands (e.g. EDTA) is usually greater than that of complexes involving monodentate ligands.

5.2 Acid-base reactions of hydrated ions

It is important to take account of the water molecules in hydrated ions. At first sight, the formation of iron(III) hydroxide $Fe(OH)_3(s)$, when sodium hydroxide solution is added to a solution containing $Fe^{3+}(aq)$ ions, looks like a simple precipitation reaction:

$$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$$

This suggests that the reaction is similar to the precipitation, for example, of barium sulfate when sulfate ions and Ba^{2+} ions are mixed together:

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

However, such a treatment ignores the role of the water molecules. The $Fe(H_2O)_6^{3+}$ ion acts as a weak acid, $K_a = 10^{-5}$ mol dm^{-3}, because it undergoes an acid-base reaction with water molecules:

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

If the H_3O^+ ions are removed by the addition of a strong base such as hydroxide ions, further acid-base reactions can take place:

$$[Fe(H_2O)_5(OH)]^{2+}(aq) + H_2O(l) \rightarrow [Fe(H_2O)_4(OH)_2]^+(aq) + H_3O^+(aq)$$
$$[Fe(H_2O)_4(OH)_2]^+(aq) \rightarrow Fe(OH)_3(s) + H_3O^+(aq) + 2H_2O(l)$$

The overall reaction with hydroxide ions is:

$$Fe(H_2O)_6^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s) + 6H_2O(l)$$

The net result is that the ion has been deprotonated by a series of acid-base reactions and water ligands have been released. Source: Chemistry for Advanced Level, Peter Cann and Peter Hughes

5.3 Effect of ligands on $E^\ominus$ values

Different ligands can affect the **relative stabilities of oxidation states** in transition elements.

Example: $[Co(H_2O)_6]^{3+} + e^- \rightleftharpoons [Co(H_2O)_6]^{2+}$ $E^\ominus = +1.81$ V

$[Co(NH_3)_6]^{3+} + e^- \rightleftharpoons [Co(NH_3)_6]^{2+}$ $E^\ominus = +0.11$ V

Observe the difference in the $E^\ominus$ values (and thus the difference in the ease of reduction of Co(III) to Co(II)) when different ligands are bonded to the same metal ion.

Two deductions can be made from the $E^\ominus$ values:

1. $[Co(H_2O)_6]^{3+}$ is more easily reduced / a stronger oxidising agent than $[Co(NH_3)_6]^{3+}$.
2. NH_3 ligand stabilises Co(III) more relative to Co(II). Hence, **Co(III)** is **less readily reduced to Co(II) when it is bonded to NH_3 ligands**.