eunoia
JUNIOR COLLEGE

2023 JC2 H2 CHEMISTRY (9729)
EXTENSION TOPIC:
INTRODUCTION TO TRANSITION ELEMENTS CHEMISTRY

Name: ____ Civics Group: _________

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 (see **Topic: Electrochemistry**)

(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 exchange in haemoglobin

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

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

(m) explain how some transition elements and/or their compounds can act as catalysts (see also Reaction Kinetics **6(j)**)

REFERENCES

1. **Chemistry (for CIE AS & A Level)** by Peter Cann & Peter Hughes
2. **Cambridge International AS and A Level Chemistry Revision Guide** by Judith Potter and Peter Cann

LECTURE CONTENT

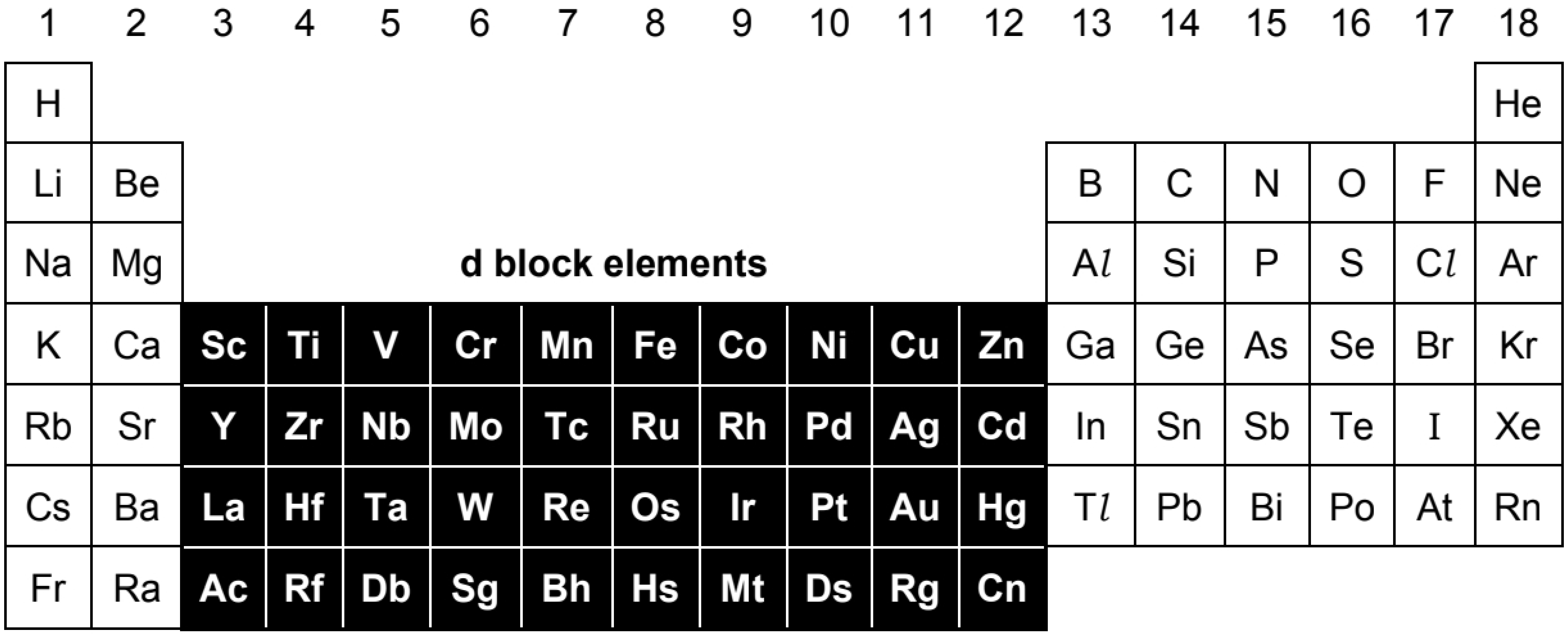
1 Introduction

LO **(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

1.1 Definition of Transition Elements

By definition, d block elements refer to elements occurring at that point in the periodic table where the d subshell (comprising of five d orbitals) is being filled, from d^1 to d^{10}.

- d block elements are located between Group 3 and Group 12 of the periodic table, inclusive.



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	**d block elements**										Al	Si	P	S	Cl	Ar
K	Ca	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	Ga	Ge	As	Se	Br	Kr
Rb	Sr	**Y**	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**	In	Sn	Sb	Te	I	Xe
Cs	Ba	**La**	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**Ac**	**Rf**	**Db**	**Sg**	**Bh**	**Hs**	**Mt**	**Ds**	**Rg**	**Cn**						

A **transition element** (or transition metal) is a d block element that forms **at least one stable ion** with **a partially filled d subshell**.

In this topic, the focus would be on the first row (period 4) transition elements:

Ti	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**
Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper

- Although scandium (Sc) and zinc (Zn) are d block elements in the first row, they are **<u>not considered</u>** transition elements. This can be explained by looking at the electronic configurations of Sc and Zn, as well as their respective stable ions:

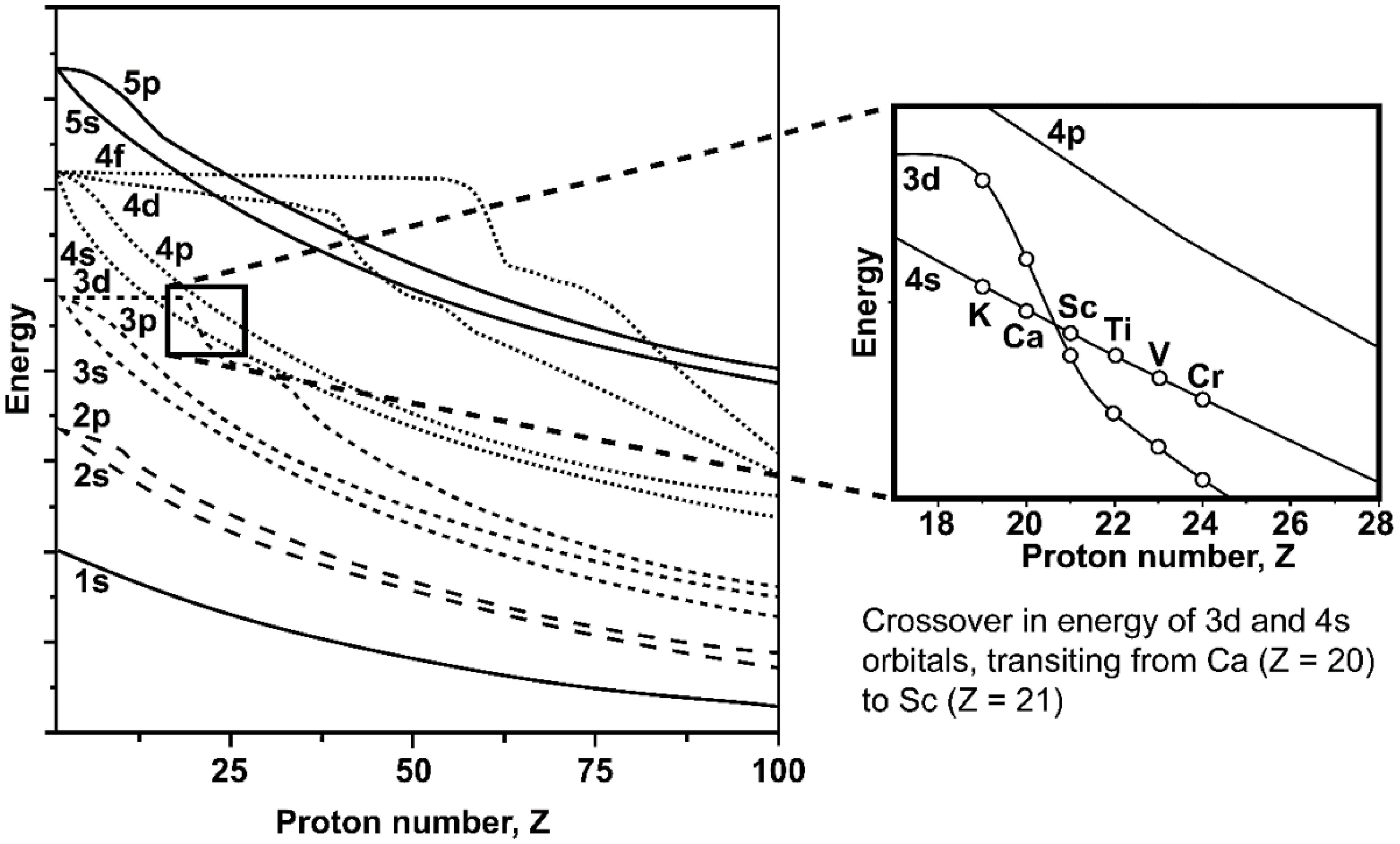
Sc	[Ar] $3d^1\ 4s^2$	Zn	[Ar] $3d^{10}\ 4s^2$
Sc^{3+}	[Ar]	Zn^{2+}	[Ar] $3d^{10}$

  - Sc^{3+} has **<u>no d electrons</u>**,
  - Zn^{2+} has a **<u>completely filled d subshell</u>**.
  - Hence, these ions **<u>do not</u>** have **<u>partially-filled</u>** d subshells.

1.2 Writing Electronic Configuration

1.2.1 Writing Electronic Configuration for Atoms of Transition Elements

There is a crossover between energy of the 3d and 4s orbitals between $_{20}$Ca and $_{21}$Sc (**Figure 1**). Up till Ca, the 4s is lower in energy than the 3d orbital. From Sc onwards, the **4s** is actually the **outermost (higher energy) orbital**, while the **3d** orbital is **penultimate**.



Crossover in energy of 3d and 4s orbitals, transiting from Ca (Z = 20) to Sc (Z = 21)

Figure 1 Crossover between energy of 3d and 4s orbitals between Ca and Sc

- When representing the electronic configuration in writing, **<u>3d is written before 4s</u>**.
- However, spectroscopic results show that Sc has the electronic configuration [Ar] $3d^1\ 4s^2$, instead of [Ar] $3d^3$ or [Ar] $3d^2\ 4s^1$. To understand this observation, we have to consider the nature of inter-electronic repulsions in 3d and 4s orbitals (Refer to **Appendix 1** on page 387).
  - This effect is generally true for Sc through Zn, so their electron configurations are of the form **[Ar] $3d^n\ 4s^2$**, where n = 1 for scandium and n = 10 for zinc (See **Table 1**).
  - Two exceptions, which are observed experimentally, are **chromium** (Cr), with electronic configuration **[Ar] $3d^5\ 4s^1$**, and **copper** (Cu), with electronic configuration **[Ar] $3d^{10}\ 4s^1$**. The anomaly is attributed to the exchange energy associated with electrons having parallel spins (Refer to **Appendix 2** on page 38).

1.2.2 Writing Electronic Configuration for Cations of Transition Elements

To write the electronic configuration for cations:

- Begin by writing the electron configuration of the corresponding atom of the respective element before forming the cation.
- Electrons are removed from the **<u>highest energy orbital</u>** first.
  - The **4s electrons** (further away from nucleus) are **<u>removed first</u>** before the **3d electrons**.
- Paired electrons are **<u>removed first</u>** before unpaired electrons.

Example:	$_{26}$Fe	[Ar]	⥮	↿	↿	↿	↿	⥮	[Ar] $3d^6$ $4s^2$
	$_{26}$Fe^{3+}	[Ar]	↿	↿	↿	↿	↿		[Ar] $3d^5$

Table 1 Electronic configuration of some Period 4 elements (Shaded are non-transition elements)

Atomic No.	Element	Electronic Configuration							
20	Ca	[Ar]						⥮	[Ar] $4s^2$
21	Sc	[Ar]	↿					⥮	[Ar] $3d^1$ $4s^2$
22	Ti	[Ar]	↿	↿				⥮	[Ar] $3d^2$ $4s^2$
23	V	[Ar]	↿	↿	↿			⥮	[Ar] $3d^3$ $4s^2$
24	Cr	[Ar]	↿	↿	↿	↿	↿	↿	[Ar] $3d^5$ $4s^1$
25	Mn	[Ar]	↿	↿	↿	↿	↿	⥮	[Ar] $3d^5$ $4s^2$
26	Fe	[Ar]	⥮	↿	↿	↿	↿	⥮	[Ar] $3d^6$ $4s^2$
27	Co	[Ar]	⥮	⥮	↿	↿	↿	⥮	[Ar] $3d^7$ $4s^2$
28	Ni	[Ar]	⥮	⥮	⥮	↿	↿	⥮	[Ar] $3d^8$ $4s^2$
29	Cu	[Ar]	⥮	⥮	⥮	⥮	⥮	↿	[Ar] $3d^{10}$ $4s^1$
30	Zn	[Ar]	⥮	⥮	⥮	⥮	⥮	⥮	[Ar] $3d^{10}$ $4s^2$

Checkpoint / Pen down own notes

- Definition of a transition element.
- Writing of electronic configurations of transition metal and their ions.

2 Physical Properties of Transition Elements

LO **(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

Similar to the lighter Group 1 and 2 metals, the transition elements from Group 8–12 are good conductors of heat (**Figure 2**) and electricity (**Figure 3**), particularly Cu, Ag and Au in Group 11.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li 44	Be 210											B 27.4	C	N	O	F	Ne
Na 131	Mg 156	**d block elements**										A*l* 247	Si 156	P	S	C*l*	Ar
K 108	Ca 201	Sc 15.8	Ti 11.4	V 31	Cr 67	Mn 7.79	Fe 80.4	Co 69	Ni 82.9	Cu 398	Zn 113	Ga 40.6	Ge 60	As 50.2	Se	Br	Kr
Rb 58.2	Sr 35.4	Y 17.2	Zr 21.1	Nb 52.3	Mo 142	Tc 50.2	Ru 117	Rh 150	Pd 70	Ag 428	Cd 97	In 83.7	Sn 62.8	Sb 25.9	Te 6	I	Xe
Cs 35.9	Ba 18.4	La 13.4	Hf 23	Ta 54.4	W 160	Re 71.2	Os 87.6	Ir 147	Pt 71.1	Au 318	Hg 8.21	T*l* 47	Pb 34	Bi 8.2	Po 42	At 1.7	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn						

Figure 2 Room temperature thermal conductivity of metals (W m^{-1} K^{-1})

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li 18.4	Be 43.1											B 0.27	C	N	O	F	Ne
Na 36.1	Mg 38.6	**d block elements**										A*l* 66	Si 0	P	S	C*l*	Ar
K 24	Ca 49.6	Sc 3.07	Ti 4.11	V 6.63	Cr 13	Mn 0.9	Fe 17.6	Co 27.6	Ni 25.2	Cu 103	Zn 28.3	Ga 11.5	Ge 0	As 6.63	Se	Br	Kr
Rb 13.4	Sr 13.1	Y 2.89	Zr 4.1	Nb 13.2	Mo 34	Tc 9.32	Ru 22.7	Rh 38.2	Pd 16	Ag 108	Cd 25	In 20.5	Sn 15.2	Sb 4.66	Te	I	Xe
Cs 8.62	Ba 5.35	La 2.8	Hf 5.21	Ta 13	W 32.5	Re 9.3	Os 18.2	Ir 36.6	Pt 16.3	Au 73.4	Hg 1.8	T*l* 11.5	Pb 8.35	Bi 1.64	Po 4.31	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn						

Figure 3 Room temperature electrical conductivity of metals (%IACS, International Annealed Copper Standard)

Yet they show properties different from them, for example, transition metals are hard, have a higher density and have higher melting and boiling points. The various physical properties of transition elements will be explored in this section.

2.1 Trend in Atomic Radii of Transition Elements

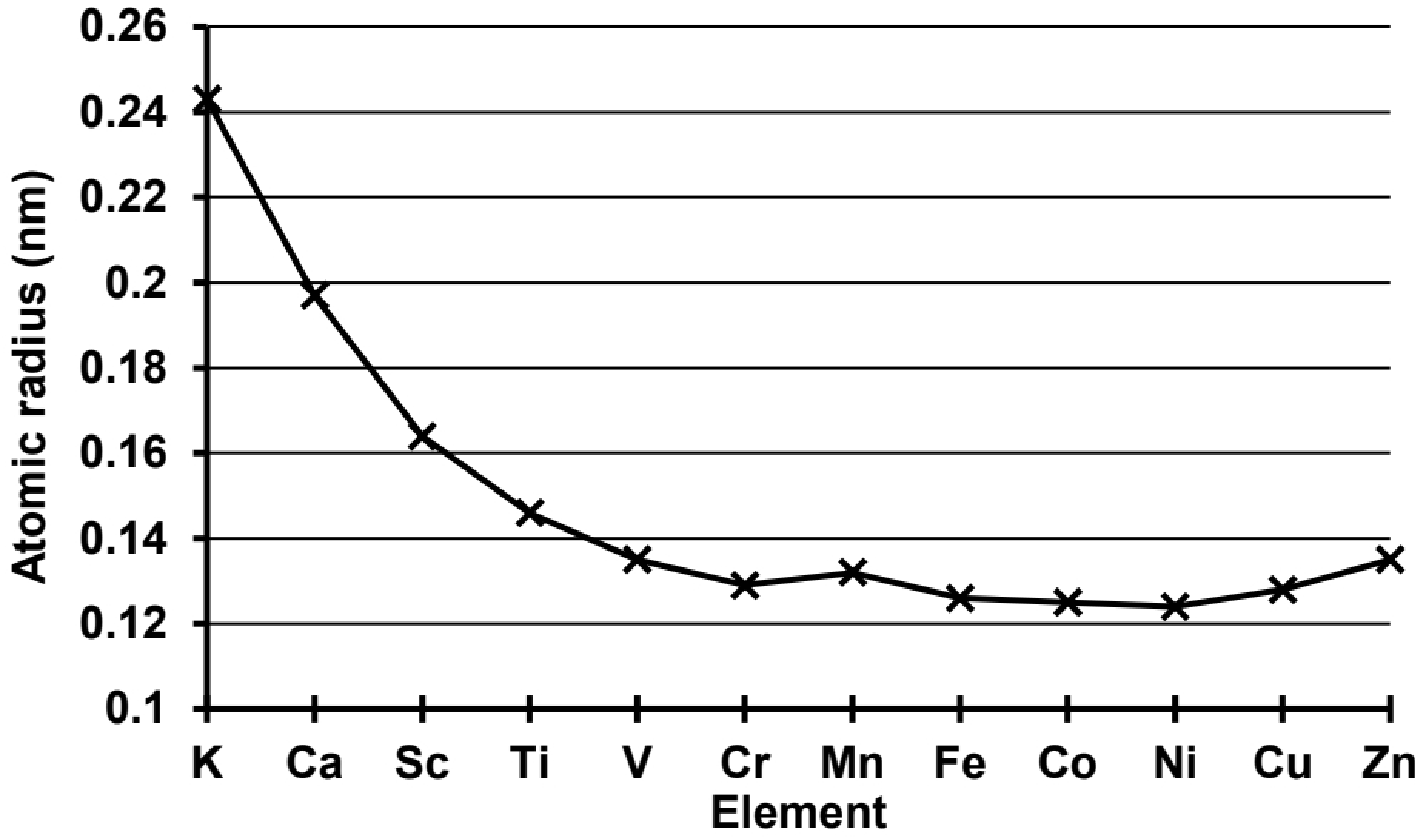


Figure 4 Variation in atomic radii of selected period 4 elements

Atomic radii of the first row transition elements are **<u>smaller than those of the period 4 s block elements K and Ca</u>**

- Moving from s block to the d block,
  - **<u>nuclear charge increases</u>**.
  - Despite electrons being added to the **<u>inner 3d orbitals</u>**,
  - the 3d electrons nonetheless, are **<u>ineffective in shielding</u>** the 4s electrons from the nucleus, due to the **diffused** 4-lobed shape of the d orbitals.
  - **<u>Effective nuclear charge increases</u>**,
  - hence **<u>electrostatic forces of attraction</u>** between the nucleus and valence electrons **<u>increase</u>**,
  - Atomic radii of the first row transition elements are smaller than those of the period 4 s block elements, K and Ca.

Atomic radii of transition elements are **<u>relatively invariant (remain relatively constant)</u>**.

- Across the period 4 transition elements,
  - **<u>nuclear charge increases</u>**.
  - Since electrons are being added to the **<u>inner 3d orbitals</u>**, **<u>shielding effect also increases</u>** (Refer to **Appendix 3** on page 38 for a more detailed discussion),
  - the **<u>increase</u>** in shielding effect **<u>almost cancels</u>** the **<u>increase</u>** in nuclear charge.
  - **<u>Effective nuclear charge increases very gradually</u>**,
  - hence **<u>electrostatic forces of attraction</u>** between the nucleus and valence electrons **<u>increase only slightly</u>**.
  - Atomic radii remain relatively constant across the period 4 transition element.

2.2 Trend in First Ionisation Energy of Transition Elements

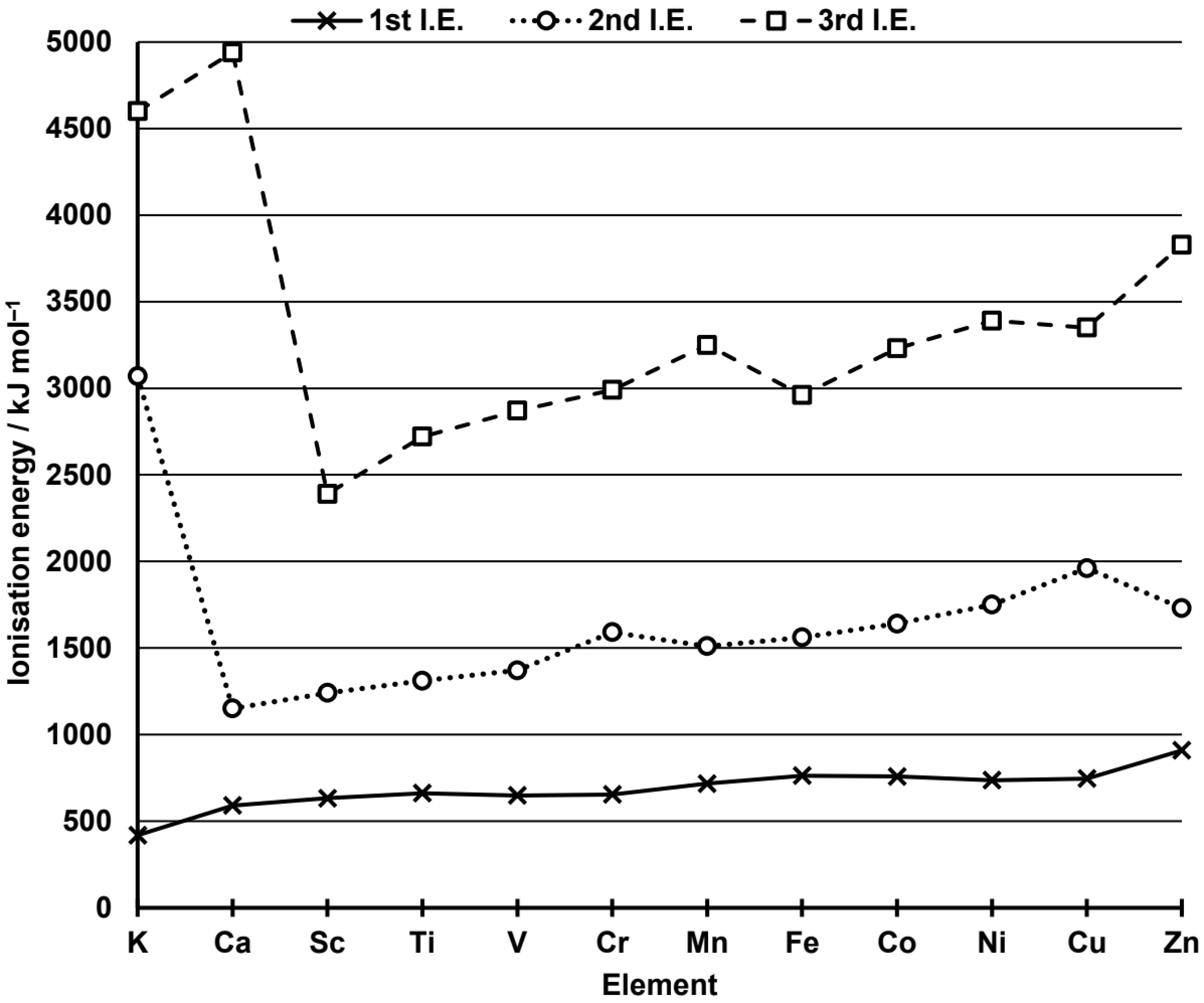


Figure 5 Variation in first, second and third ionisation energies for selected Period 4 elements

First ionisation energies of transition elements are **relatively invariant (remain relatively constant)**.

Across the Period 4 transition elements,

- **nuclear charge increases**.
- Since electrons are being added to the **inner 3d orbitals, shielding effect also increases**,
- the **increase** in shielding effect **almost cancels** the **increase** in nuclear charge.
- **Effective nuclear charge increases very gradually**,
- hence **electrostatic forces of attraction** between the nucleus and valence electrons **increase only slightly**.
- **Energy** required to remove the valence electrons **increases only slightly**.

Example 2A

Explain the following trends seen in **Figure 5**.

1 3rd I.E. of Fe is lower than expected (in fact, true for Co, Ni, Cu as well).

2.3 Trend in Melting and Boiling Points of Transition Elements

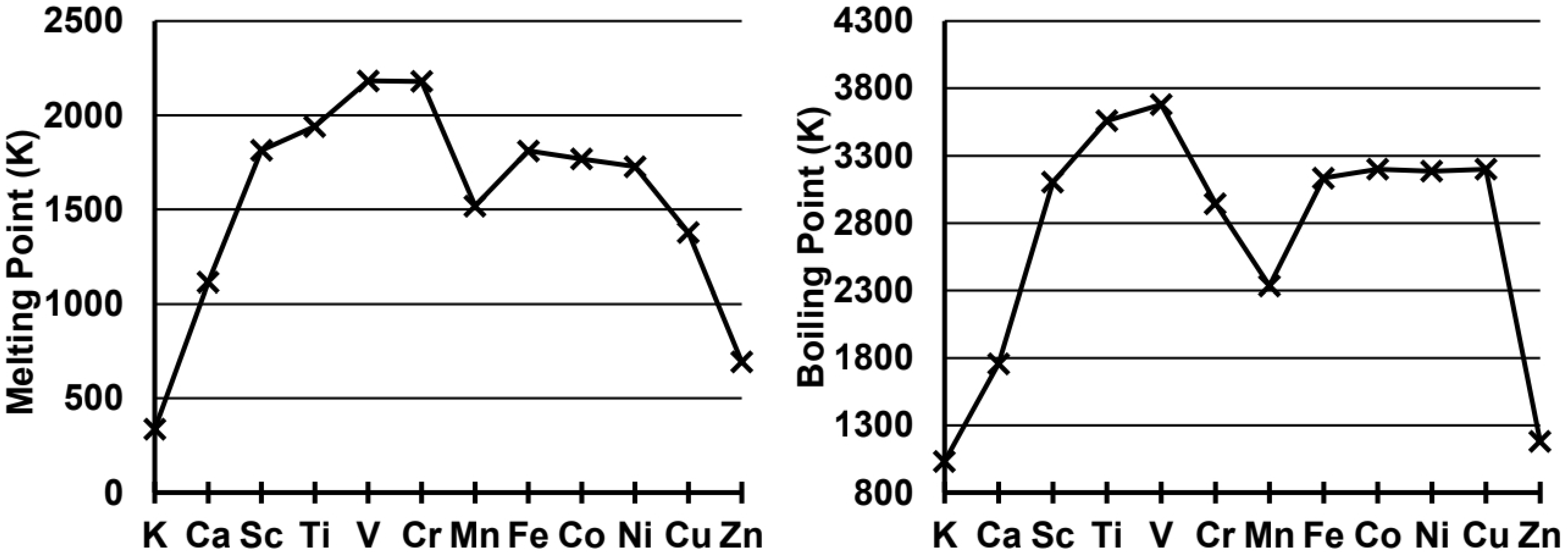


Figure 6 Variation in melting and boiling points of selected period 4 elements

Transition elements have **higher melting and boiling points** than s block elements.

- Both s block elements and transition elements have **giant metallic lattice structures** held together by **strong metallic bonds**
- In transition elements, the sea of delocalised electrons is contributed by **3d and 4s electrons**, since the energy level difference between the 3d and 4s orbitals is small.
- In s block elements, only **one or two 4s electrons** can be delocalised.
- Thus, transition elements have **higher** melting and boiling points than s block elements.

2.4 Trend in Density of Transition Elements

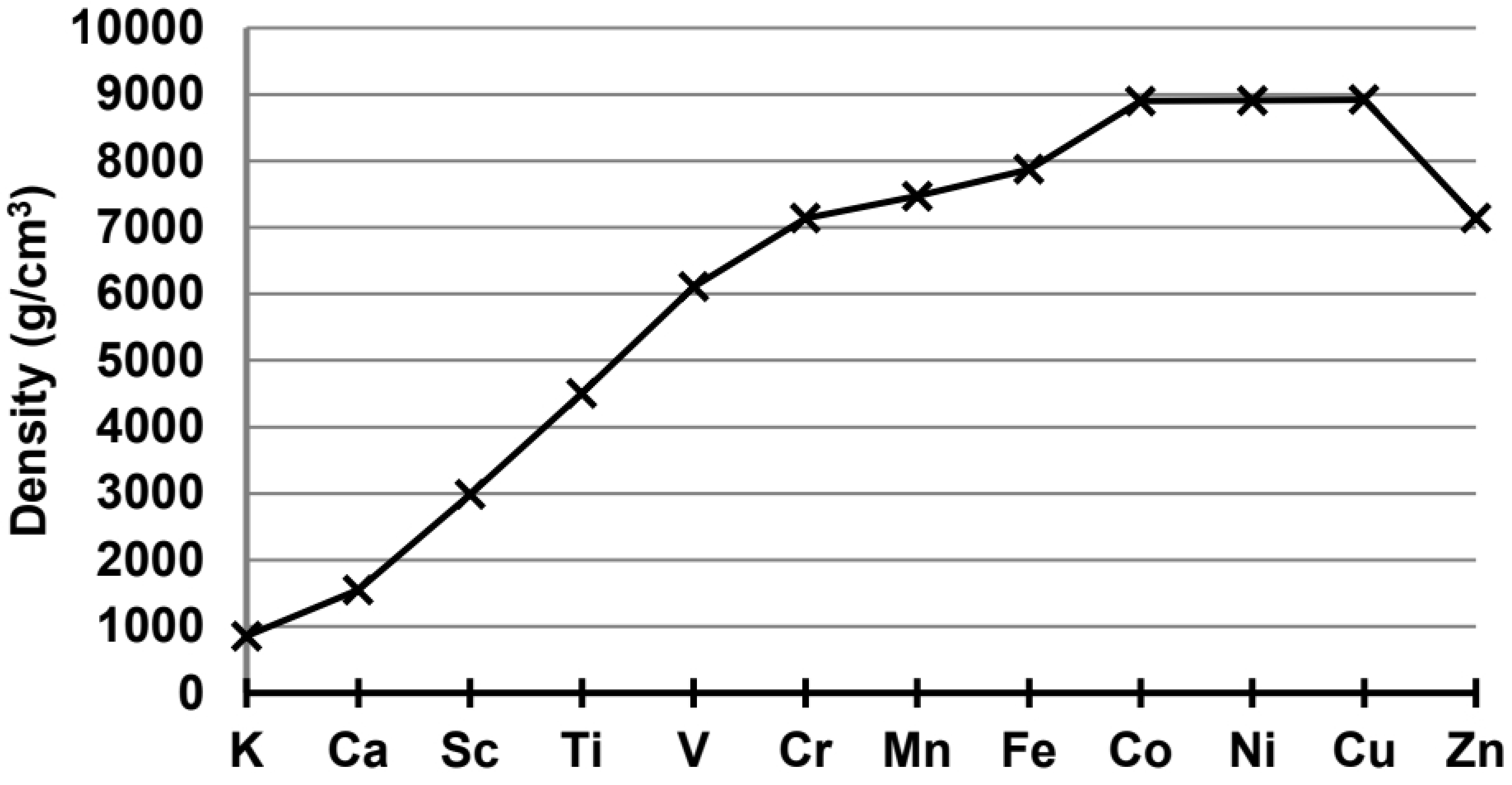


Figure 7 Variation in density of selected period 4 elements

Transition elements are **denser** than s block elements.

- Transition metal cations have relatively **smaller atomic radii** and **higher atomic mass** compared to s block elements
- Transition elements have **more closely packed structures** due to their stronger metallic bonding as compared to s block elements
- **More atoms** of the d block elements are packed in a **unit volume** compared to the s block elements within the same period
- Transition elements are **denser** than s block elements

Checkpoint / Pen down own notes

- Understand the trends of transition elements in terms of
  - Atomic radii, first ionisation energy, melting & boiling points, density

3 Chemical Properties of Transition Elements

Transition elements have characteristic chemical properties which s block elements do not have. They are as follows:

1. Displaying variable oxidation states
2. Forming stable complexes
3. Forming coloured complexes and ions
4. Exhibiting catalytic properties

LO **(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

3.1 Variable Oxidation States

Table 2 Transition elements and their variable oxidation states (most common oxidation states are in **bold**)

Ti	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**
+1	+1	+1	+1	+1	+1	+1	**+1**
+2	**+2**	**+2**	**+2**	**+2**	**+2**	**+2**	**+2**
+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 above summarises the known oxidation state of the period 4 transition elements.

- Transition elements possess **variable oxidation states** due to the **small energy level difference between the 3d and 4s orbitals**.
- Different numbers of 3d and 4s electrons **can be lost to form stable ions or utilised in bonding to form compounds** of different oxidation states.
- s block elements are restricted to oxidation numbers +1 (Group 1) and +2 (Group 2) respectively.
- Further removal of inner shell electrons will involve too much energy.

3.1.1 Predicting Likely Oxidation States

All the transition elements in **Table 1** on page 5 can have +2 oxidation state, where two 4s electrons are lost. For Cr and Cu, the one 4s electron and one of the 3d electrons are lost.

The **maximum** oxidation state a transition element can have is the **number of 4s electrons** plus the number of ***unpaired* 3d electrons**.

Example:

Maximum oxidation state of Cr = 1 + (10 – 5) = +6

Other oxidation states of transition elements usually vary between +2 and the maximum oxidation state of the element (see **Table 2** above). These oxidation states are usually rare.

3.1.2 Characteristics of Transition Element Compounds or Ions

Transition elements form different types of compounds or ions depending on their oxidation states:

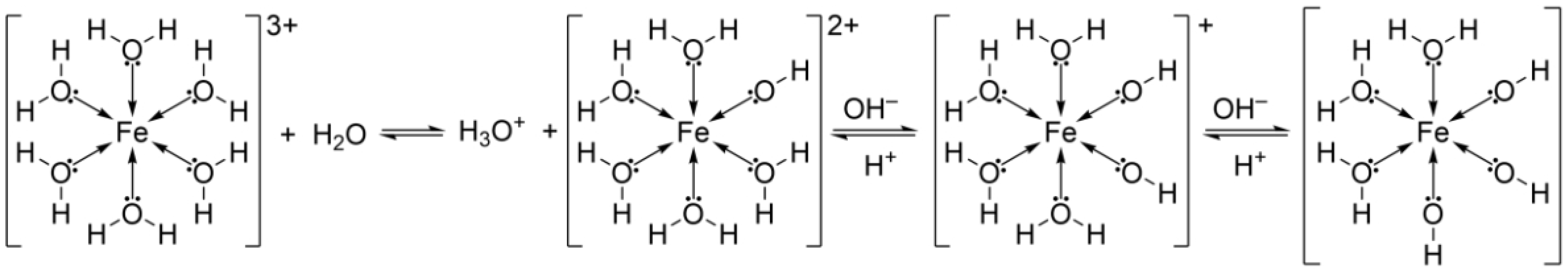
- Compounds of transition elements in **low** oxidation states are usually **ionic**. The lower oxides are thus **basic**, *e.g.* $Mn^{II}O$, $Cr^{II}O$.
- Compounds of transition elements in **high** oxidation states are usually form **covalent**. The higher oxides are thus **acidic**, *e.g.* $Mn_2^{VII}O_7$, $Cr^{VI}O_3$.
    - ➢ At higher oxidation states, transition element cations have **high charge density** and are **highly polarising**, thus they form **covalent** compounds and ions, *e.g.* $Mn_2^{VII}O_7$, $Mn^{VI}O_4^{2-}$.
- Oxides of transition elements in **intermediate** oxidation states are usually **amphoteric**, *e.g.* $Cr_2^{III}O_3$.

Note:

- Transition metal cations such as Fe^{3+}, Cr^{3+} are able to undergo hydrolysis in water to form acidic solutions of pH 3. (Similar to $A\ell^{3+}$)

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

- This is due to the **smaller cation size** and a **larger positive charge (3+),** and hence a **higher charge density** of these ions (**high polarising power**), it is able to **draw electrons to itself** from the oxygen atoms of the neighbouring water molecules, which **further weakens** the O–H bonds, thereby producing H^+ in the solution.



only **in the presence of added base / acid**

$$[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} [Fe(H_2O)_4(OH)_2]^{+} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} Fe(H_2O)_3(OH)_3(s)$$

3.1.3 Relative Stability of Oxidation States

In Period 4 transition elements, stability of the **+2 oxidation state** relative to the +3 oxidation state **increases** across the series.

Relative stability of the oxidation states are reflected by their standard electrode potential, $E^\ominus$, as shown in **Figure 8**.

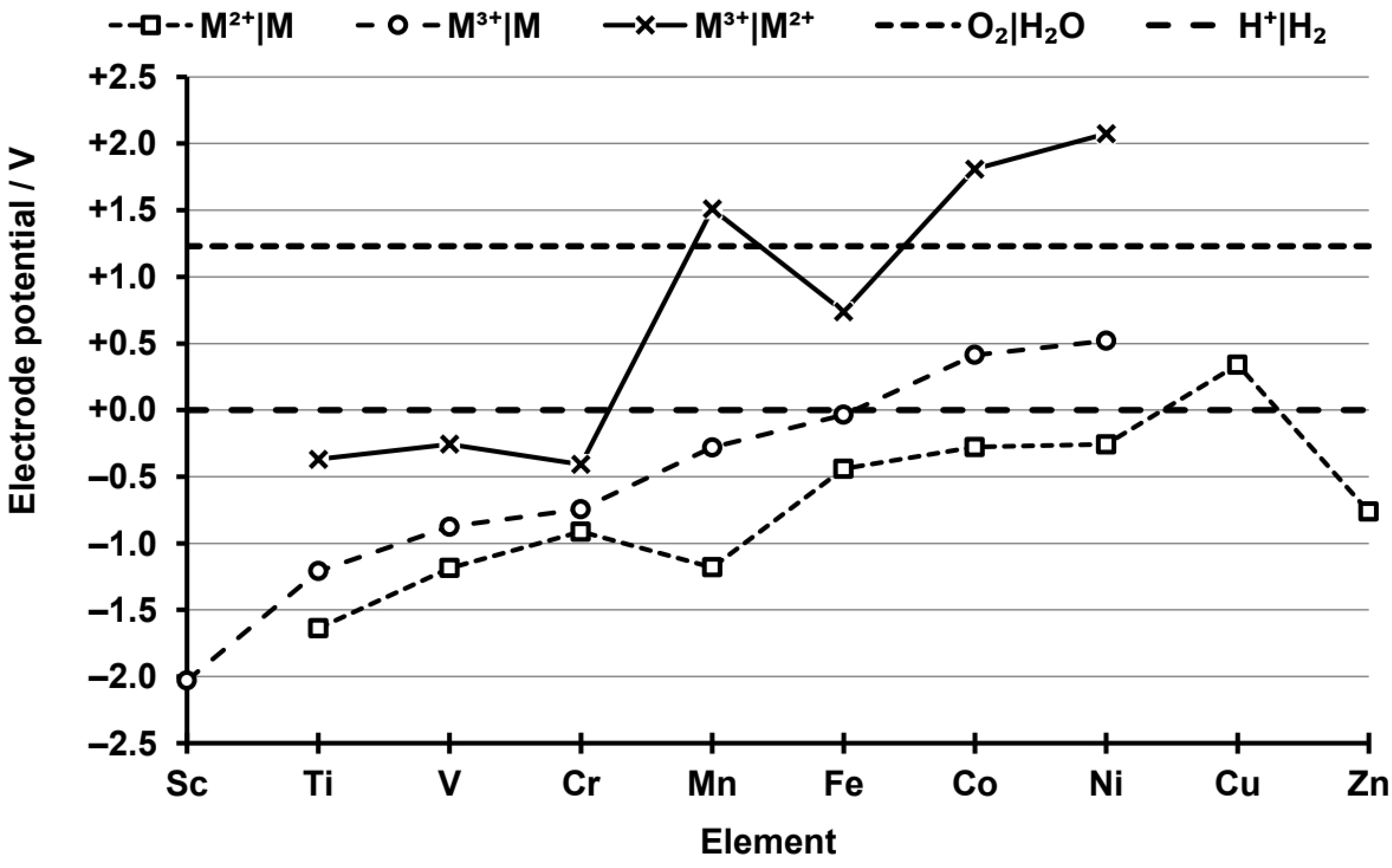


Figure 8 Electrode potentials for the $M^{3+}|M^{2+}$, $M^{2+}|M$ and $M^{3+}|M$ couple

$\boxed{E^{\ominus}\left(M^{2+}(aq)|M(s)\right)}$

- M^{2+}(aq) ion is known for all the elements from Ti to Zn.

  Note: The more negative the $E^{\ominus}$ value, the less spontaneous for the reduction to take place!

  - With the exception of Cu^{2+}, M^{2+}(aq) is more stable relative to M(s) as seen from the negative $E^{\ominus}\left(M^{2+}(aq)|M(s)\right)$ for the other elements, i.e. M^{2+} less likely to undergo reduction.

  - Since $E^{\ominus}\left(M^{2+}(aq)|M(s)\right)$ is negative compared to $E^{\ominus}\left(H^{+}(aq)|H_2(g)\right) = 0.00$ V, all the metals except Cu are expected to react with aqueous acids to give M^{2+}(aq), although the M^{2+}(aq) ion can undergo further oxidation to higher oxidation states, i.e. M undergoes oxidation to form M^{2+} while H^{+} undergoes reduction to form H_2(g).

  - Generally, the value of $E^{\ominus}\left(M^{2+}(aq)|M(s)\right)$ becomes increasingly less negative from left to right of the d-block, i.e. the reduction of M^{2+} becomes increasingly more spontaneous from left to right of the d-block. This would mean that the oxidation of the metal to form M^{2+} becomes decreasingly less spontaneous from left to right of the d-block.

  - In short, M^{2+}(aq) is increasingly less stable relative to M(s) from left to right of the d-block, **oxidation of M to M^{2+} is decreasingly likely** to occur, *i.e.* the metals are less reactive towards oxidation.

$\boxed{E^{\ominus}\left(\mathrm{M^{3+}(aq)}\middle|\mathrm{M(s)}\right)}$

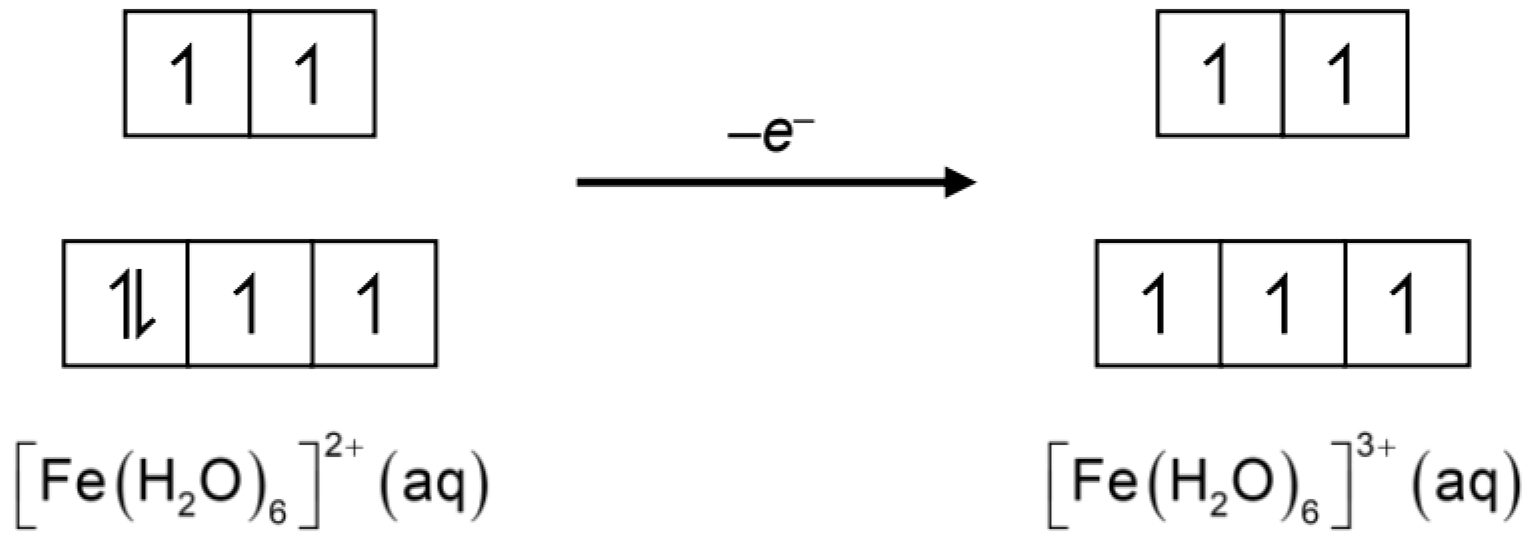
- M^{3+}(aq) ion is known only for the elements Sc to Ni. In fact, Sc^{3+} is the only stable ions formed by Sc.
  - ➢ With the exception of Co^{3+} and Ni^{3+}, M^{3+}(aq) is more stable relative to M(s) as seen from the negative $E^{\ominus}\left(\mathrm{M^{3+}(aq)}\middle|\mathrm{M(s)}\right)$ for the elements.
  - ➢ Generally, the value of $E^{\ominus}\left(\mathrm{M^{3+}(aq)}\middle|\mathrm{M(s)}\right)$ becomes increasingly less negative, meaning that M^{3+}(aq) is increasingly less stable relative to M(s), **oxidation of M to M^{3+} is decreasingly likely** to occur, *i.e.* the metals are less reactive towards oxidation.

$\boxed{E^{\ominus}\left(\mathrm{M^{3+}(aq)}\middle|\mathrm{M^{2+}(aq)}\right)}$

- From the discussion above, both M^{2+} and M^{3+} decreases in stability generally across the series. However, stability of M^{3+} decreases much faster than that of M^{2+}, hence stability of the +2 oxidation state **relative** to the +3 oxidation state **increases** across the series. This is seen in the general increasingly less negative $E^{\ominus}\left(\mathrm{M^{3+}(aq)}\middle|\mathrm{M^{2+}(aq)}\right)$, indicating that **reduction is increasingly likely** to occur.
- The general trend in $E^{\ominus}\left(\mathrm{M^{3+}(aq)}\middle|\mathrm{M^{2+}(aq)}\right)$ is broadly similar to that of the third ionisation energies (**Figure 5** on page 8):

$$\begin{array}{ccccc} \mathrm{M^{2+}} & \rightarrow & \mathrm{M^{3+}} & + & e^{-} \\ [\mathrm{Ar}]\,3\mathrm{d}^{n} & & [\mathrm{Ar}]\,3\mathrm{d}^{n-1} & & \end{array}$$

  - ➢ Across the period, **effective nuclear charge increases** for the M^{2+} ions as **nuclear charge increases** while **shielding effect remains essentially constant**.
  - ➢ The **electrostatic forces of attraction** between the nucleus and the valence d electron to be removed **increases**.
  - ➢ Thus, there is **increasing difficulty of removing a d electron** and the stability of the +2 oxidation state increases across the series.
- Like the trend in third I.E., there is a dip in $E^{\ominus}\left(\mathrm{M^{3+}(aq)}\middle|\mathrm{M^{2+}(aq)}\right)$ from Mn to Fe, corresponding to inter-electronic repulsion in the d^6 system of Fe^{2+}, where two electrons are forced to occupy the same d orbital:



(Refer to **page 23** to understand the splitting of d orbitals in the aqua complexes)

- **Negative** $E^\ominus$ values for Ti, V and Cr indicate that the reduction $M^{3+}(aq) + e^- \rightarrow M^{2+}(aq)$ is **not** thermodynamically favourable. (Equilibrium tends towards the oxidation process i.e. the +3 oxidation state)
  - Hence, $M^{3+}(aq)$ is **more stable** w.r.t. $M^{2+}(aq)$.
  - $M^{2+}(aq)$ would be **easily oxidised**, hence M^{2+} is a **good reducing agent**.
  - *E.g.* $Cr^{2+}(aq)$ will be oxidised by oxygen in air to $Cr^{3+}(aq)$
- **Positive** $E^\ominus$ values for Mn to Ni indicate that the reduction $M^{3+}(aq) + e^- \rightarrow M^{2+}(aq)$ is thermodynamically favourable. (Equilibrium tends towards the reduction process)
  - Hence, $M^{2+}(aq)$ is **more stable** w.r.t. $M^{3+}(aq)$.
  - $M^{3+}(aq)$ would be **easily reduced**, hence M^{3+} is a **good oxidising agent**.
  - In fact, with the exception of Fe^{3+}, the $E^\ominus\left(M^{3+}(aq)\middle|M^{2+}(aq)\right)$ for Mn, Co and Ni are all more positive than $E^\ominus\left(O_2(g)\middle|H_2O(l)\right) = +1.23V$. This means that $Mn^{3+}(aq)$, $Co^{3+}(aq)$ and $Ni^{3+}(aq)$ are all unstable in water, oxidising H_2O to give O_2, while themselves reduced to M^{2+}.

Example 3A

The iron(II) state is much more strongly reducing in alkaline medium, than in acidic medium. Explain.

Checkpoint / Pen down own notes

- Understand the reasons why transition elements tend to have variable oxidation states.
- Ability to predict the likely oxidation states of transition elements.
- Understand the characteristic of transition element compound or ions in terms of the oxidation states exhibited.
- Relative stability of the oxidation state of transition elements.

LO **(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)

3.2 Formation of Complexes

A **complex** consists of a **central metal atom or ion** surrounded by other ions or molecules called **ligands** bonded to the central atom/ion by **dative covalent bonds**.

All cations have some tendency to form complexes, since they attract the electron clouds on surrounding groups. However, this tendency is particularly strong amongst d block elements.

- Due to their relatively small size and high charge, transition metal ions have **high charge density** and hence, **high polarising power** to attract ligands.
- Transition metal ions also have **low-lying vacant d orbitals** (*i.e.* empty d orbitals of low energy).
- These accept the lone pair(s) of electrons on ligands *via* **dative covalent bonds** (see **Table 4**)
  - ➢ represented by an arrow, →, showing the direction of electron flow from each of the lone pairs on the ligands to the central metal atom or ion

Cations of s-block elements, in contrast, are larger, have a lower polarising power and thus tend to become involved in **ion-dipole** attraction, rather than covalency.

Two important features of a complex are as follows:

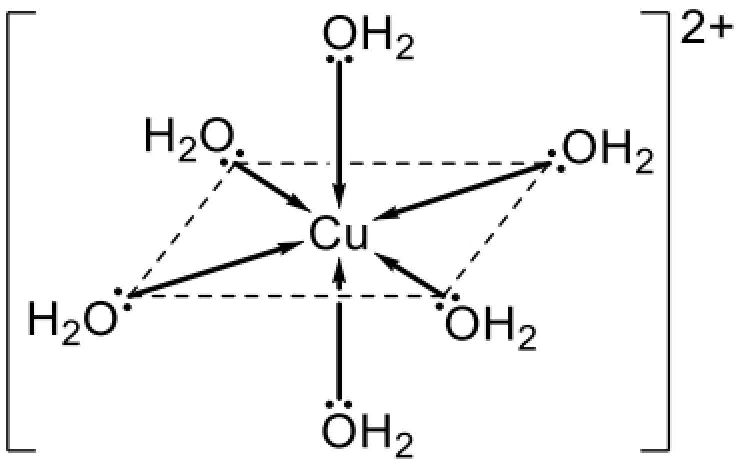
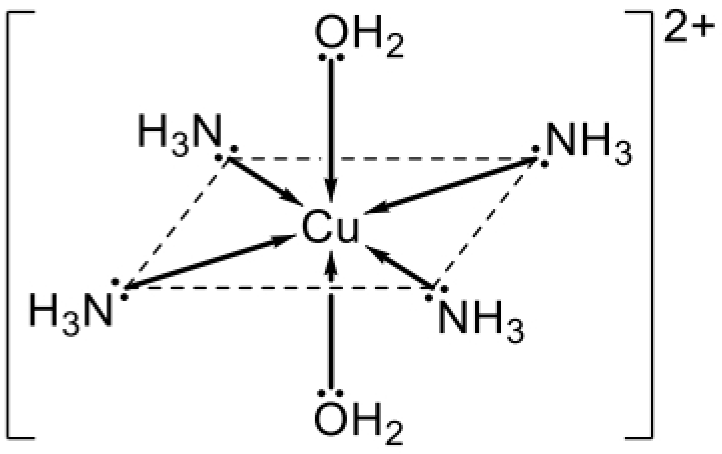
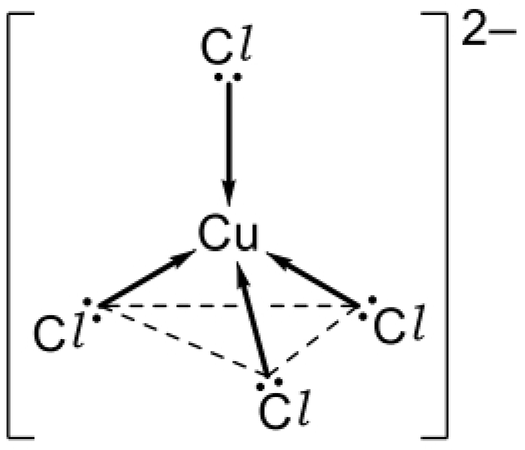
- *The **net charge** on the complex* (see **Table 3**): this is the resultant of the charge contributions from the ligands and from the central transition metal ion/atom. The "charge" on the central metal ion is, of course, the oxidation number of the metal in that complex ion.
  - ➢ A complex may be **cationic**, **neutral**, or **anionic**.

Table 3 Charges of Complexes

Example	Oxidation number of metal cation	Charge of ligand	Net charge	Complex
$[Cu(H_2O)_6]^{2+}$	Cu = +2	H_2O = 0	+2 + 6(0) = +2	Cationic
$[Fe(OH)(H_2O)_5]^{2+}$	Fe = +3	H_2O = 0 OH = –1	+3 + (–1) = +2	
$Ni(CO)_4$	Ni = 0	CO = 0	0	Neutral
$Pt(NH_3)_2Cl_2$	Pt = +2	NH_3 = 0 C*l* = –1	+2 + 2(–1) = 0	
$[Fe(CN)_6]^{4-}$	Fe = +2	CN = –1	+2 + 6(–1) = –4	Anionic
$[CuCl_4]^{2-}$	Cu = +2	C*l* = –1	+2 + 4(–1) = –2	

- *The **co-ordination number*** (see 4): this indicates the number of ligand groups around the central atom or ion. The most common values are four and six, but two is also widespread and is particularly important in the chemistry of copper(I) and silver(I) compounds.

Table 4 Examples of Complexes of Copper(II) ion with Water, Ammonia and Chloride ions

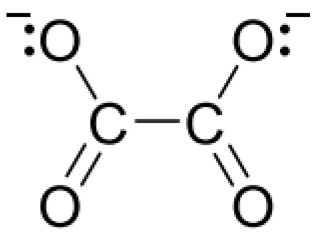
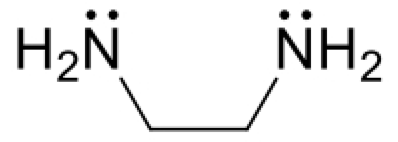
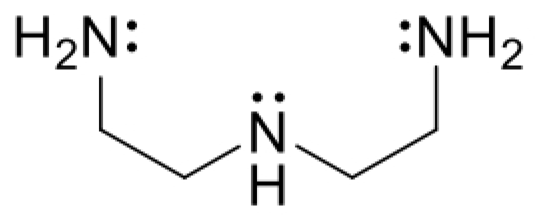
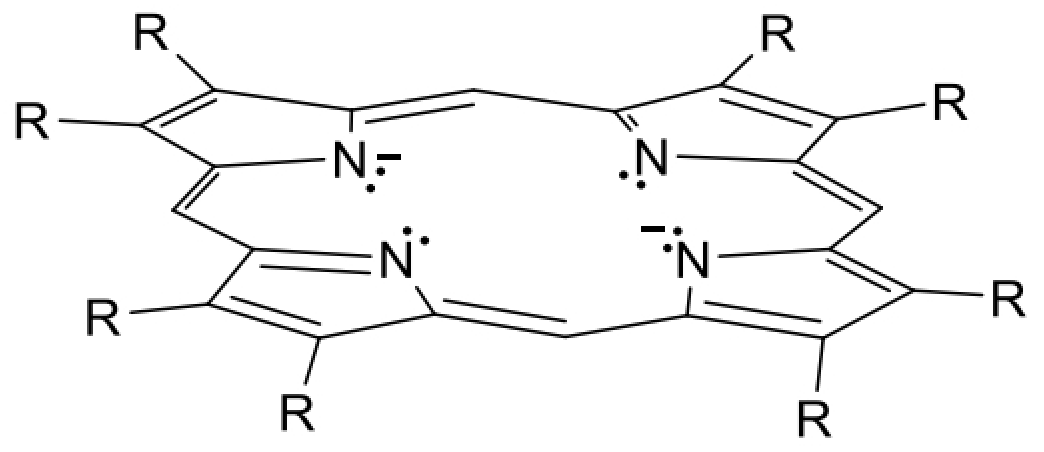
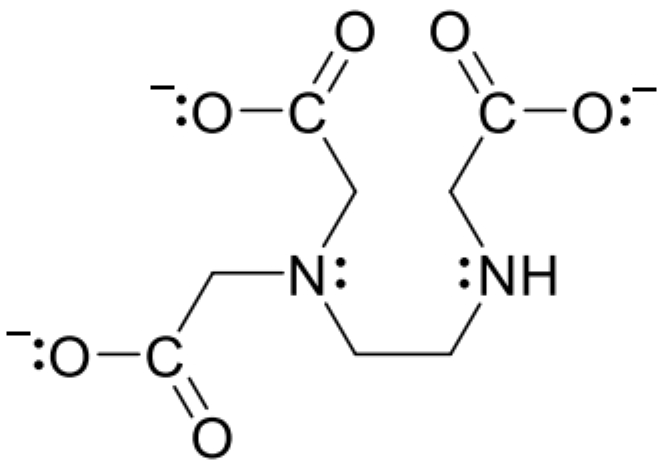
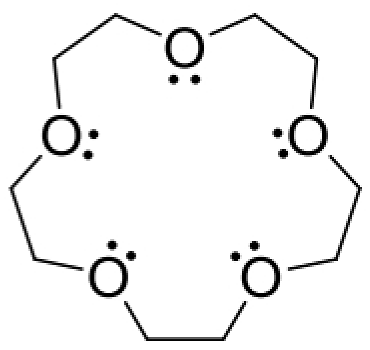
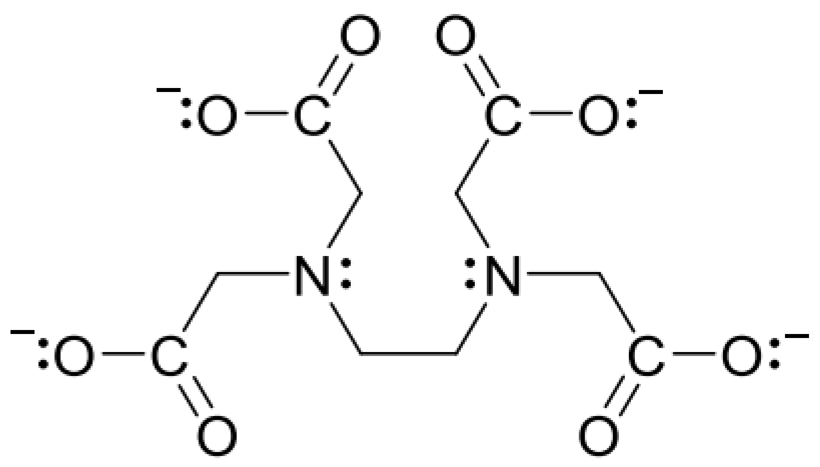
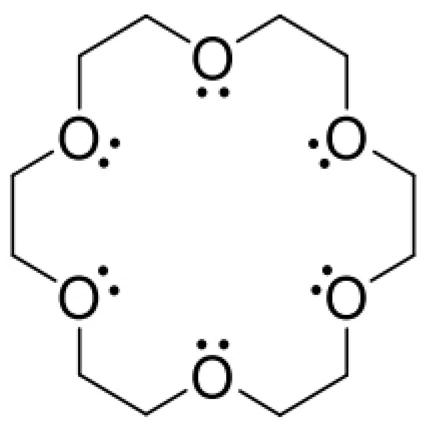
Metal Centre	Ligands	Complex	Co-ordination Number
Cu^{2+}	6×H_2O water	 hexaaquacopper(II) ion, $[Cu(H_2O)_6]^{2+}$	6
	4×NH_3 ammonia 2×H_2O water	 tetraamminediaquacopper(II) ion, $[Cu(NH_3)_4(H_2O)_2]^{2+}$	6
	4×Cl^- chloride	 tetrachlorocuprate(II) ion, $[CuCl_4]^{2-}$	4

3.2.1 Ligands

A **ligand** can be either a neutral molecule or an anion that contains at least one atom bearing **a lone pair of electrons** to be used in **dative covalent bond formation** with a metal atom or ion.

- Ligands (from the Latin word *ligare*, which means to bind) can be **neutral** molecules or **negatively-charged** anions.
- All ligands are **Lewis bases** as they are lone pair donors.
- A ligand can be classified according to the ***number of dative bonds*** (*per ligand*) formed with the central metal atom or ion (See **Table 5**), known as the **denticity**.
  - ➢ The number of bonds formed must not be equated with the number of lone pairs of electrons in the ligand – each co-ordinating atom can only donate one lone pair to the central metal, even if it has more, and there may be atoms with lone pairs in the ligand that donate none.
  - ➢ If *two or more* of the donor atoms are interacting with the *same* metal centre, that is, ligands with denticity of 2 and higher, are described as **chelating** and the complexes as **chelates**.
  - ➢ Polydentate ligands are also called chelating agents. The term chelate comes from the Greek work *Chela*, meaning “crab’s claw”. 

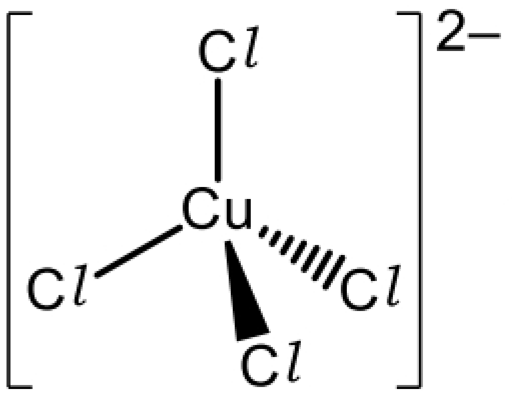
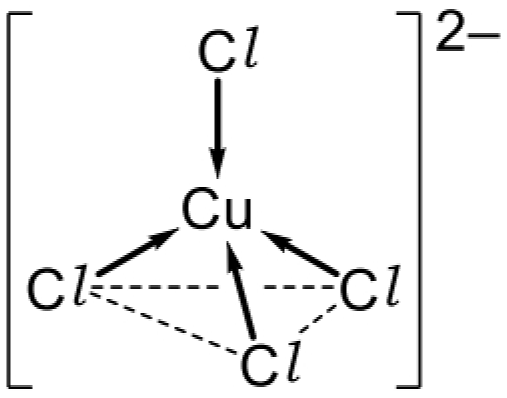
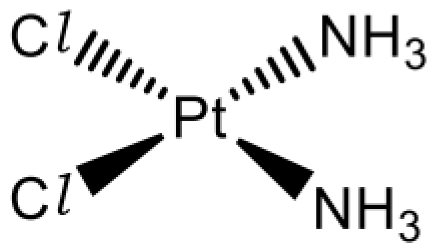
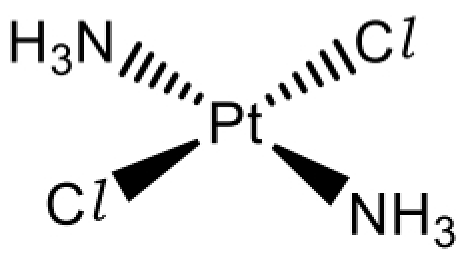
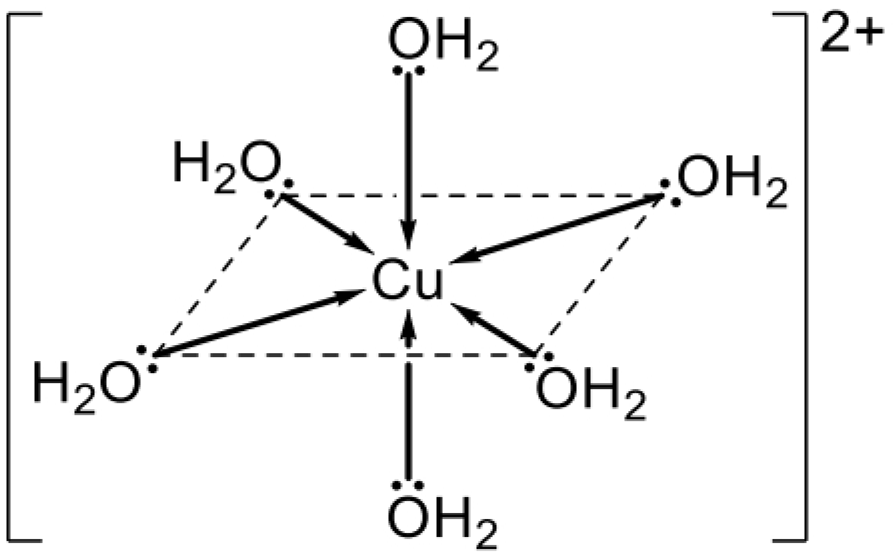
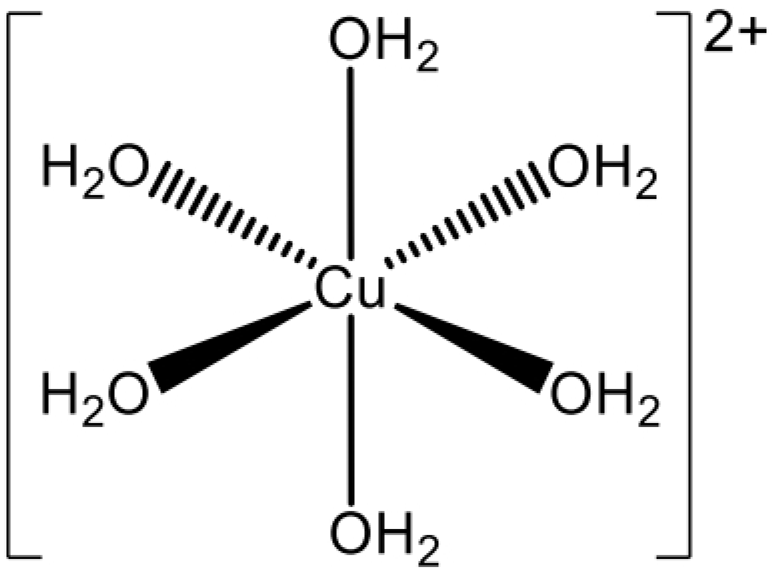
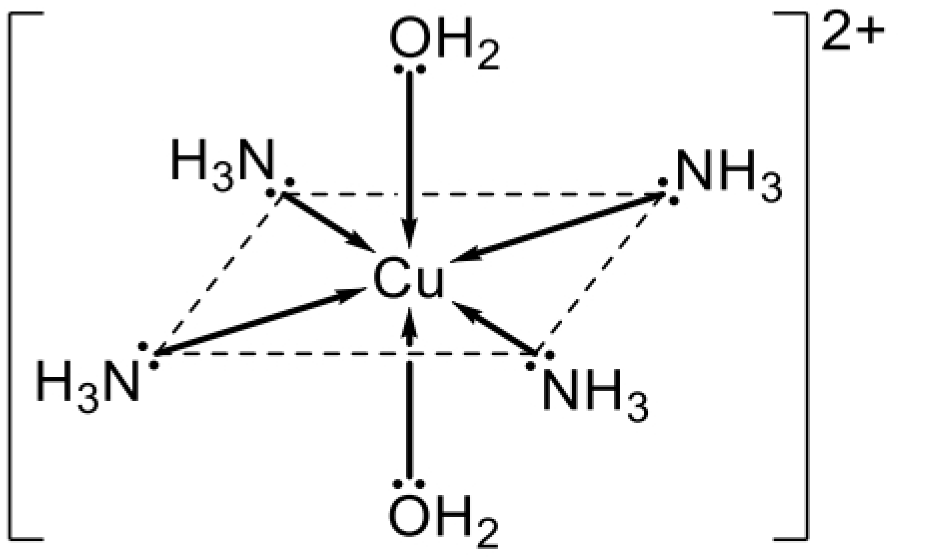
Table 5 Examples of Ligands

Denticity	Number of dative bonds	Examples
monodentate	1	$:NH_3$, $H_2O:$, $:CN^-$, $:Cl^-$, $:F^-$, SCN^- (Note: for SCN^-, the lone pair on either the S or the N atom can be used for formation of dative bond. It is said to be ***ambidentate***. This is due to resonance within the ion : $S{=}C{=}\ddot{N}\!:^- \longleftrightarrow {}^-\!:\!\ddot{S}{-}C{\equiv}N:$)
bidentate	2	 ethanedioate $(C_2O_4^{2-})$  1,2-diaminoethane (en)
tridentate	3	 diethylenetriamine (dien)
tetradentate/ quadridentate	4	haeme group in the haemoglobin molecule 
pentadentate / quinquidentate	5	 ethylenediaminetriacetate  15-crown-5
hexadentate	6	 ethylenediaminetetraacetate ($EDTA^{4-}$)  18-crown-6

3.2.2 Shapes of Complexes

Complexes show a wide variety of regular, and an infinite range of irregular, geometries for the arrangement of the ligands about the metal centre. They can adopt *linear*, *square planar*, *tetrahedral* or *octahedral* geometry depending on the electronic configuration and co-ordination number of the central metal atom or ion.

Table 6 Shapes of some complexes

Co-ordination Number	Shape	Example	Lewis structure
2	linear	$\left[Ag(NH_3)_2\right]^+$	$\left[H_3N{:}\longrightarrow Ag \longleftarrow {:}NH_3\right]^+$
4	tetrahedral	$\left[CuCl_4\right]^{2-}$	 ***or*** 
	square planar	$Pt(NH_3)_2Cl_2$	 *cis*-platin  *trans*-platin
6	octahedral	$\left[Cu(H_2O)_6\right]^{2+}$	 ***or*** 
		$\left[Cu(NH_3)_4(H_2O)_2\right]^{2+}$	

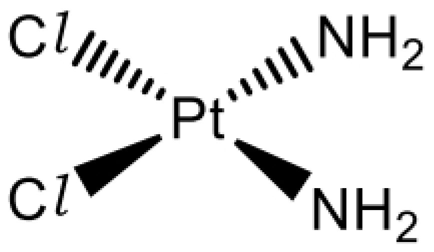
3.2.3 Isomerism in Complexes (For Your Information)

One of the consequences of complexes adopting specific geometries is the occurrence of isomers.

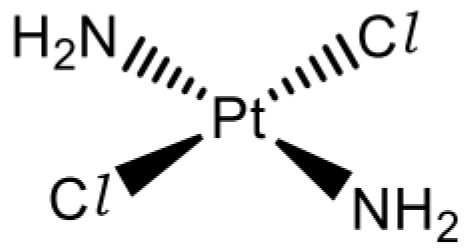
Structural isomerism: These are compounds related by the *interchange of ligands* inside the co-ordination sphere for those outside it. A classical example of this phenomenon is observed in compounds of formula $CrCl_3(H_2O)_6$.

As usually obtained from chemical suppliers, this is a green solid in which only two of the chloride ions are co-ordinated to the metal. This is formulated $[Cr(H_2O)_4Cl_2]Cl{\bullet}2H_2O$. Solutions of this compound in water slowly turn blue-green as a co-ordinated chloride ligand is replaced by a water molecule and the complex $[Cr(H_2O)_5Cl]Cl_2{\bullet}H_2O$ may be isolated.

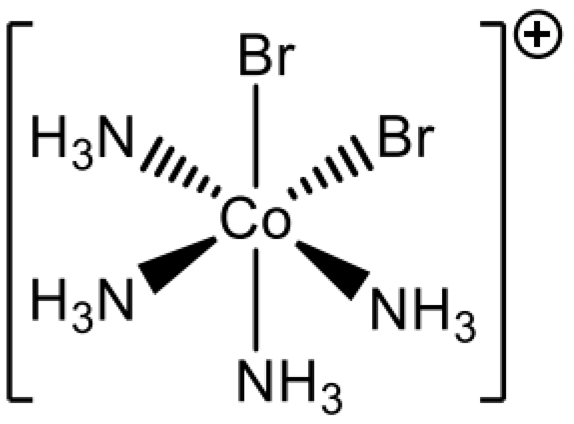
Cis-trans isomerism: A planar complex of the type $[Pt(NH_3)_2Cl_2]$ can exist in two forms depending upon the relative spatial orientation of the two Cl^- ligands (see **Table 6**). They can be at 90° to give the *cis* form, or at 180° to give the *trans* isomer.



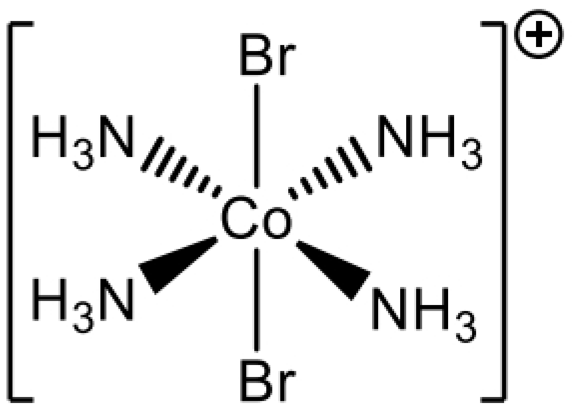
cis



trans



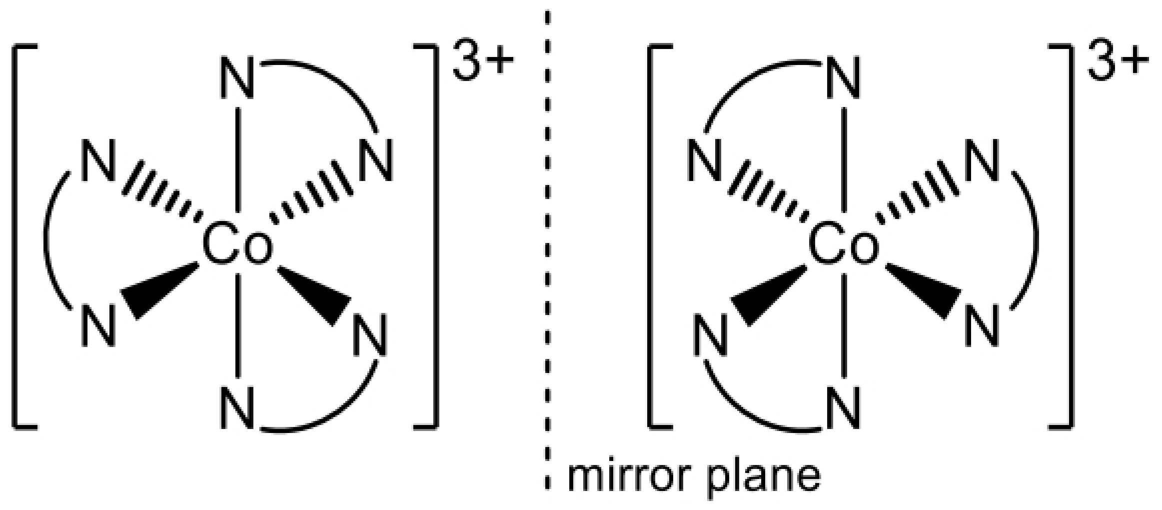
cis



trans

In six co-ordinate complex ions such as $[Co(NH_3)_4Br_2]^+$, a similar situation exists, in which the Br^- ligands adopt either a *cis* or a *trans* arrangement.

Enantiomerism: This type of isomerism arises most commonly when chelating ligands are present. If a molecule possesses neither a plane nor a centre of symmetry, it is usually ***chiral***. *Enantiomers* are non-superimposable mirror images. A typical example of a chiral complex is found when three chelating ligands are coordinated to an octahedral centre, as in the cation $[Co(en)_3]^{3+}$:



represents the ethylenediamine ligand (en), $H_2NCH_2CH_2NH_2$

Enantiomers rotate plane-polarised light in ***opposite direction***.

3.2.4 Nomenclature of Complexes

The naming of transition metal complexes takes a standard format, which consists of four components:

- Number of a certain ligand
- Name of ligand

} Can be repeated if there is more than one type of ligand in the complex, listed *alphabetically*

- Name of transition element
  - Cationic complex: Name of the metal is used
  - Anionic complex: Name of the metal is modified to end with *-ate*
- Oxidation state in roman numerals within round brackets

All the components are combined into one word as shown in the example below.

tetrachlorocuprate(II) : $[CuCl_4]^{2-}$

Number of ligands

di-	2
tri-	3
tetra-	4
penta-	5
hexa-	6

Type of ligands

H_2O	aqua
NH_3	ammine
CO	carbonyl
Cl^-	chloro
CN^-	cyano
OH^-	hydroxo
SCN^-	thiocyanato

Oxidation state of metal ion

Name of metal in anionic complex

Ti	titanate	Co	cobaltate
V	vanadate	Ni	nickelate
Cr	chromate	Cu	cuprate
Mn	manganate	Zn	zincate
Fe	ferrate		

Some common transition metal complexes:

(a) Hexacyanomanganate(IV) ion $[Mn(CN)_6]^{2-}$

(b) Potassium tetrachlorocuprate(II) $K_2[CuCl_4]$

(c) Tetraamminediaquacopper(II) sulfate $[Cu(NH_3)_4(H_2O)_2]SO_4$

(d) Pentaaquahydroxoiron(III) ion $[Fe(H_2O)_5(OH)]^{2+}$

(e) Tetracarbonylnickel(0) $Ni(CO)_4$

Self Check 3A

Name the following complexes.

$Pt(NH_3)_2Cl_2$	$[Ag(NH_3)_2]Br$	$[Cr(H_2O)_4Cl_2]Cl$

Checkpoint / Pen down own notes

- Definition of complexes; how complexes are formed.
- Definition of ligands; how ligands bond with metal ions; denticity; examples of ligands.
- Shapes of complexes; how isomerism can exist in some complexes.
- Proper naming of complex ions and salts.

LO **(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]

3.3 Colour of Transition Metal Ions and Complexes

Transition metal complexes and compounds are often coloured in both **solid** and **aqueous** states.

3.3.1 Crystal Field Theory – d orbital splitting

The Crystal Field Theory, first introduced by Bethe and Van Vleck, was extended mainly by Orgel to cover transition metal chemistry. It uses simple electrostatic consideration to explain how the energies of 3d orbitals are affected by the presence of surrounding ligands.

- In an isolated atom or ion, the five d orbitals are **degenerate** (have the same energy).

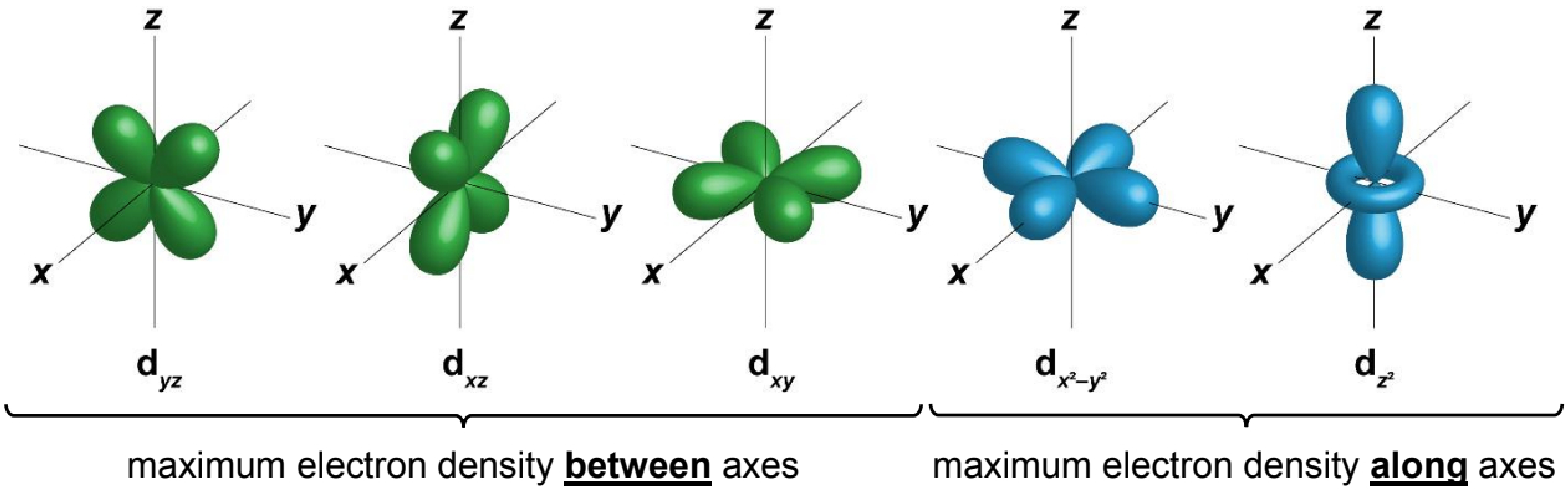


Figure 9 Shapes of the d orbitals in transition metal ions

- In an **octahedral** complex, the ligands are modelled as six **point negative charges** that surround the positively charged transition metal ion:

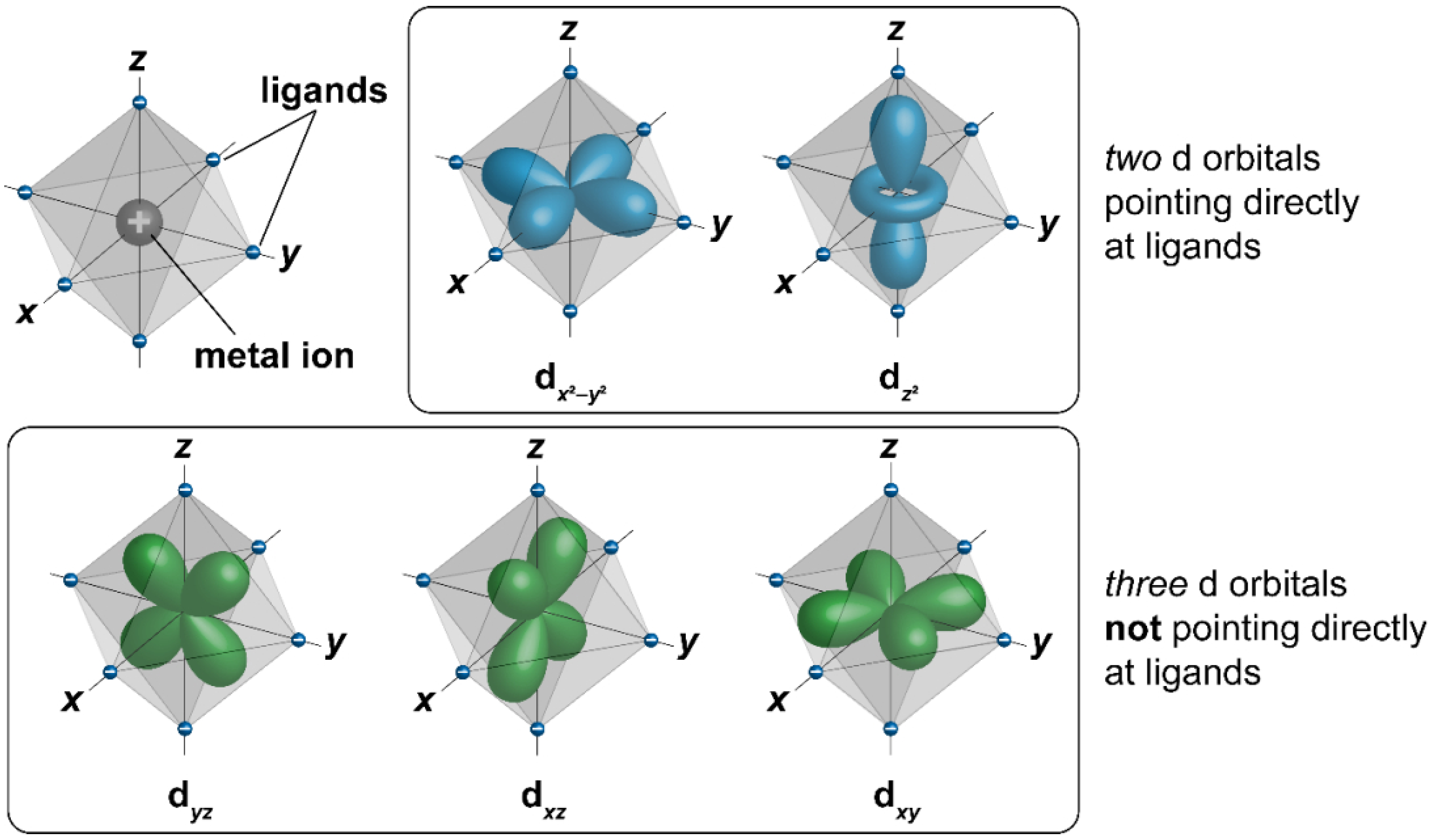


Figure 10 Interaction between the d orbitals and ligands in an octahedral complex

- Each ligand forms a **dative bond** with the transition metal ion *via* a lone pair of electrons along the ***x*, *y* and *z* axes**.
- When the ligands approach the transition metal ion along the *x*, *y*, and *z* axes, there is **inter-electronic repulsion between the lone pair of electrons from the donor atom of the ligand and the electrons in the d orbitals of the transition metal ion**. This causes the energies of these d electrons to increase to different extents.
- When ligands approach the *x*, *y* and *z* axes, the electrons in the $d_{x^2-y^2}$ and d_{z^2} orbitals will experience **greater repulsion** than those in the d_{xy}, d_{yz} and d_{xz} orbitals.
- Hence, the five d orbitals will be split into 2 energy levels – the d_{z^2} and $d_{x^2-y^2}$ orbitals at a **higher energy level** than the d_{xy}, d_{xz} and d_{yz} orbitals as shown in **Figure 11** below.

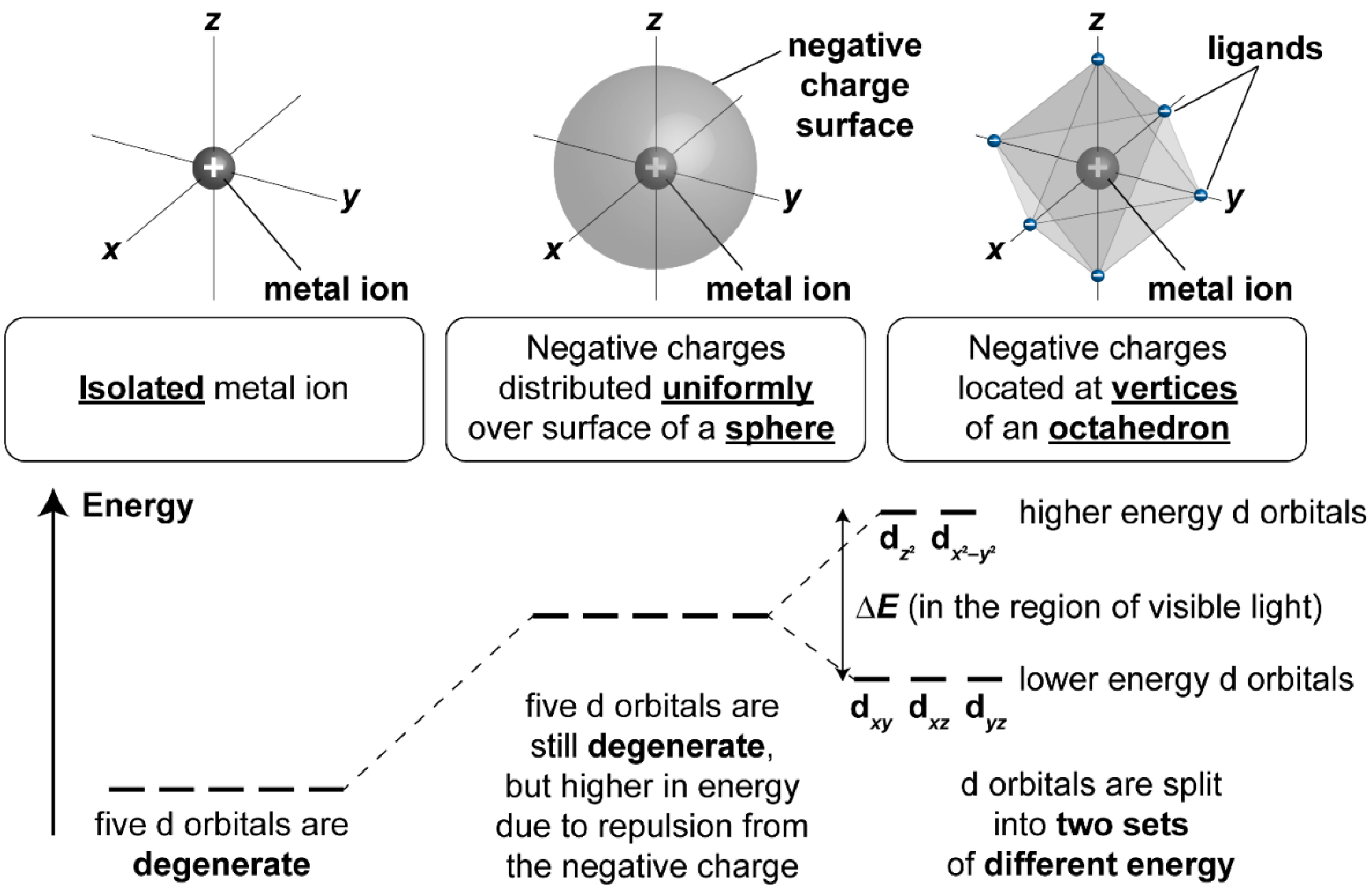
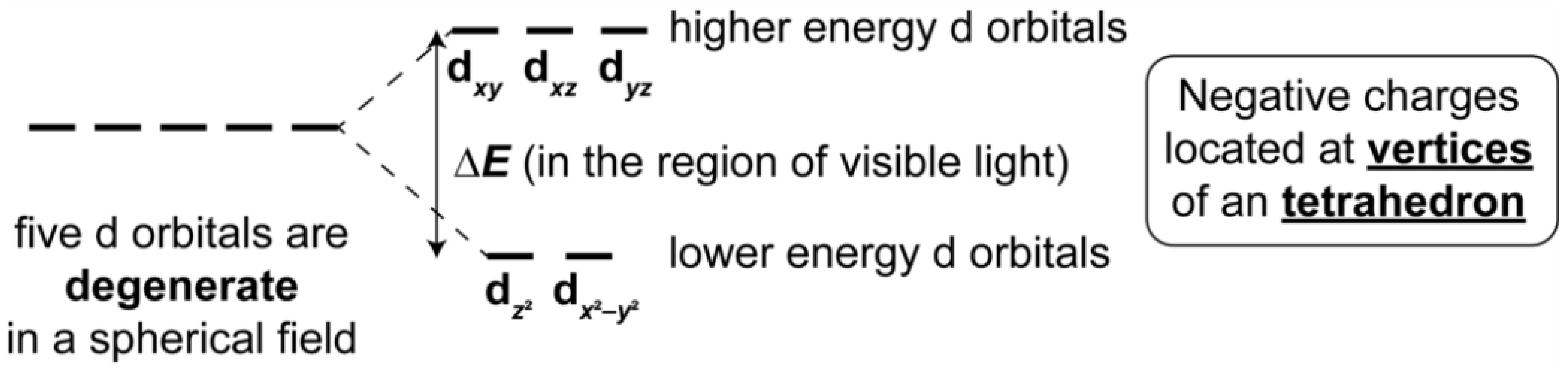


Figure 11 d orbitals splitting in the presence of ligands in an octahedral complex

It is this **splitting of the d orbitals** that helps to explain for the spectra (colour), stability and magnetic properties of transition metal complexes.

Note: (For Information Only)

In **tetrahedral** complexes, four ligands are arranged around the transition metal ion. As these ligands are arranged differently in space relative to the d orbitals, the splitting is different:



3.3.2 d-d Transition

The colours of transition metal complexes and compounds are due to **d-d transition**.

- In a complex, the presence of **ligands splits the d orbitals** of the transition metal atom or ion into **two different energy levels**. This is called d orbital splitting.
- An **electron in the lower energy d orbital absorbs certain wavelengths of light energy** from the **visible region of the electromagnetic spectrum**, and is **promoted to a higher energy d orbital**. This is called **d-d transition** (**Figure 12**).
- The **remaining wavelengths** are **transmitted** and the **complementary colour is observed**.

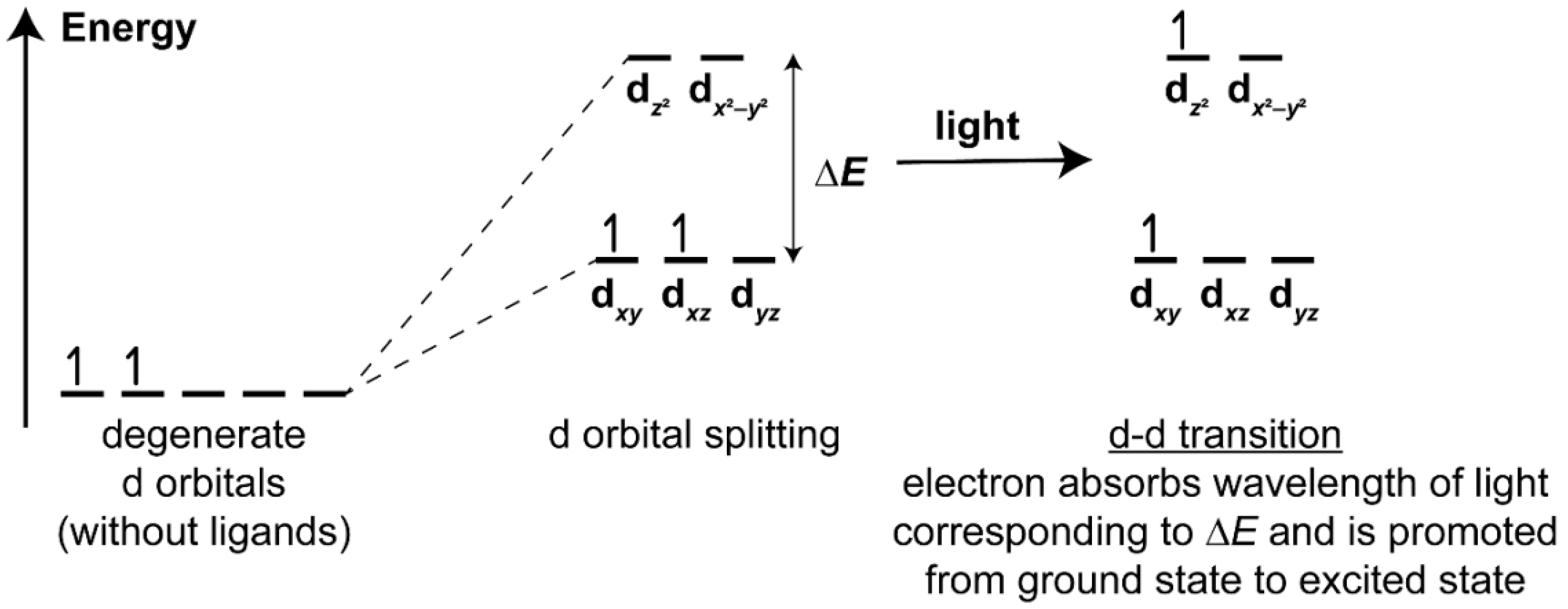


Figure 12 d-d transition

- For d-d transition to take place, at least one of the d orbitals must be occupied by an electron, and the d subshell must **not** be fully filled. Hence, complexes of Sc(III), Cu(I) and Zn(II) are **not coloured**.
  - Sc(III) has an electronic configuration of **[Ar]**.
    - The 3d orbitals are **empty** and there are **no electrons for d-d transition** to occur.
  - Cu(I) and Zn(II) have an electronic configuration of **[Ar] 3d^{10}**.
    - The 3d orbitals are **fully occupied** with electrons and it is **not possible for d-d transition** to occur.

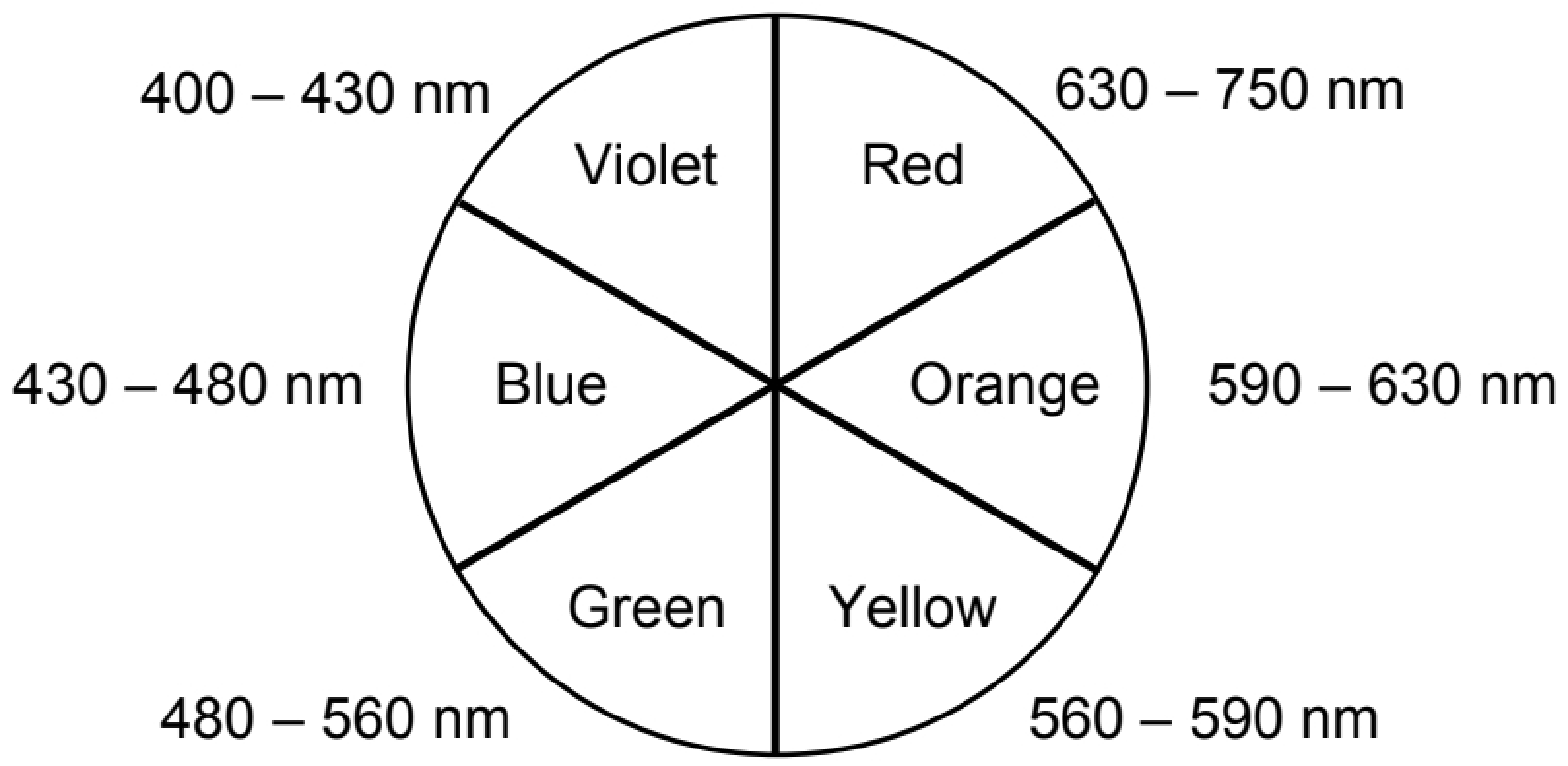
- d-d transition is not the only mechanism that gives rise to colours of transition metal complexes. There are some transition metal complexes which are intensely coloured in solution but possess *no d electrons*. *E.g.* $Mn^{VII}O_4^-$, $Cr^{VI}O_4^{2-}$, $V^{V}O_2^+$, $Cu^{I}I$, *etc.* The colours in these complexes arises due to the promotion of electrons from either metal-to-ligand or from ligand-to-metal, rather than between the d orbitals, known as charge-transfer.

3.3.3 Determination of Colours

The energy gap, ΔE, between the two groups of d orbitals determines the wavelength of visible light absorbed, λ:

$$\boxed{\Delta E \propto \frac{1}{\lambda}}$$

- For **large ΔE**: **short** λ absorbed, remaining λ transmitted, complementary colour observed.
- For **small ΔE**: **long** λ absorbed, remaining λ transmitted, complementary colour observed.
- The colour wheel below shows the wavelengths, λ, of different colours of light. **Complementary colours are opposite each other** in the colour wheel.



Example 3B

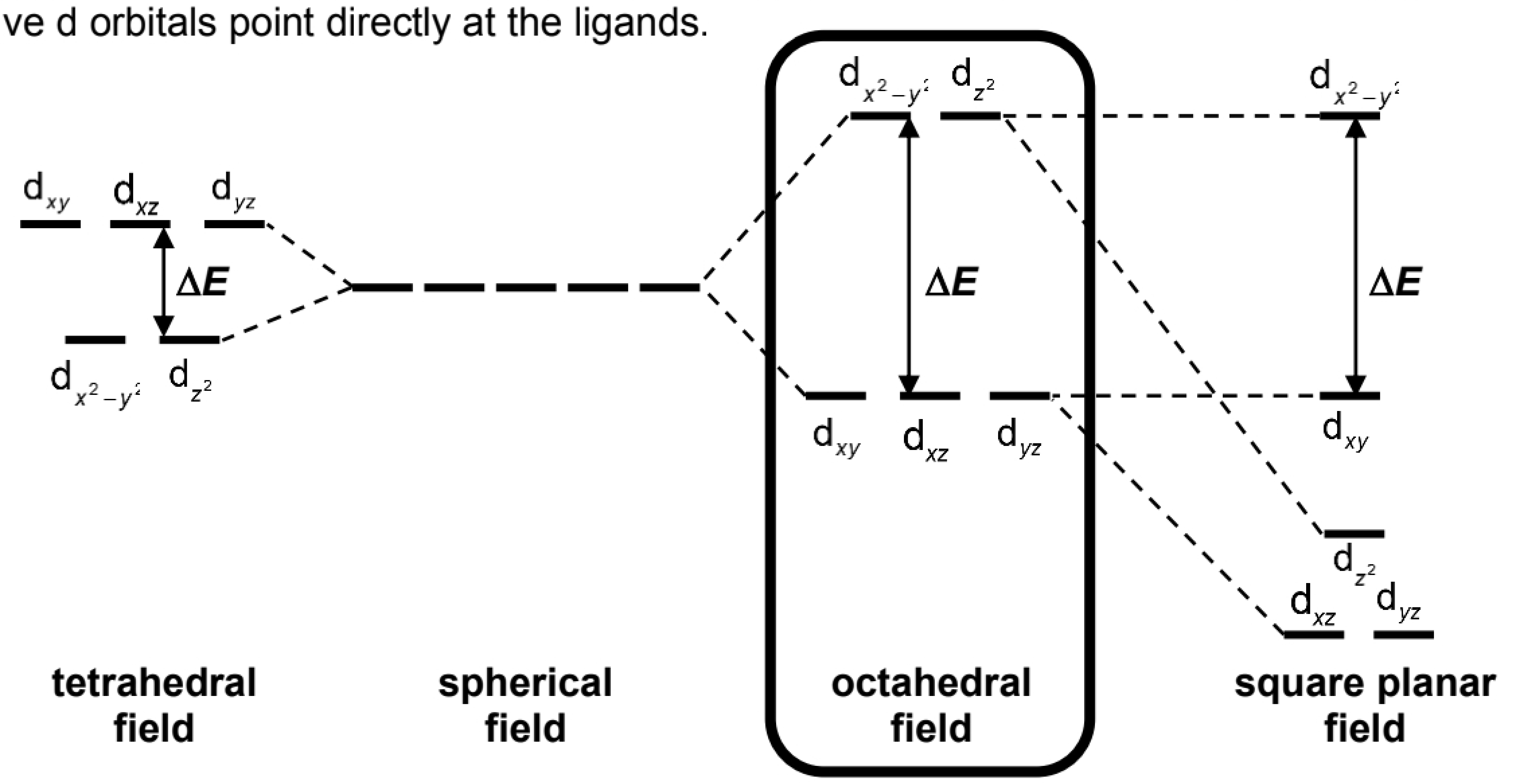
Explain why $[Cu(H_2O)_6]^{2+}$ solution is blue.

- Cu^{2+} has a ____________________.
- In $[Cu(H_2O)_6]^{2+}$, the presence of ____________ **the 3d orbitals of the Cu^{2+}** metal ion into ____________________.
- A ____________ **in the** ____________ **energy level absorbs light energy corresponding to the wavelengths for** ____________, and is **promoted to a** ____________ **energy 3d orbital** (d-d transition).
- The ____________ **wavelengths are transmitted** and the ____________ **colour** is observed.

3.3.4 Factors Affecting ΔE

The energy gap, ΔE, that results from the splitting of the d orbitals, depends on the following factors:

- **Identity of the transition metal and its oxidation state** (see **Table 2** on page 5) **(For your information)**
  - Generally, ΔE increases with oxidation state, which reflects the electrostatic nature of d orbital splitting. The higher the charge density of the metal ion, the stronger the attraction for the ligands, and hence the stronger the repulsion, leading to a larger ΔE.
    - *E.g.* $\left[Fe(H_2O)_6\right]^{2+}$ is pale green, absorbing lower energy red light, whereas $\left[Fe(H_2O)_6\right]^{3+}$ is pale violet, absorbing higher energy yellow light, corresponding to a larger ΔE.
  - For the same oxidation state, variation in ΔE across the first row transition elements is irregular.
    - $Mn^{3+} > Co^{3+} > Ti^{3+} > V^{3+} > Cr^{3+} > Fe^{3+} > Cr^{2+} > Cu^{2+} > V^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+} > Mn^{2+}$
- **Shape of the complex (For your information)**
  - The shape of the complex results in different *numbers* of ligands, *positioned differently* relative to the orientation of the d orbitals.
  - This results in different extent of the interactions between the lone pairs of electrons on ligands and the d orbitals, and thus different magnitudes of ΔE.
    - *E.g.* the extent of d orbital splitting, ΔE, in a tetrahedral complex is generally smaller than that in an octahedral complex, due to the lesser number of ligands and that none of the five d orbitals point directly at the ligands.



- **Nature of the ligands (crystal field)**
  - The magnitude of ΔE changes as the *strength of the repulsions* between d electrons and point charges changes. As such, ΔE thus measures the **strength** of the crystal field.
    - **Weak field** ligands ⇒ smaller ΔE (refer to **Appendix 4** on page 38)
    - **Strong field** ligands ⇒ larger ΔE

Spectrochemical series in order of increasing ΔE: **(for your information)**

$I^- < Br^- < Cl^- <$ **S**$CN^- < F^- < OH^- < C_2O_4^{2-} < O^{2-} < H_2O <$ **N**$CS^- < EDTA^{4-} < NH_3 <$ en $< CN^- < CO$

←

Weak field ligand results in **small ΔE and long λ absorbed**

→

Strong field ligand results in **large ΔE and short λ absorbed**

- **Different ligands** split the energy level of d orbitals to **different extent**.
- Known as the **spectrochemical series**, reflecting colour variations in chemical compounds of individual cations with different ligands.
- The order is difficult to rationalise fully in terms of electrostatic energies embodied in the simple point-charge model of crystal field theory. For example, why the charged O^{2-} anion precedes the polar H_2O molecule in the series.
- Crystal field theory qualitatively describes the strength of the metal-ligand bonds.
    - **Weak field** ligands ⇒ weaker metal-ligand bonds
    - **Strong field** ligands ⇒ stronger metal-ligand bonds

Table 7 Colours of some common complexes in solution

O.S. T.E	+1	+2	+3	+4	+5	+6	+7
V		$[V(H_2O)_6]^{2+}$ Violet	$[V(H_2O)_6]^{3+}$ Green	$[VO(H_2O)_5]^{2+}$ Blue	$[VO_2(H_2O)_4]^+$ Yellow		
Cr		$[Cr(H_2O)_6]^{2+}$ Blue	$[Cr(H_2O)_6]^{3+}$ Purple (usually appears **green** due to ligand exchange with Cl^-) $[Cr(OH)_6]^{3-}$ Dark Green $[Cr(NH_3)_6]^{3+}$ Purple			CrO_4^{2-} **Yellow** $Cr_2O_7^{2-}$ **Orange**	
Mn		$[Mn(H_2O)_6]^{2+}$ **Pale pink / colourless**	$[Mn(H_2O)_6]^{3+}$ Red	MnO_2 **Brown solid**	MnO_4^{3-} Deep blue	MnO_4^{2-} Dark green	MnO_4^- **Purple**
Fe		$[Fe(H_2O)_6]^{2+}$ **Pale green** $[Fe(CN)_6]^{4-}$ Yellow	$[Fe(H_2O)_6]^{3+}$ Violet (usually appears **yellow** due to hydrolysis) $[Fe(CN)_6]^{3-}$ Orange-red $[Fe(H_2O)_5(SCN)]^{2+}$ **Deep red**			FeO_4^{2-} Red-purple	

Co		$[Co(H_2O)_6]^{2+}$ Pink $[Co(NH_3)_6]^{2+}$ Pale brown $[CoCl_4]^{2-}$ Blue	$[Co(H_2O)_6]^{3+}$ Blue green $[Co(NH_3)_6]^{3+}$ Brown				
Ni		$[Ni(H_2O)_6]^{2+}$ Green $[Ni(NH_3)_6]^{2+}$ Blue $[Ni(CN)_6]^{4-}$ Yellow					
Cu	CuI **White** solid Cu_2O **Brick red** solid	$[Cu(H_2O)_6]^{2+}$ **Blue** $[Cu(NH_3)_4(H_2O)_2]^{2+}$ **Dark blue** $[CuCl_4]^{2-}$ **Yellow**					

Example 3C

Explain why a solution of $[Fe(H_2O)_6]^{2+}$ is pale green, while a solution of $[Fe(CN)_6]^{4-}$ is yellow.

- H_2O is a ________ ligand that causes **smaller d orbital splitting** resulting in a ________ΔE.
- ____________________ **of** ____________________ **wavelength** is **absorbed** and the ____ **colour** is **observed**.
- Thus, the solution of $[Fe(H_2O)_6]^{2+}$ appears pale green.
- CN^- is a ____________ ligand that causes **larger d orbital splitting** resulting in a________ΔE.
- ____________________ **of** ____________________ **wavelength** is **absorbed** and the ____ **colour** is **observed**.
- Thus, the solution of $[Fe(CN)_6]^{4-}$ appears yellow.

LO **(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

3.3.5 Ligand Exchange

In a complex ion, the ligand can be replaced by a different ligand. This is known as **ligand exchange**. As the nature of the ligand affects ΔE, a **change in colour** of the solution is usually seen.

There are two competing factors which can affect ligand exchange:

- **Strength of the Ligands**

  In the presence of **stronger** ligands, the **weaker** ligands in a complex ion are replaced by the stronger ligands. (Note: You do not need to know the relative order of the ligand strengths)

  E.g. hexaaquacopper(II) to tetraamminediaquacopper(II)

  When **aqueous NH_3** is added to the **light blue** $[Cu(H_2O)_6]^{2+}$ complex ion, a new complex ion, tetraamminediaquacopper(II), is formed, producing a **dark blue solution**. Below is the main equilibrium:

$$\underset{\textbf{light blue}}{\left[Cu(H_2O)_6\right]^{2+}}(aq) + 4NH_3(aq) \rightleftharpoons \underset{\textbf{dark blue}}{\left[Cu(NH_3)_4(H_2O)_2\right]^{2+}}(aq) + 4H_2O(l)$$

  - A **ligand exchange** reaction occurs.
  - When aqueous NH_3 is added, **$[NH_3]$ increases**, causing the position of equilibrium to shift to the **right** to form $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex.
  - The presence of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ cause the solution to appear dark blue.

  Since the formation of a complex is ***reversible***, it is possible to revert back to hexaaquacopper(II) by removing the NH_3 ligands *via* neutralisation using dilute sulfuric acid:

  - $H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2SO_4$
  - When sulfuric acid is added, **$[NH_3]$ decreases**, causing the position of equilibrium to shift to the **left** to reform $[Cu(H_2O)_6]^{2+}$.
  - The reformation of $[Cu(H_2O)_6]^{2+}$ cause the solution to turn light blue.

$$\underset{\textbf{light blue}}{\left[Cu(H_2O)_6\right]^{2+}}(aq) \underset{H_2SO_4(aq)}{\overset{NH_3(aq)}{\rightleftharpoons}} \underset{\textbf{dark blue}}{\left[Cu(NH_3)_4(H_2O)_2\right]^{2+}}(aq)$$

- **Concentration of the Ligands**

  In the presence of a **large concentration** of a different ligand, ligand exchange can occur for a complex ion.

  E.g. hexaaquacopper(II) to tetrachlorocuprate(II)

  When **concentrated solution of HCl** is added to the **light blue** $[Cu(H_2O)_6]^{2+}$ complex ion, a new complex ion, tetrachlorocuprate(II), is formed, producing a **green solution**.

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

  - A **ligand exchange** reaction occurs.
  - When concentrated HCl is added, **$[Cl^-]$ increases**, causing the position of equilibrium to shift to the **right** to form **$[CuCl_4]^{2-}$** complex.

- The presence of **<u>both blue $[Cu(H_2O)_6]^{2+}$ and yellow $[CuCl_4]^{2-}$</u>** causes the solution to appear yellow-green.

[***Important***: $[CuCl_4]^{2-}$ is NOT green but yellow in solution]

Since the formation of a complex is ***reversible***, it is possible to revert back to hexaaquacopper(II) by adding water to dilute the mixture:

- Since there are **<u>more concentration terms</u>** on the **<u>left hand side</u>** of the equilibrium, when the mixture is diluted, the position of equilibrium to shift to the **<u>left</u>** to reform $[Cu(H_2O)_6]^{2+}$.
- The reformation of $[Cu(H_2O)_6]^{2+}$ cause the solution to turn light blue.

$$\underset{\textbf{light blue}}{\left[Cu(H_2O)_6\right]^{2+}(aq)} \underset{H_2O}{\overset{\text{conc. HC}l}{\rightleftharpoons}} \underset{\textbf{yellow}}{\left[CuCl_4\right]^{2-}(aq)}$$

There are many examples in which a compound that is insoluble in water is 'solubilised' by conversion into a complex.

$$\underset{\textbf{green}}{Cr^{3+}(aq)} \xrightarrow{NaOH(aq)} \underset{\textbf{grey-green ppt}}{Cr(OH)_3(s)} \xrightarrow{\text{excess }NaOH(aq)} \underset{\textbf{dark green}}{\left[Cr(OH)_6\right]^{3-}(aq)}$$

$$\underset{\textbf{colourless}}{Zn^{2+}(aq)} \xrightarrow{NaOH(aq)} \underset{\textbf{white ppt}}{Zn(OH)_2(s)} \xrightarrow{\text{excess }NaOH(aq)} \underset{\textbf{colourless}}{\left[Zn(OH)_4\right]^{2-}(aq)}$$

$$\underset{\textbf{colourless}}{Zn^{2+}(aq)} \xrightarrow{NH_3(aq)} \underset{\textbf{white ppt}}{Zn(OH)_2(s)} \xrightarrow{\text{excess }NH_3(aq)} \underset{\textbf{colourless}}{\left[Zn(NH_3)_4\right]^{2+}(aq)}$$

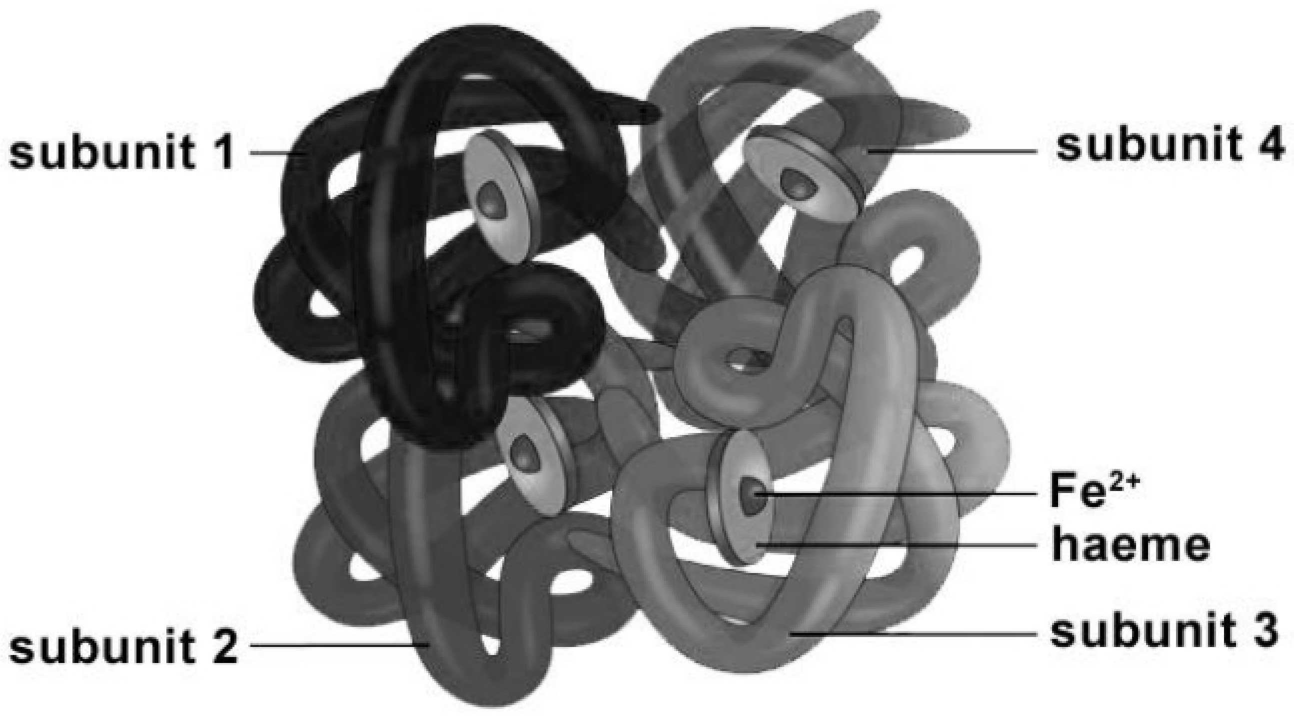
$$\underset{\textbf{light blue}}{Cu^{2+}(aq)} \xrightarrow{NH_3(aq)} \underset{\textbf{blue ppt}}{Cu(OH)_2(s)} \xrightarrow{\text{excess }NH_3(aq)} \underset{\textbf{dark blue}}{\left[Cu(NH_3)_4(H_2O)_2\right]^{2+}(aq)}$$

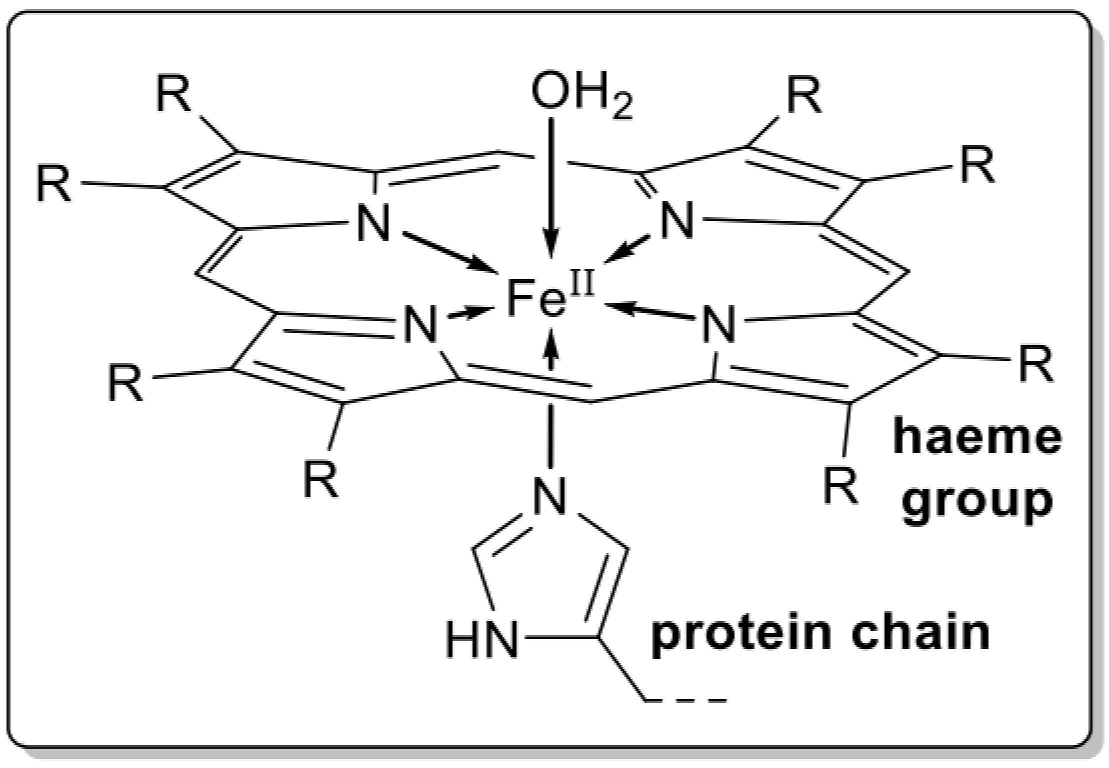
$$\underset{\textbf{pink}}{Co^{2+}(aq)} \xrightarrow{NH_3(aq)} \underset{\textbf{blue ppt}}{Co(OH)_2(s)} \xrightarrow{\text{excess }NH_3(aq)} \underset{\textbf{pale brown}}{\left[Co(NH_3)_6\right]^{2+}(aq)}$$

$$\underset{\textbf{green}}{Ni^{2+}(aq)} \xrightarrow{NH_3(aq)} \underset{\textbf{green ppt}}{Ni(OH)_2(s)} \xrightarrow{\text{excess }NH_3(aq)} \underset{\textbf{dark blue}}{\left[Ni(NH_3)_6\right]^{2+}(aq)}$$

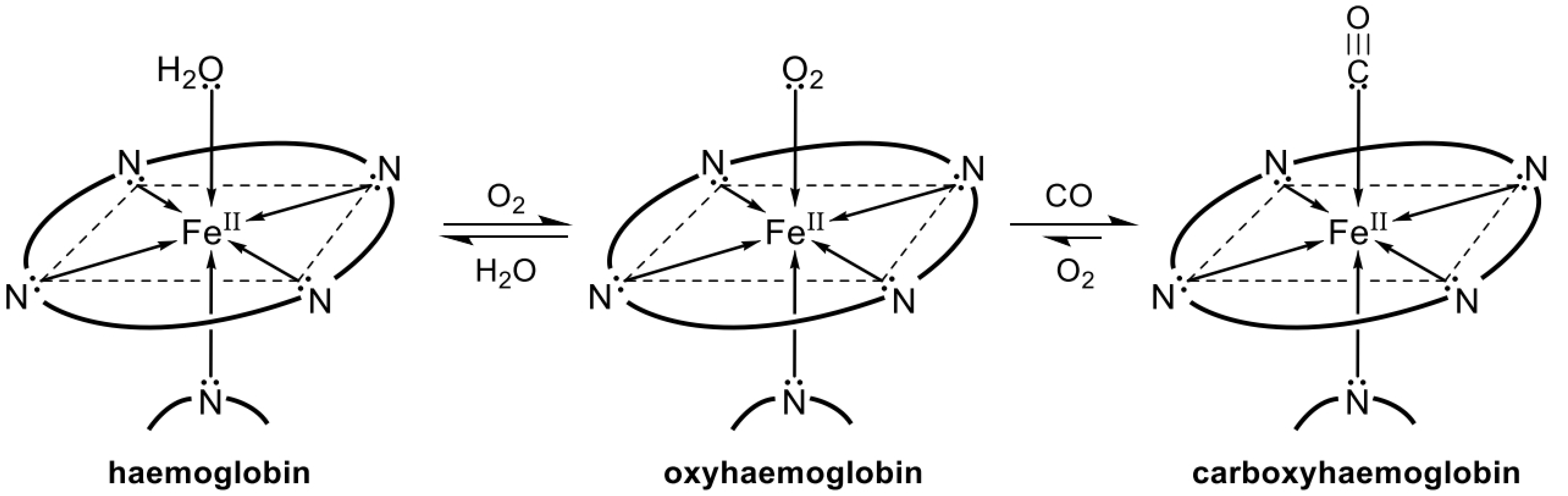
3.3.5.1 CO/O_2 Exchange in Haemoglobin

- In humans, haemoglobin molecule, the vital oxygen-carrying constituent of the blood, is an assembly of four protein subunits.
  - Each subunit is composed of a protein chain tightly associated with a non-protein prosthetic **haeme group**.
  - The haeme group contains **iron** in oxidation state **(II)**, and exhibits **hexaco-ordination**. Five of the co-ordination sites are occupied by nitrogen, four from the porphyrin ring system in the haeme group and the fifth from the protein.





- 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:



- Carbon monoxide binds to haemoglobin at the same sites as oxygen, but approximately **210 times** more tightly, to give **carboxyhaemoglobin**.
  - Normally, oxygen would bind to haemoglobin in the lungs and be released in areas with low oxygen partial pressure (*e.g.* active muscles). When carbon monoxide binds to haemoglobin, it cannot be released as easily as oxygen.
  - The slow release rate of carbon monoxide (half-life in the blood of 4 to 6 hours) causes an accumulation of carboxyhaemoglobin molecules as exposure to carbon monoxide continues. Because of this, fewer haemoglobin particles are available to bind and deliver oxygen, thus causing the **gradual suffocation** associated with carbon monoxide poisoning.
  - Conversion of most haemoglobin to carboxyhaemoglobin results in death – known medically as carboxyhemoglobinemia or **carbon monoxide poisoning**.
  - Smaller amounts carboxyhaemoglobin lead to oxygen deprivation of the body causing tiredness, dizziness, and unconsciousness.
- Ligand such as cyanide also **strongly** bind at this site which accounts for its toxic nature.

Example 3D

1 When dilute ammonia is gradually added to a solution containing copper(II) ions, a blue precipitate is formed, which re-dissolves on adding more dilute ammonia. Explain.

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

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

- When dilute NH_3 is added gradually, $[OH^-]$ increases.
- ____
- Blue precipitate of $Cu(OH)_2$ is formed.

$$\left[Cu(H_2O)_6\right]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons \underset{\text{dark blue}}{\left[Cu(NH_3)_4(H_2O)_2\right]^{2+}(aq)} + 4NH_3(l) \text{ -------- eqm (2)}$$

- When excess NH_3 is added, ________ ligands ________________ ligands from $[Cu(H_2O)_6]^{2+}$ to form the ______________________________ complex (eqm(2)).
- ________________ as it is used to form the complex.
- The equilibrium position in eqm (1) shifts to the ________________ to ________________ Thus, the blue precipitate dissolves.

2 When H_2O ligands in an aqua-complex of cobalt are replaced by other ligands, large changes in $E^\ominus$ values are observed. Comment on the oxidising power of the following cobalt(III) complexes.

$$[Co(H_2O)_6]^{3+}(aq) + e^- \rightleftharpoons [Co(H_2O)_6]^{2+} \qquad E^\ominus = +1.89V$$

$$[Co(NH_3)_6]^{3+}(aq) + e^- \rightleftharpoons [Co(NH_3)_6]^{2+} \qquad E^\ominus = +0.10V$$

$$[Co(CN)_6]^{3-}(aq) + e^- \rightleftharpoons [Co(CN)_6]^{4-} \qquad E^\ominus = -0.80V$$

From the $E^\ominus$ values, it can be seen that Co(III) is more stable compared to Co(II) in the presence of CN^- ligands, while Co(II) is more stable than Co(III) in the presence of H_2O ligands and marginally so in the presence of NH_3 ligands. This means that $[Co(H_2O)_6]^{3+}$ is a ______________________________ (capable of oxidising the solvent H_2O to O_2; $E^\ominus(O_2|H_2O) = +1.23V < +1.89V$), and $[Co(NH_3)_6]^{3+}$ is only ______________________, while $[Co(CN)_6]^{3-}$ is ________________ unless in the presence of a strong reducing agent $\left(E^\ominus < -0.80V\right)$.

Note:

1) In a complex with several ligands originally bonded to the metal centre, one, more than one or all ligands can be replaced in a ligand exchange reaction.
2) The coordination number of the metal centre can change after ligand exchange.
3) Strong and weak ligands are **<u>not the same</u>** as strong field and weak field ligands.

Checkpoint / Pen down own notes

- How colours of transition metal ions and complexes come about; d orbital splitting; d-d transitions; determination of colours.
- Relationship between the energy gap ΔE between the d-orbital splitting, the energy absorb and the colours of metal ions and complexes perceived.
- Factors that affect the energy gap ΔE between the d-orbital splitting: the type of transition metal and its oxidation state; the shape of the complex; the nature of the ligands involved.
- Ligand exchange – dependent on strengths of ligands; concentration of the ligands.
- Ligand exchange as exemplified by the CO/O2 exchange in the haemoglobin system.

LO **(m)** explain how some transition elements and/or their compounds can act as catalysts (see also Reaction Kinetics **8(j)**)

3.4 Catalytic Activity

Transition elements and their compounds are important catalysts. There are two types of catalysts that transition elements can form, namely:

- Heterogeneous catalysts
- Homogeneous catalysts

3.4.1 Heterogeneous Catalysis

- The **catalyst and reactants are in different physical phases**.
  - The catalyst is usually in the solid phase while the reactants are usually liquids or gases.
- For heterogeneous catalysis to occur, the reactant molecules **adsorbed** onto the **active sites** on its surface through the **formation of weak bonds between the reactant molecules and the surface catalyst atoms**.

Note: **Adsorption** is the **adhesion** of a substance to the surface of another substance

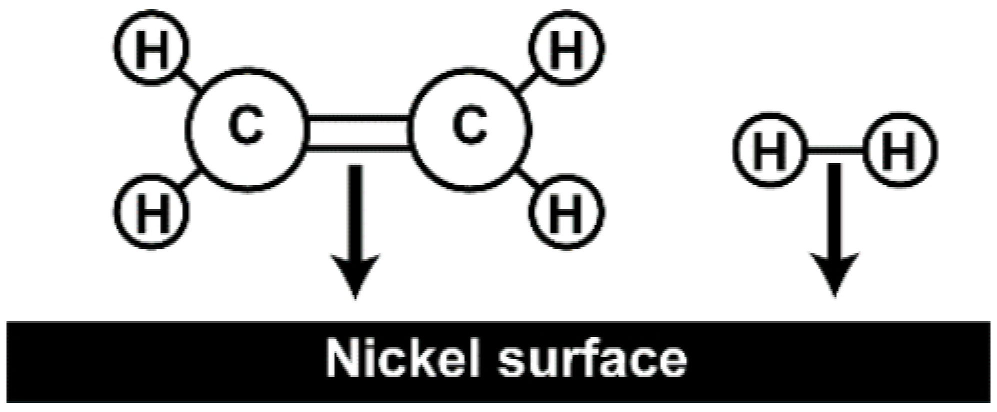
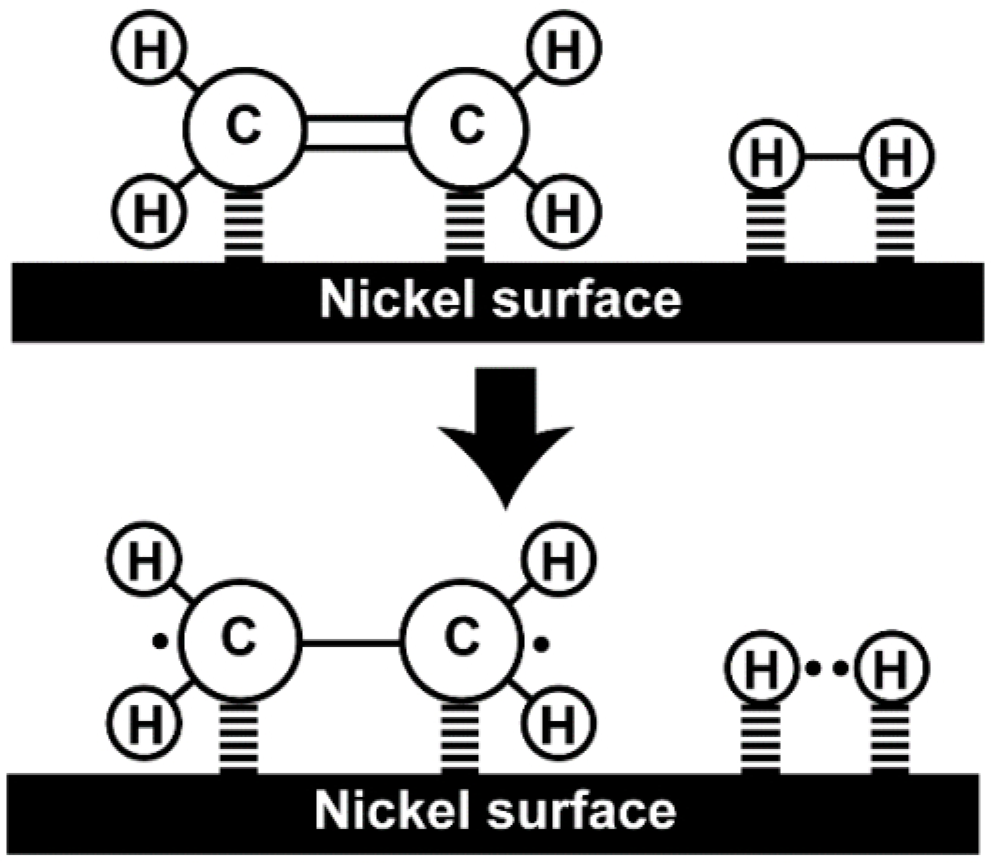
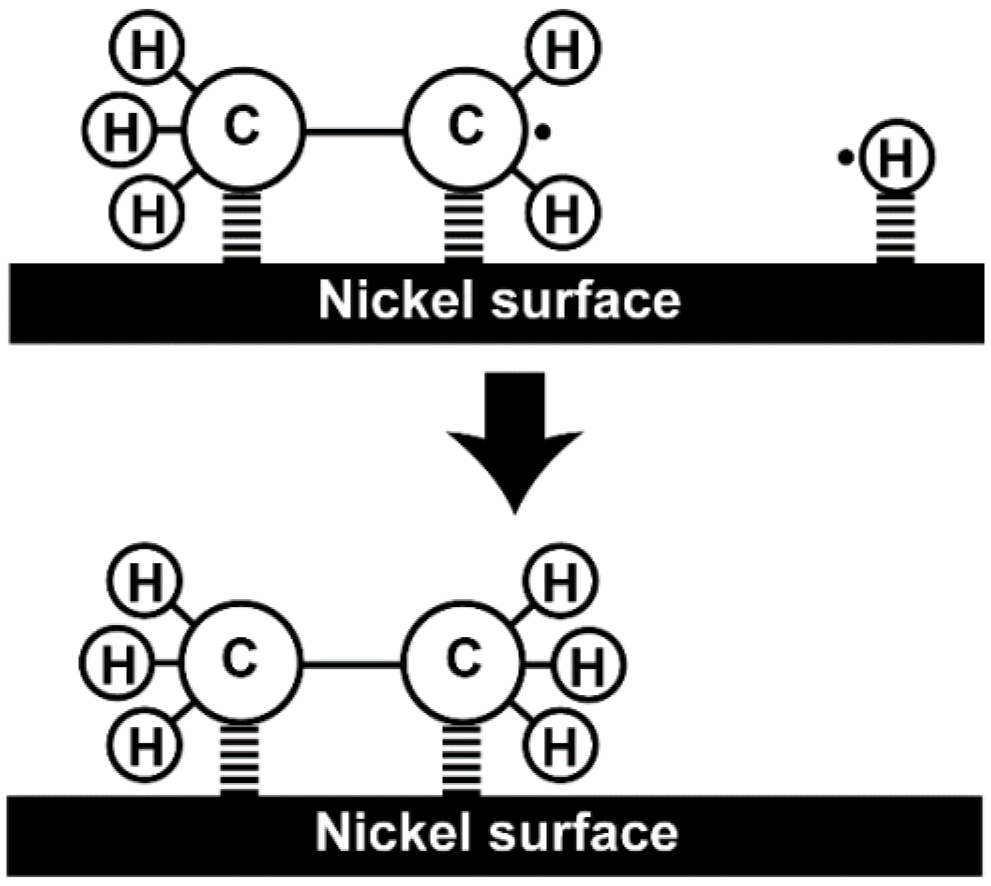
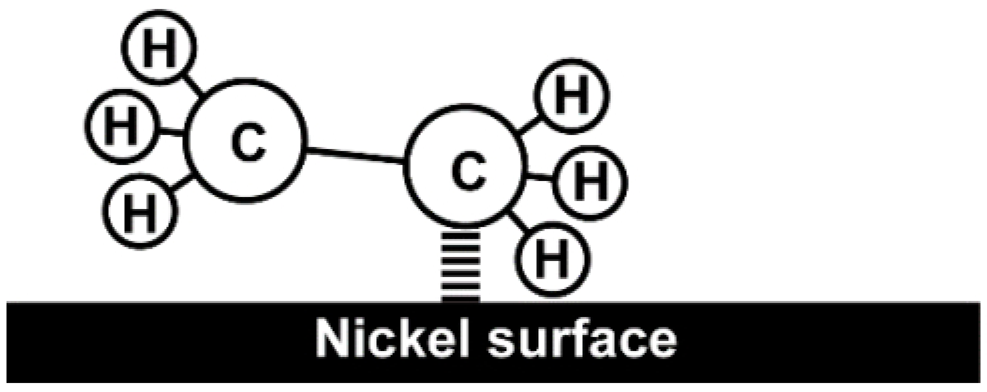
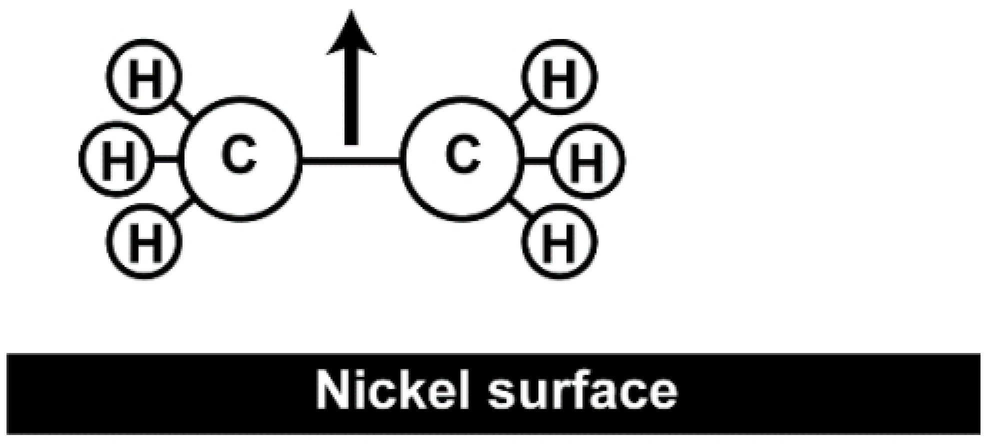
- **Adsorption weakens the covalent bonds within the reactant molecules**, thereby reducing the activation energy for the reaction.
- **Adsorption increases the concentration of the reactant molecules** at the catalyst surface and allows the reactant molecules to come into close contact with proper orientation for reaction.

Transition **metal and their ions** are effective heterogeneous catalysts because they have **partially filled 3d orbitals** which allows the reactant particles to be adsorbed onto the catalyst surface.

- The d electrons can be used to form bonds with the reactant molecules.
- Energetically accessible and available orbitals can be used to accommodate lone pairs of electrons from reactant molecules to form bonds.

E.g.: Hydrogenation of ethene catalysed by nickel metal

Adsorption Theory

Step 1: Diffusion Reactant molecules diffuse towards the solid catalyst surface.	Example: $CH_2{=}CH_2 + H_2 \rightarrow CH_3{-}CH_3$ 
Step 2: Adsorption These molecules physically adsorbed on solid catalyst surface by intermolecular forces of attraction. Chemical bonds are formed between molecules on the active sites, thereby weakening the bonds in the adsorbed reactant molecules.	
Step 3: Chemical Reaction Adjacent reactant molecules react to form products.	
Step 4: Desorption This is the reverse of adsorption. After the reaction, the adsorbed product molecules leave the nickel surface.	
Step 5: Diffusion The product molecules diffuse away from the surface.	

[Refer to Chemical Kinetics lecture notes for more examples of heterogeneous catalysts]

3.4.2 Homogeneous Catalysis

- The **catalyst and reactants are in the same physical phase,** either liquid or gaseous
- A **homogeneous** catalyst provides an alternative pathway with **lower activation energy** by **forming an intermediate** which is later consumed in the reaction.
- The **catalytic** activity of a homogeneous catalyst depends on its ability to exist in **variable oxidation states**.

> Transition metal ions are effective homogeneous catalysts because they can **exist in different oxidation states** and undergo conversion from one oxidation state to another oxidation state relatively easily.

Example 3E

(a) Explain why the oxidation of $I^-(aq)$ by $S_2O_8^{2-}(aq)$ needs to be catalysed using $Fe^{2+}(aq)$.

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

[R] $S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ $E^\ominus = +2.01V$

[O] $I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\ominus = +0.54V$

$E^\ominus_{cell} =$

- Due to the ________________________________, the reaction has ________________. Therefore, this reaction is ________________________ even though it is energetically favourable.
- $Fe^{2+}(aq)$ ions can be used as the ________________ for this reaction.
- The rate of the catalysed reaction is faster as activation energy is ________________ due to the mechanism involving ________________________________ each other.

(b) With the aid of the *Data Booklet*, show how $Fe^{2+}(aq)$ can be used to catalyse the reaction.

Step 1: Reaction of Fe^{2+} catalyst with $S_2O_8^{2-}$

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

[R] $S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ $E^\ominus = +2.01V$

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

$E^\ominus_{cell} =$.

Step 2: Regeneration of Fe^{2+} catalyst

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

[O] $I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\ominus = +0.54V$

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

$E^\ominus_{cell} =$

Example 3E (cont'd)

(c) Draw an energy profile diagram for both the catalysed and uncatalysed reaction.

(d) Using $E^\ominus$ values from the *Data Booklet*, suggest two other transition metal ions that could catalyse the reaction between $S_2O_8^{2-}$ and I^-.

Concept : **Choose other couples involving *<u>transition metal cations</u>* *with* $E^\ominus$ values <u>between 2.01V and 0.54V</u>**

Possible ions: Co^{2+} or Mn^{2+}

$$Co^{3+}(aq) + e^- \rightleftharpoons Co^{2+}(aq) \qquad E^\ominus = +1.89V$$

Step 1: **Co^{2+}** reacts with **$S_2O_8^{2-}$**

Equation 1 :

$E^\ominus_{cell} =$

Step 2: **Co^{3+}** reacts with **I^-**

Equation 2 :

$E^\ominus_{cell} =$

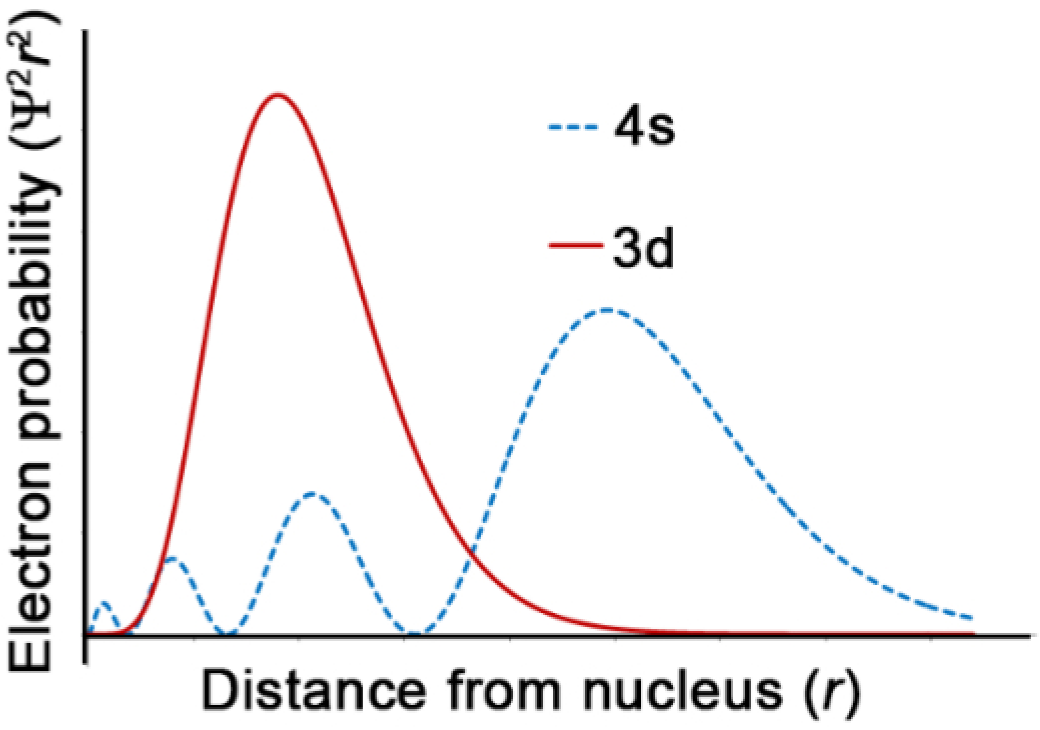
Overall equation :

Checkpoint / Pen down own notes

- How transition elements and their compounds can function as catalysts, as exemplified in heterogeneous and homogeneous catalysis – the role of partially filled 3d orbitals and the variable oxidation states of transition metal ions.

APPENDIX

Appendix 1 – Filling of 3d versus 4s orbital



The most probable distance of a 3d electron from the nucleus is less than that for a 4s electron, *i.e.* the 3d electrons are more likely to be found closer to the nucleus, so two 3d electrons repel each other more strongly than two 4s electrons.

In other words, because the 3d subshell is rather compact, in contrast to the diffuse 4s orbital, the electron repulsion in the d subshell increases strongly with increasing d occupation.

Hence, Sc has the configuration [Ar] $3d^1$ $4s^2$ rather than the two alternatives, [Ar] $3d^3$ or [Ar] $3d^2$ $4s^1$, for then the strong inter-electronic repulsions in the 3d orbitals are minimised.

The total energy of the atom is least despite the cost of allowing electrons to populate the higher energy 4s orbital.

Appendix 2 – Stability of Half-filled and Fully-filled d Subshell

The Pauli exclusion principle, a rule, complementary to the aufbau principle, of building up the electronic configuration of atoms and molecules state that a maximum of two electrons can occupy an orbital and then only providing that the spins of the electrons are paired, *i.e.* opposed. Hence, there is zero probability of finding two electrons with parallel spin at the same distance from the nucleus, while there is a higher probability of finding two spin-paired electrons.

Electrons with parallel spins do not physically repel each other any more (or less) than electrons with paired spins. But the mutual avoidance can be predicted to have two effects on the energy of the system:

- the electrostatic repulsion between parallel-spin electrons should be reduced, and
- each electron in a parallel-spin assembly is shielded from the nucleus less by its neighbours than is the case with paired electrons.

Each of these effects helps to stabilise a collection of electrons whose spins are parallel, conferring extra stability to a half- and fully-filled 3d subshell.

Appendix 3 – Variation in atomic radius across the d block elements

Although the atomic radius of the d block elements are relatively invariant, on a closer look, the atomic radius *initially decreases*, then *remains constant*, and *finally increases* at the end.

The overall trend can be explained based on two factors, namely the nuclear attractions and inter-electronic repulsions of the 3d electrons (shielding), where former results in a decrease in atomic radii and the latter an increase in atomic radii. From Sc to Zn, the nuclear charge increases while electrons are entering the penultimate 3d orbitals:

- Initially (Sc to V), the low shielding power of the 3d orbital, coupled with the small number of 3d electrons, means that the increase in nuclear charge is more significant than the shielding by the 3d electrons, resulting in a decrease in atomic radii.
- In the middle (V to Ni), as explained in **Appendix 1**, electron repulsion in the d subshell increases strongly with increasing d occupation. Hence, increase in shielding from the electron repulsion as

more 3d electrons are being added, offset the increase in nuclear charge, resulting in invariance in atomic radii.

- Towards the end (Ni to Zn), as the number of inner 3d elections increases further, shielding from the electronic repulsion becomes more dominant, resulting in an increase in the atomic radii.

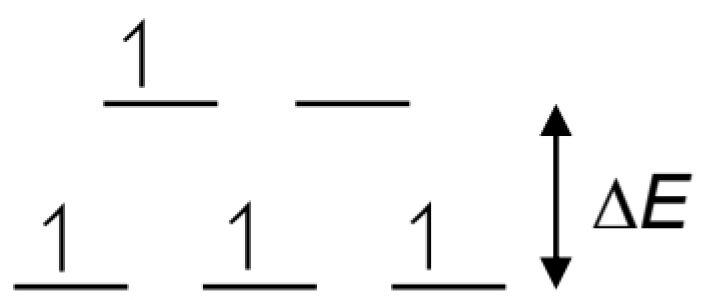
Appendix 4 – Ligand Field Strength, Pairing and Hund's Rule

Consider transition metal complexes having one, two and three d-electrons, which fill the degenerate d_{xy}, d_{xz} and d_{yz} orbitals singly. The spins align parallel according to Hund's rule, giving the lowest energy state.

For transitional metal complexes with four d-electrons, the situation is more complicated. Now we can have a **high spin** configuration in which all the electrons are unpaired, or a **low spin** configuration in which two of the electrons are paired.

Putting two electrons in the same orbital gives rise to an energy penalty known as the **pairing energy**, **P**, resulting from the electrostatic repulsion between electrons. Whether a high spin or a low spin configuration is adopted, depends on the relative magnitude of the energy gap, ΔE, and the pairing energy, P, for the complex:

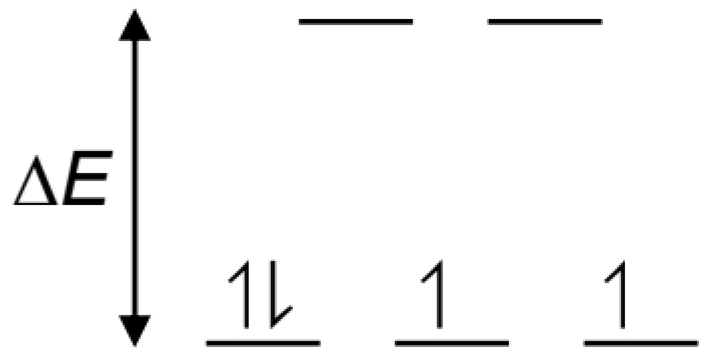
high spin



ΔE < P

Weak field ligands

low spin



ΔE > P

Strong field ligands

Ligands that result in a *small d orbital splitting*, *i.e.* small ΔE, give rise to *high spin* complexes are said to be **weak field ligands**, while those that result in a *large d orbital splitting*, *i.e.* large ΔE, give rise to low spin complexes are said to be **strong field ligands**.

Appendix 5 – Complex Stability Constant, K_{stab}

Whether a ligand is able to replace another ligand in a reaction depends on the complexation stability constant (K_{stab}) of the equilibrium reaction.

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

K_{stab} is essentially the *equilibrium constant* for the reaction.

$$K_{\text{stab}} = \frac{\left[\text{Ni}(\text{NH}_3)_6^{2+}\right]}{\left[\text{Ni}(\text{H}_2\text{O})_6^{2+}\right]\left[\text{NH}_3\right]^6}$$

The value of K_{stab} for this equilibrium is 5×10^7 mol^{-6} dm^{18}, which is very large. This shows that

- The position of the 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 bond with Ni^{2+} than H_2O