Nanyang Junior College
Chemistry (9729)

Lecture Notes 20
An Introduction to the Chemistry of Transition Elements

H2

Lecturer: Ms Theresia Line Ishak **JC2/2025**

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 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

References

Peter Cann and Peter Hughes. (2002). *Chemistry for Advanced Level* (pp. 563-581). John Murray (Publishers) Ltd

1. INTRODUCTION

Our study focuses on the **first row** of the transition elements (in Period 4).

Group																	
1	2											13	14	15	16	17	18
							1 H hydrogen 1.0										2 He helium 4.0
3 Li lithium 6.9	4 Be beryllium 9.0	Key: atomic number / atomic symbol / name / relative atomic mass										5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0	10 Ne neon 20.2
11 Na sodium 23.0	12 Mg magnesium 24.3	**d block elements**										13 Al aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 Cl chlorine 35.5	18 Ar argon 39.9
		3	4	5	6	7	8	9	10	11	12						
19 K potassium 39.1	20 Ca calcium 40.1	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4	31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8
37 Rb rubidium 85.5	38 Sr strontium 87.6	39 Y yttrium 88.9	40 Zr zirconium 91.2	41 Nb niobium 92.9	42 Mo molybdenum 95.9	43 Tc technetium –	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57–71 anthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium –	85 At astatine –	86 Rn radon –
87 Fr francium –	88 Ra radium –	89–103 actinoids	104 Rf rutherfordium –	105 Db dubnium –	106 Sg seaborgium –	107 Bh bohrium –	108 Hs hassium –	109 Mt meitnerium –	110 Ds darmstadtium –	111 Rg roentgenium –	112 Cn copernicium –		114 Fl flerovium –		116 Lv livermorium –		
lanthanoids		57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium –	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0	
actinoids		89 Ac actinium –	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium –	94 Pu plutonium –	95 Am americium –	96 Cm curium –	97 Bk berkelium –	98 Cf californium –	99 Es einsteinium –	100 Fm fermium –	101 Md mendelevium –	102 No nobelium –	103 Lr lawrencium –	

1.1 Electronic Configuration

- Apply Hund's Rule, Aufbau's Rule and Pauli's Exclusion Principle when filling electrons into the orbitals. (Refer to Atomic Structure Lecture Notes)

- The **4s** subshell is filled with electrons first **before** the **3d** subshell.

  Reason: The **empty** 4s subshell has a lower energy than the 3d subshell.

  Example: $_{21}Sc$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$
  $_{22}Ti$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
  $_{23}V$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$

  Note that even though we fill 4s subshell with electrons before 3d subshell, **we write 3d first, then 4s**.

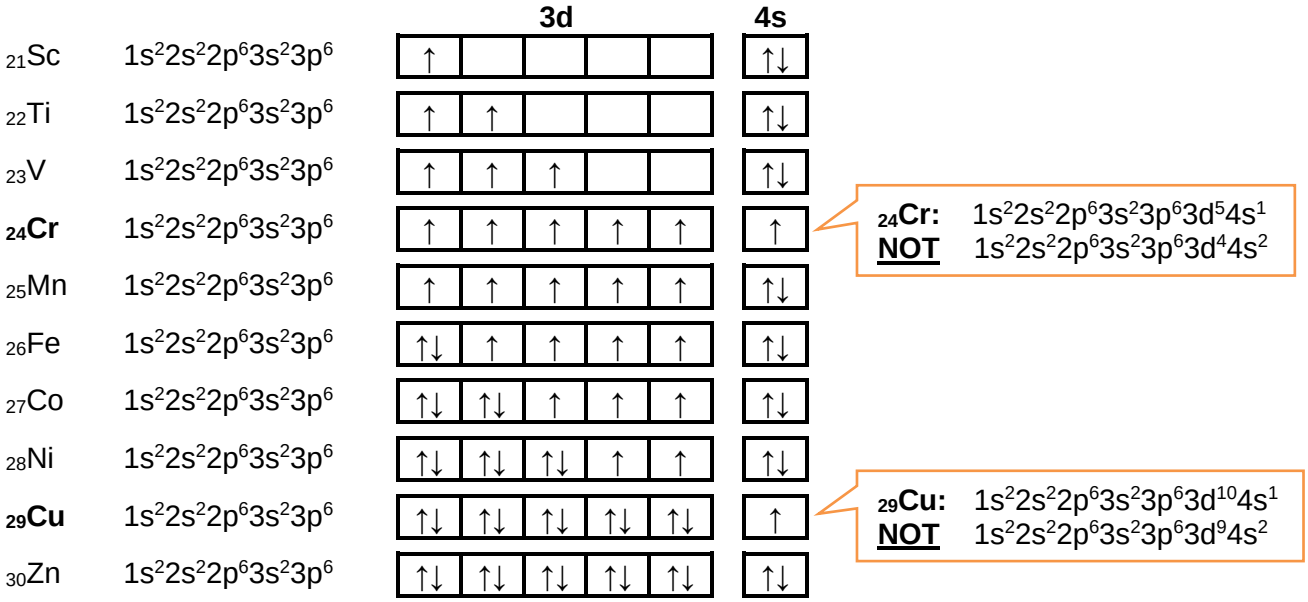
- **Exception: Cr and Cu**

  $_{24}Cr$: $[Ar]3d^5 4s^1$ ✓ **NOT** $[Ar]3d^4 4s^2$ ✗
  $_{29}Cu$: $[Ar]3d^{10} 4s^1$ ✓ **NOT** $[Ar]3d^9 4s^2$ ✗

  Reason: An exactly half-filled or completely filled d subshell is more favoured than a partially filled d subshell.

  When exactly half-filled or fully filled, the **distribution of electron density is more symmetrical around the nucleus**. This is more stable compared to the partially filled d subshell.

- Electronic configuration of d-block elements



- Electronic configuration of d-block cations

When we write the electronic configuration of d-block cations, we first write the electronic configuration of the **neutral atom**, then we **remove electrons from the 4s subshell**, followed by the 3d subshell.

Example: $_{22}Ti$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$ ⟹ $_{22}Ti^{2+}$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$

$_{23}V$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$ ⟹ $_{23}V^{2+}$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$

$_{24}Cr$: $[Ar]3d^5 4s^1$ ⟹ $_{24}Cr^{3+}$: $[Ar]3d^3$

$_{29}Cu$: $[Ar]3d^{10} 4s^1$ ⟹ $_{29}Cu^{2+}$: $[Ar]3d^9$

Example 1

(a) Complete the following to show the ground state electronic configuration of the following ions.

(i) Ti^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6$ $3d^1$

(ii) Ni^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6$ $3d^8$

(iii) Cr^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6$ $3d^3$

(b) What is the charge of the following ions?

(i) a cobalt ion with d^6 configuration: 3+

(ii) an iron ion with d^6 configuration: 2+

(c) Which of the following species does not have either a half-filled or a fully filled 3d subshell?

A Zn **B** Mn^{2+} **C** Fe^{3+} **D** Co

1.2 Definition of Transition Element

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

- Example: Fe is a transition element.

  Fe can form Fe^{2+} and Fe^{3+}, which are stable ions with a partially filled d-subshell.

  $_{26}Fe^{2+}$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$
  $_{26}Fe^{3+}$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

- **Sc and Zn** are **NOT** transition elements (even though they are in the d-block). Compounds of Sc and Zn do not show the characteristic properties of transition metals.

  Reason: **Sc** forms only one stable ion, Sc^{3+} that has no electrons in the 3d subshell.

  $_{21}Sc$: $[Ar]3d^1 4s^2$ $_{21}Sc^{3+}$: $[Ar]$ ► empty 3d subshell

  Zn forms only one stable ion, Zn^{2+} that has a fully filled 3d subshell.

  $_{30}Zn$: $[Ar]3d^{10} 4s^2$ $_{30}Zn^{2+}$: $[Ar]3d^{10}$ ► fully filled 3d subshell

- Hence, the first transition metal series consists of Ti to Cu in the first row of the d-block.

Example 2

Element X has 29 electrons and forms ions with 1+ and 2+ charge.

Write the electronic configuration of X^+ and X^{2+} and explain if element X is a transition element.

X^+ : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

X^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$

Note that element X is Cu.
$_{29}Cu$: $[Ar]3d^{10} 4s^1$

Answer:

Element X is a transition element as X can form 2 stable ions and X^{2+} has a partially filled 3d subshell.

2. PHYSICAL PROPERTIES

Across the d-block, the elements have similar physical properties, but they show **significant differences from s-block elements** such as Ca. The d-block elements are harder, have higher densities and have higher melting points.

2.1 Comparison across Transition Elements

(a) First Ionisation Energies

$$M(g) \rightarrow M^+(g) + e^-$$

	Across Transition Elements	**Across Period 3 Elements**
Trend	Relatively invariant	Generally increase
Explanation	• From Sc to Cu, as number of protons increases, nuclear charge increases. • Each additional electron is added to the penultimate 3d subshell. Shielding effect increases as the presence of 3d orbitals shield the 4s electrons from the nuclear attraction. • Hence, effective nuclear charge remains almost constant (only increases very slightly). • Attraction between the nucleus and the outermost electron remains almost constant. • Energy required to remove the outermost 4s electron is relatively invariant.	• As number of protons increases, nuclear charge increases. • As successive electrons are added to the same outermost shell, shielding effect remains approximately the same. • Hence, effective nuclear charge increases and attraction between the nucleus and outermost electron increases. • More energy is required to remove the outermost electron. • Exceptions: - ns^2 vs ns^2 np^1 configuration - ns^2 np^3 vs ns^2 np^4 configuration

(b) Atomic Radii

	Across Transition Elements	**Across Period 3 Elements**
Trend	Relatively invariant	Decreases
Explanation	• From Sc to Cu, as number of protons increases, nuclear charge increases. • Each additional electron is added to the penultimate 3d subshell. Shielding effect increases as the presence of 3d orbitals shield the 4s electrons from the nuclear attraction. • Hence, effective nuclear charge remains almost constant (only increases very slightly). • Attraction between the nucleus and the outermost shell remains almost constant. • Thus, the transition elements have similar atomic radius.	• As number of protons increases, nuclear charge increases. • As successive electrons are added to the same outermost shell, shielding effect remains approximately the same. • Hence effective nuclear charge increases. • The outermost shell is attracted more closely towards the nucleus and atomic radius decreases across a period.

(c) Ionic Radii (FYI)

	Across Transition Elements	**Across Period 3 Elements**
Trend	Relatively invariant	Decreases
Explanation	M^{2+} and M^{3+} ions are formed with electrons removed from the outermost shell (4s and 3d subshell).	Na^{+}, Mg^{2+}, Al^{3+} and Si^{4+} are isoelectronic. P^{3-}, S^{2-} and Cl^{-} are isoelectronic.
	• Across the d-block, as number of protons increases, nuclear charge increases. • For the 2+ and 3+ ions, there are no more 4s electrons. Hence, the 3d electrons are the outermost electron. Shielding effect remains approximately constant across the d-block elements. • Effective nuclear charge only increases very slightly. • Thus, transition metal ions of the same charge are similar in size (only decreases very slightly across the period).	Within each isoelectronic series, • As number of protons increases, nuclear charge increases. • As the species are isoelectronic, shielding effect remains the same. • Hence effective nuclear charge increases. • The outermost shell is attracted more closely towards the nucleus, and the ionic radius decreases across the isoelectronic series.

2.2 Comparison between Transition Elements and s-block Elements

(a) Density

	Transition Elements	**s-block Elements (e.g. calcium)**
Trend	High	Low
Explanation	• Higher relative atomic mass compared to the s-block elements. • Smaller atomic radius, hence the atoms have a smaller volume. • This results in transition elements having a larger mass per unit volume.	• Lower relative atomic mass compared to the transition elements. • Larger atomic radius, hence the atoms have a larger volume. • This results in s-block elements having a smaller mass per unit volume.

(b) Melting Point

	Transition Elements	**s-block Elements (e.g. calcium)**
Trend	Higher than s-block elements	Generally low
Explanation	• The 3d and 4s electrons are close in energies and are available to contribute to the sea of delocalised electrons around the metal cations, resulting in stronger metallic bonding. • More energy is required to break the stronger metallic bonds.	• Only two valence electrons are delocalised around the metal cations, resulting in weaker metallic bonding. • Less energy is required to break the weaker metallic bonds.

(c) Electrical Conductivity (FYI)

	Transition Elements	s-block Elements (e.g. calcium)
Trend	Higher than s-block elements	Low
Explanation	• The 3d and 4s electrons are close in energies and are available to contribute to the sea of delocalised electrons around the metal cations. • More mobile charge carriers are present.	• Only two valence electrons are delocalised around the metal cations. • Less mobile charge carriers are present.

(d) Atomic Radii (FYI)

	Transition Elements	s-block Elements (e.g. calcium)
Trend	Smaller than s-block elements	Larger than transition elements
Explanation	• From Ca to Sc, number of protons increases. Hence, nuclear charge increases. • In Sc, the additional electron is added to the penultimate 3d subshell. Since the shielding provided by the inner d electrons is less efficient than s and p electrons, • there is an increase in effective nuclear charge. • The outermost shell in Sc is attracted more closely towards the nucleus compared to the outermost shell in Ca. *(For the same quantum shell, s electrons provide the best shielding: s > p > d > f. This is because the s electron has more density near the nucleus of an atom than a p electron.)*	

Example 3

The following data refer to copper as a typical transition element and to calcium as an s-block element.

For which property are the data under the correct element?

	Property	*copper*	*calcium*
A	Density (g cm^{-3})	8.92	1.54
B	Electrical conductivity (MS m^{-1})	50	80
C	Melting point (^oC)	810	1083
D	Metallic radius (nm)	0.197	0.117

3. CHEMICAL PROPERTIES

The transition elements and their compounds display chemical behaviour that differs from the s-block elements and their compounds.

The characteristic properties of transition metals are:
1) Variable Oxidation States
2) Catalytic Properties
3) Complex Ion Formation
4) Formation of Coloured Compounds and Ions

3.1 Variable Oxidation States

Oxidation numbers of the elements from Sc to Zn

Sc $3d^14s^2$	**Ti $3d^24s^2$**	**V $3d^34s^2$**	**Cr $3d^54s^1$**	**Mn $3d^54s^2$**	**Fe $3d^64s^2$**	**Co $3d^74s^2$**	**Ni $3d^84s^2$**	**Cu $3d^{10}4s^1$**	**Zn $3d^{10}4s^2$**
	+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					

Those in **bold** represent the oxidation numbers that are more common

- From Sc to Mn, there is an increase in the number of oxidation states exhibited by the elements. From Mn to Zn, there is a decrease in the number of oxidation states exhibited by the elements.

- Electrons in the d orbitals start to pair up after Mn ($3d^5$).
  Thus, the number of unpaired d electrons available for bonding decreases.

- **Maximum oxidation state = number of 4s electrons + unpaired 3d electrons**
  (*exception: Cu)

3.1.1 Comparing Oxidation States of Transition Elements with s-block Elements

❖ *S-block elements have fixed oxidation states that correspond to their group numbers*

This is because once the outermost electrons in the s orbitals are removed, subsequent removal of the electrons will be from the inner quantum shell that requires a large amount of energy and hence is not favoured.

Element	**Electronic Configuration**	**Ionisation Energies / kJ mol^{-1}**			
		1st	**2nd**	**3rd**	**4th**
K	$1s^22s^22p^63s^23p^64s^1$	418	3070	4600	5860
Ca	$1s^22s^22p^63s^23p^64s^2$	590	1150	4940	6480
V	$1s^22s^22p^63s^23p^63d^34s^2$	648	1370	2870	4600

❖ *Transition elements have variable oxidation states*

This is due to the similarity in the energies of the 3d and 4s electrons. Once the 4s electrons are removed, some or all the 3d electrons may also be removed or shared without requiring much more energy. Therefore, different number of electrons from the 4s and 3d subshells can be used for bonding to form stable compounds (ionic or covalent).

e.g.

Fe^{2+} (+2) Fe^{3+} (+3)	Cr^{3+} (+3) $Cr_2O_7^{2-}$ (+6)	Mn^{2+} (+2) MnO_2 (+4) MnO_4^{2-} (+6) MnO_4^{-} (+7)

For transition elements with lower oxidation states: (e.g. +2, +3 oxidation states)

- Due to loss of 4s electrons, followed by 3d electrons.
- Ionic bonds are found in compounds such as $FeCl_3$ and $FeSO_4$.

For transition elements with higher oxidation states:

- Maximum oxidation states correspond to the number of 4s and unpaired 3d electrons.
- Electrons are shared with other atoms to form covalent bonds.
  Covalent bonds are found in compounds such as TiO_2, V_2O_5, Mn_2O_7 and oxoanions such as VO_3^-, CrO_4^{2-}, $Cr_2O_7^{2-}$, MnO_4^-.

Example 4

The electronic configuration of vanadium is $[Ar]3d^34s^2$. Which of the following ions does not exist?

A VO^{2+} **B** VO_2^+ **C** VO_3^{2-} **D** VO_4^{2-}

Maximum oxidation state = number of 4s electrons + unpaired 3d electrons = +5
Oxidation state of V in VO_4^{2-} = +6 ⇒ VO_4^{2-} does not exist

Example 5

Ti has the electronic structure $1s^22s^22p^63s^23p^63d^24s^2$. Which of the following compounds is **unlikely** to form?

A TiO **B** K_2TiO_4 **C** $TiCl_3$ **D** $Fe_2(TiO_3)_3$

Maximum oxidation state = number of 4s electrons + unpaired 3d electrons = +4
Oxidation state of Ti in TiO_4^{2-} = +6 ⇒ K_2TiO_4 is unlikely to form

Example 6

Explain why Cr^{6+} does not exist but CrO_4^{2-} is formed instead.

Answer:

Forming Cr^{6+} would require a **very high ionisation energy**. The high charge of Cr^{6+} would result in **high polarising power** that polarises water to form CrO_4^{2-}.

3.1.2 $E^{\ominus}$ of Transition Metal Ions

$E^{\ominus}$ is used to compare relative stability of the metal ions.

$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	–0.41 V
$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$	+1.54 V
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77 V
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	+1.89 V

Note: Anomaly at Fe^{3+}/ Fe^{2+}
- $E^{\ominus}$ is less positive than expected.
- Formation of Fe^{3+} from Fe^{2+} is more favoured than expected (i.e. Fe^{3+} is more stable than expected).
- This is due to the stability of the half-filled d subshell in $Fe^{3+}(d^5)$.

Across the transition metal series, $E^{\ominus}$ generally becomes more positive.
- The reduction of M^{3+} to M^{2+} is more favoured.
- The oxidation of M^{2+} to M^{3+} is less favoured.
- M^{3+} gets relatively less stable.
- It becomes more difficult to lose the 3rd electron from M as the effective nuclear charge increases across the transition metal series.

3.1.3 Predicting and Explaining Redox Reactions Involving Transition Elements

- Species involving transition element with high oxidation states tend to be good oxidising agents. E.g. MnO_4^-, $Cr_2O_7^{2-}$

  Species involving transition element with low oxidation states tend to be good reducing agents. E.g. Cr^{2+}, V^{2+}

- Redox reactions involving transition metals are usually accompanied by colour changes.

- Recall:
  - The likelihood of redox reactions can be predicted using $E^{\ominus}$ values, but it gives no information about the rate of reaction.
  - The more positive the $E^{\ominus}$ value, the more the reduction is favoured.
  - **$E^{\ominus}_{cell} = E^{\ominus}_{red} - E^{\ominus}_{oxd} > 0$** indicates that the reaction is **thermodynamically feasible.**

Example 7

Write balanced chemical equations for the reactions between:
(a) acidified manganate(VII) and iron(II) ions.
(b) acidified dichromate(VI) ions and iron(II) ions.

Which is a better titrant in the volumetric analysis of Fe^{2+}?

Answer:

(a) Between acidified manganate(VII) and iron(II) ions:

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ +0.77 V
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$ +1.52 V

$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{oxd}$ = +1.52 – (+0.77) = +0.75 V (> 0, feasible)

Overall equation: $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$
(Note: the purple acidified MnO_4^- is reduced to Mn^{2+}.)

(b) Between acidified dichromate(VI) ions and iron(II) ions

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ +0.77 V
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$ +1.33 V

$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{oxd}$ = +1.33 – (+0.77) = +0.56 V (> 0, feasible)

Overall: $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$
(Note: the orange acidified $Cr_2O_7^{2-}$ is reduced to the green Cr^{3+}.)

MnO_4^- is a better titrant as the colour change is more distinct.

Example 8

Which of the following are chemically stable when left to stand in the atmosphere?

1 a solution of potassium hexacyanoferrate(III)

2 a mixture of aqueous sodium hydroxide and iron(II) sulfate

3 a mixture of aqueous sodium chloride and vanadium(II) chloride

Reduction of O_2 from the atmosphere: $O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$ +0.40 V

$\mathbf{[Fe(CN)_6]^{3-}} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$ +0.36 V
$\Rightarrow [Fe(CN)_6]^{3-}$ does not undergo oxidation.

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$
$Fe(OH)_3 + e^- \rightleftharpoons \mathbf{Fe(OH)_2} + 4OH^-$ –0.56 V
$\Rightarrow E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{oxd}$ = +0.40 – (–0.56) = +0.96 V (> 0, feasible)
$\Rightarrow Fe(OH)_2$ can be oxidised by O_2 in the atmosphere

$V^{3+} + e^- \rightleftharpoons \mathbf{V^{2+}}$ –0.26 V
$\Rightarrow E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{oxd}$ = +0.40 – (–0.26) = +0.66 V (> 0, feasible)
$\Rightarrow V^{2+}$ can be oxidised by O_2 in the atmosphere

3.2 Catalytic Properties

A **catalyst** is a substance which increases the rate of a reaction by providing a different reaction pathway with a lower activation energy without itself undergoing any permanent chemical change.

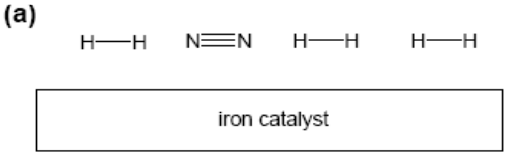
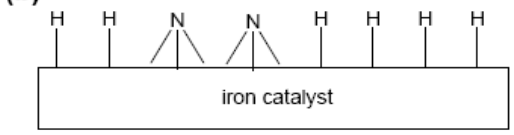
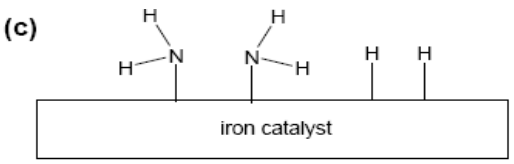
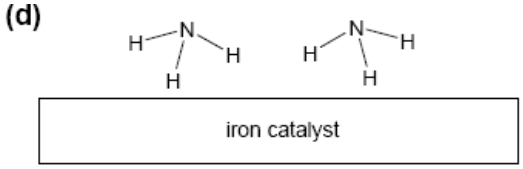
Many transition metals and their compounds show catalytic activities as they are able to provide an **alternative pathway for the reaction** with **lower activation energy E_a**, either through *homogeneous catalysis* or *heterogeneous catalysis*.

3.2.1 Heterogeneous catalyst – catalyst and reactants are in **different phases**

The catalyst is usually in the solid phase and the reactants are usually liquids or gases.

e.g. **V_2O_5** in Contact process, $2SO_2 + O_2 \rightarrow 2SO_3$
Fe / Fe_2O_3 in Haber process, $N_2 + 3H_2 \rightleftharpoons 2NH_3$
Ni in hydrogenation of alkenes
Pt and **Pd** in catalytic converters in car engines

Recall from Kinetics – Adsorption Theory in Heterogeneous Catalysis

Example (The Haber Process)	Process
(a) 	**a. Diffusion** The reactant molecules **diffuse** towards the catalyst surface.
(b) 	**b. Adsorption** Reactant molecules are **adsorbed on the active site** of the catalyst, i.e. weak temporary bonds are formed between reactant molecules and the catalyst surface. The process **(i)** brings reactant molecules closer together, thus **increasing their concentration at the catalyst surface**. **(ii) weakens the bonds** in the reactant molecules **(iii)** allows these molecules to be **orientated** in the right positions for reaction, ⇨ Thus **increasing the frequency of effective collisions**.
(c) 	**c. Chemical Reaction** Adjacent reactant molecules react to form products.
(d) 	**d. Desorption** Once the product is formed, it is **desorbed** and it diffuses away from the catalyst surface. The **active site on the catalyst is regenerated** and now free to adsorb another reactant molecule.

How does a transition metal work as a heterogeneous catalyst?

- Heterogeneous catalysis is explained by **Adsorption Theory**.
- Transition metals are good heterogeneous catalysts because they **possess partially filled d subshells**.
  - ✓ The **d electrons are available for the formation of weak temporary bonds** with the reactant molecules.
  - ✓ The **energetically low-lying vacant d orbitals** can be used to accommodate electron pairs from reactant molecules, resulting in weak temporary bond formation.

Example 9

Transition metals like platinum and rhodium are found in catalytic converters fitted into cars. Which of the following statements best explains the role of transition metals in this use?

A Transition metals can exhibit variable oxidation states in their compounds as 3d and 4s electrons have similar energies.

B Transition metals form coloured ions due to absorption of energy in the visible light region to promote an electron from a lower to a higher energy 3d orbital.

C Transition metals have very high melting points because both 3d and 4s electrons are involved in forming strong metallic bond.

D Transition metals have available and partially filled 3d orbitals for adsorption of reactant molecules.

3.2.2 Homogeneous catalysts – catalyst and reactants are in the **same phase**

Recall from Electrochemistry – Homogeneous Catalysis

Example: Oxidation of I^- by $S_2O_8^{2-}$ using Fe^{2+} catalyst

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

	E^θ / V
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+2.01

Uncatalysed reaction: $E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{oxd} = (+2.01) - (+0.54) = +1.47$ V (> 0, feasible)

- This reaction has **high activation energy** as both reactants are **negatively charged** and they **repel each other**. The presence of **small amounts** of $Fe^{2+}(aq)$ can catalyse the reaction by providing an **alternative pathway** with a **lower activation energy**.

$$\mathbf{S_2O_8^{2-}(aq) + 2I^-(aq) \xrightarrow{Fe^{2+}} 2SO_4^{2-}(aq) + I_2(aq)}$$

If the same reaction is carried out with Fe^{2+}(aq) as a catalyst, the mechanism proceeds as follows:

<u>Step 1</u>: $2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \rightarrow 2Fe^{3+}(aq) + SO_4^{2-}(aq)$

$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{oxd} = +2.01 - (+0.77) = +1.24$ V (> 0, feasible)

Fe^{2+} is oxidised to Fe^{3+} (intermediate compound).

<u>Step 2</u>: $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{oxd} = +0.77 - (+0.54) = +0.23$ V (> 0, feasible)

Fe^{3+} is reduced to Fe^{2+}, hence regenerating the Fe^{2+} catalyst.

- The two steps in this mechanism have lower E_a as the reactants have opposite charges.
- During the reaction, the oxidation number of the iron ion changes from +2 → +3 → +2. Since most transition metals have variable oxidation states, their ions are often useful as homogeneous catalyst in redox reactions.

How does a transition metal work as a homogeneous catalyst?

- Homogeneous catalysis is explained by the Intermediate Compound Theory.
- The catalyst provides an alternative pathway for the reaction with a lower activation energy.
- **Transition metal ions** function well as homogeneous catalysts because they can exhibit **variable oxidation states** and can be easily oxidised or reduced.

Example 10

Using the $E^\ominus$ values from the *Data Booklet*, suggest another metal cation that can be used to catalyse the above reaction.

<u>Answer</u>:

- The pair of metal cations must have +0.54 V < $E^\ominus$ < +2.01 V, to ensure that both steps 1 and 2 are feasible.
- It must be a homogeneous catalyst (i.e. in aqueous state).

Possible choices: Co^{3+} / Co^{2+} +1.89 V
Mn^{3+} / Mn^{2+} +1.54 V

3.3 Complex Ion Formation

A ***complex ion*** is a specie that contains a central metal atom/ion surrounded by molecules or anions (known as ligands) which form coordinate bonds to the metal centre.

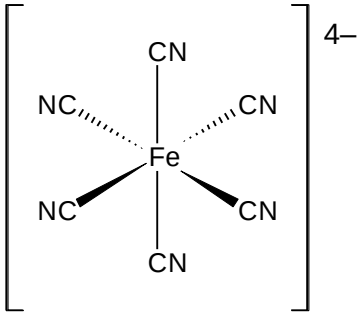
Examples of complex ions:

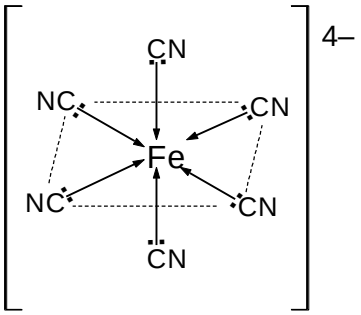
$[Ag(NH_3)_2]^+$ $[Al(H_2O)_6]^{3+}$ $[PbCl_4]^{2-}$ $[Cu(NH_3)_4(H_2O)_2]^{2+}$ $[Cr(H_2O)_6]^{3+}$

Different representions of complex ions:

Central metal ion: Fe^{2+}
Ligands: CN^-

$[Fe(CN)_6]^{4-}$





- Transition metals form stable complex ions because
  - ✓ their ions are **small** and **highly charged**, thus having high charge density.
  - ✓ they have **energetically low-lying vacant d orbitals** to accommodate the lone pairs of electrons donated by the ligands to form the dative bonds.

- E.g. When dissolved in water, iron(III) chloride dissociates in water to form Fe^{3+} ions. The Fe^{3+} ion is immediately surrounded by water molecules to form the $[Fe(H_2O)_6]^{3+}$ complex ion.

Example 11

Explain why Na^+ ions from the dissociation of sodium chloride is unable to form a complex.

Answer:

Na^+ will form ion-dipole interactions with water molecules, not dative bonds.
Na^+ has a low charge density and there are no energetically low-lying vacant d orbitals available to accommodate the lone pairs of electrons from water.

3.3.1 Ligands

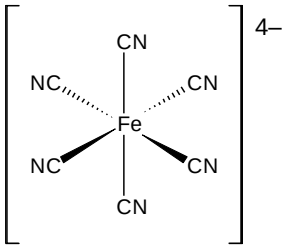
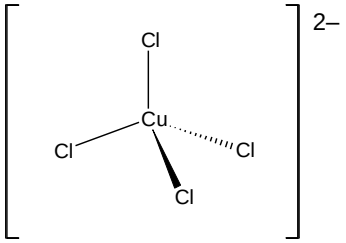
A **ligand** is a molecule or anion with at least one lone pair of electrons that can form a dative bond to the transition metal atom/ion.

- **Monodentate** ligands – forms **only one dative bond** with the central metal atom/ion in a complex.

  Example of such ligands:

  Anions → **:**C*l*$^-$ **:**F$^-$ $^-$**:**C≡N $^-$**:**SCN

  Neutral → **:**CO **:**NH_3 H_2O**:**

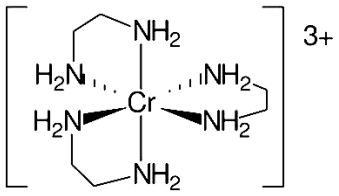
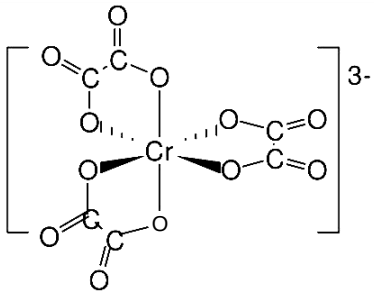
	
Fe is surrounded by 6 monodentate ligands. Each $^-$**:**C≡N ligand forms one dative bond to the central Fe^{2+} metal ion.	Cu is surrounded by 4 monodentate ligands. Each **:**C*l*$^-$ ligand forms one dative bond to the central Cu^{2+} metal ion.

Some ligands have more than one donor atom (each with at least a lone pair of electrons) and can form two dative bonds (**bidentate** ligands) or more (**polydentate** ligands) with the central metal atom/ion.

- **Bidentate** ligands – forms only **two dative bonds** per ligand.

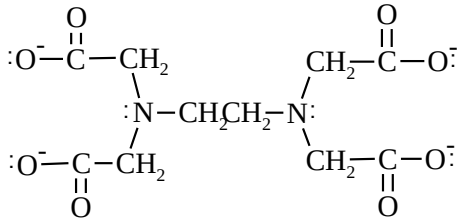
  e.g. ethane-1,2-diamine ethanedioate ion

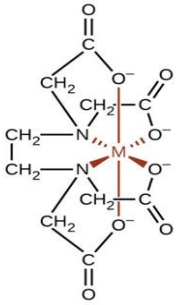
  $H_2\ddot{N}–CH_2CH_2–\ddot{N}H_2$ $^-\ddot{O}OC–CO\ddot{O}^-$

$[Cr(en)_3]^{3+}$	$[Cr(C_2O_4)_3]^{3-}$
	
Each ethane-1,2-diamine ligand forms two dative bonds to the central Cr^{3+} metal ion.	Each ethanedioate ligand forms two dative bonds to the central Cr^{3+} metal ion.

- **Hexadentate** ligands – forms **six dative bonds** per ligand.

  E.g. ethylenediaminetetraacetate ion ($EDTA^{4-}$)





  - Bidentate and other polydentate ligands can form particularly **stable complex ions** because they are able to form strong dative bonds to the metal ion and the formation of the complex ions is accompanied by an **increase in entropy**.

    E.g. $EDTA^{4-}$ is added to a solution of iron(II) sulfate:

$$[Fe(H_2O)_6]^{2+}(aq) + EDTA^{4-}(aq) \rightleftharpoons [Fe(EDTA)]^{2-}(aq) + 6H_2O(l)$$

    Entropy increase as there is an increase in number of particles in the product (from 2 mol of reactants to 7 mol of products). There is an increase in disorder of the system as there are more ways of arranging these particles.

Example 12

Explain why the oxidising power of aqueous Fe^{3+} decreases in the presence of NaCN.

Answer:

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

In both cases, iron(III) is reduced to iron(II). In the presence of cyanide (CN^-) ligands, $E^{\ominus}$ becomes less positive, i.e. the iron(III) becomes less oxidising. The CN^- ligands in $[Fe(CN)_6]^{3-}$ helps to stabilise the +3 oxidation state of iron more than the +2 state.

3.3.2 Coordination Number

Coordination number indicates the number of coordinate bonds around the central metal ion or atom in the complex.

- Complexes can be neutral, cationic or anionic.
- The **net charge** on the complex is the sum of the oxidation number of the central metal ion and the total charges of the ligands that surround it.

Complex	Central Atom/Ion	Ligand	Coordination Number
$Ni(CO)_4$	Ni	CO	4
$[Ag(NH_3)_2]^+$	Ag^+	NH_3	2
$[Cu(NH_3)_4(H_2O)_2]^{2+}$	Cu^{2+}	NH_3 and H_2O	6
$[Co(C_2O_4)_3]^{4-}$	Co^{2+}	$C_2O_4^{2-}$	6
$[Cu(EDTA)]^{2-}$	Cu^{2+}	$EDTA^{4-}$	6

- Complex salts contain cationic complexes (or anionic complexes) and oppositely charged anions (or cations) as counter ions. For example, $[Fe(NH_3)_6]Cl_2$ and $K_2[Cu(EDTA)]$.

$[Fe(NH_3)_6]Cl_2 \rightarrow [Fe(NH_3)_6]^{2+} + 2Cl^-$ *cationic complex* *counter ion*	$K_2[Cu(EDTA)] \rightarrow [Cu(EDTA)]^{2-} + 2K^+$ *anionic complex* *counter ion*

One mole of $[Fe(NH_3)_6]Cl_2$ dissociates to give one mole of $[Fe(NH_3)_6]^{2+}$ and two moles of Cl^- ions.

The complex ion behaves like a polyatomic ion: the six NH_3 ligands remain bonded to the central metal ion via the strong dative bonds. $AgNO_3$ can precipitate the two free Cl^- ions as $AgCl$.

Example 13

Cobalt(III) chloride forms a complex with ammonia in which the coordination number is 6. One mole of the compound formed reacts with two moles of silver nitrate.
Which of the following correctly shows the formula of this complex?

A $Co(NH_3)_3Cl_3$ **B** $Co(NH_3)_4Cl_3$ **C** $Co(NH_3)_5Cl_3$ **D** $Co(NH_3)_6Cl_3$

1 mol of compound reacts with 2 mol of $AgNO_3$
$\Rightarrow$ 2 free Cl^- ions precipitated as $AgCl$
$\Rightarrow$ charge on cationic complex is 2+
$\Rightarrow$ 1 Cl^- ligand and 5 NH_3 ligands (coordination number 6) are bonded to the Co^{3+} metal centre

Compound dissociates to form $[Co(NH_3)_5Cl]^{2+}$ and 2 Cl^-.

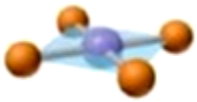
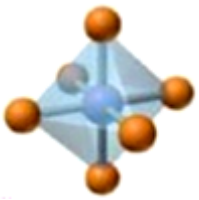
Example 14
Platinum(IV) chloride is combined with ammonia to form a single product. The product is a different platinum(IV) compound which contains a cation with a 2+ charge and has a coordination number of 6. What is the formula of this product?

A $Pt(NH_3)_3Cl_4$ **B** $Pt(NH_3)_4Cl_4$ **C** $Pt(NH_3)_6Cl_2$ **D** $Pt(NH_3)_6Cl_4$

Platinum(IV) compound containing a cation with a 2+ charge $\Rightarrow$ 2 Cl^- ligands bonded to Pt^{IV} centre
Coordination number of 6 $\Rightarrow$ 4 NH_3 ligands and 2 Cl^- ligands
Product dissociates to form $[Pt(NH_3)_4Cl_2]^{2+}$ and 2 Cl^-.

3.3.3 Shapes of Complexes

- We can determine the shape of the complex from the coordination number.

Coordination Number	Shape	Examples	Remarks
2	Linear 	$[Ag(NH_3)_2]^+$ $[CuCl_2]^-$	❖ Not common ❖ Usually in Ag(I) and Cu(I) complexes)
4	Tetrahedral 	$[CuCl_4]^{2-}$ $[CoCl_4]^{2-}$	❖ **Common**
	Square Planar 	$[Ni(CN)_4]^{2-}$ $[Pt(NH_3)_4]^{2+}$	❖ Not common ❖ Some Ni(II) and Pt(II) exhibit this shape.
6	Octahedral 	$[Fe(CN)_6]^{4-}$ $[Cu(EDTA)]^{2-}$ $[Mn(H_2O)_6]^{2+}$ $[Cu(NH_3)_4(H_2O)_2]^{2+}$	❖ **Very common**

Example 15

Given the reaction below:

$$[Co(NH_3)_6]^{3+}(aq) + 3en\ (aq) \rightleftharpoons [Co(en)_3]^{3+}(aq) + 6NH_3\ (aq)$$

where *en* represents ethane-1,2-diamine, $H_2NCH_2CH_2NH_2$

Which of the following statements are **true** about this reaction?

1 The change in entropy is positive.

2 Both complexes are octahedral.

3 ΔH is approximately 0 and the reaction is spontaneous at all temperatures.

3.3.4 Ligand Exchange Reaction

- A ligand exchange reaction is a reaction in which the **weaker ligands are substituted by stronger ligands.**

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

Weaker H_2O ligands in $[Fe(H_2O)_6]^{3+}$ are substituted by stronger CN^- ligands to form $[Fe(CN)_6]^{3-}$ in this ligand exchange reaction.

- Sometimes not all the ligands are substituted, for example:

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

$$[Fe(H_2O)_6]^{3+}(aq) + SCN^-(aq) \rightleftharpoons [Fe(SCN)(H_2O)_5]^{2+}(aq) + H_2O(l)$$
yellow → blood red

- In some cases, the coordination number changes, for example:

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

- Polydentate ligands, also known as 'chelates', form very stable complexes compared to complexes formed with monodentate ligands because the reaction is accompanied by an increase in entropy (see page 17).
So, polydentate ligands (e.g. *en* and $EDTA^{4-}$) tend to displace monodentate ligands in ligand exchange reactions.

$$[Co(NH_3)_6]^{3+}(aq) + 3en(aq) \rightleftharpoons [Co(en)_3]^{3+}(aq) + 6NH_3(aq)$$

where *en* = ethane-1,2-diammine, $H_2NCH_2CH_2NH_2$

- The relative bonding strengths of ligands are arranged in this order:

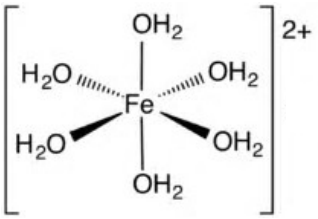
$$Cl^- < OH^- < H_2O < NH_3 < en < CN^- < EDTA^{4-}$$

3.4 Formation of Coloured Compounds and Ions

3.4.1 Crystal Field Theory

Crystal Field Theory describes the breaking of orbital degeneracy in transition metal complexes due to the presence of ligands, where the degenerate d orbitals are split into different energy levels.

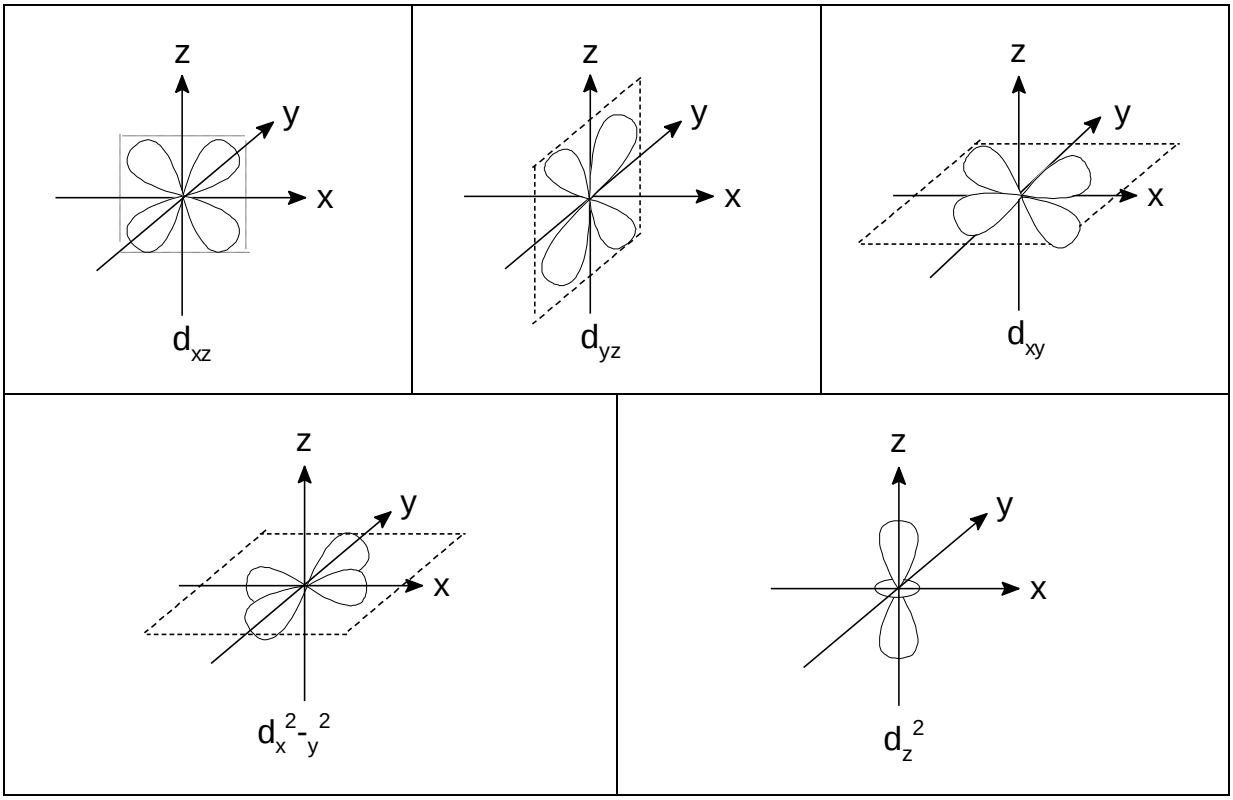
E.g. $[Fe(H_2O)_6]^{2+}$



In the gas-phase Fe^{2+} ion, all five orbitals in the 3d subshell have the same energy level (are degenerate).

In an octahedral complex, the water ligands approach Fe^{2+} along the *x, y,* and *z* axes. The electrons in the d orbitals and those in the ligands repel each other, resulting in the orbitals having a higher energy level than those in the gas-phase ion.

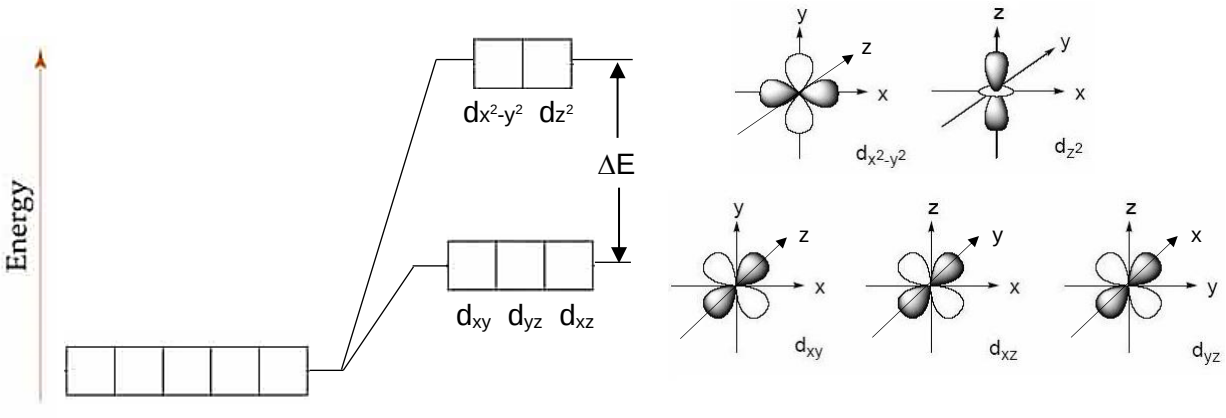
The d electrons closer to the ligands will have a higher energy than those further away which causes the d orbitals to split into different energy levels.



- d_{xy}, d_{yz} and d_{xz} orbitals have lobes that are directed between the axes which the ligands approach.
- d_{z^2} and $d_{x^2-y^2}$ orbitals have lobes that are directed along the axes pointing towards the approaching ligands.

  Thus, electrons in the $d_{x^2-y^2}$ and d_{z^2} orbitals experience stronger repulsions than those in the d_{xy}, d_{xz} and d_{yz} orbitals.

- As a result, an energy separation (or splitting) occurs, giving rise to three lower energy d orbitals and the two higher energy ones, with an energy gap ΔE. This energy gap is the crystal-field splitting energy.



Energies of the d orbitals in an octahedral crystal field

- The crystal field model accounts for the observed colours in transition metal complexes. The energy gap between the d orbitals, labeled ΔE, is of the same order of magnitude as the energy of visible light.

- Therefore, it is possible for a transition metal complex to absorb visible light, which excites an electron from the lower energy d orbitals into a higher energy d orbital.

3.4.2 Why are transition metal complexes coloured?

- White light is composed of various colours in the visible region of the electromagnetic spectrum. Our eyes can detect wavelengths in this visible region.

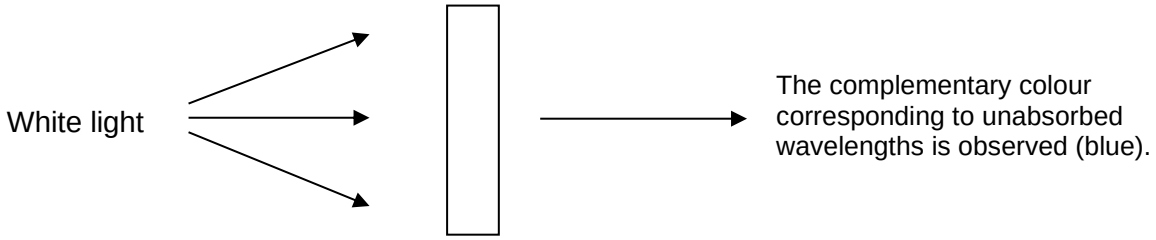
Wavelength (nm) 400 700

violet	blue	green	yellow	orange	red

- A solution under white light
  - appears colourless when none of the wavelengths is absorbed
  - appears coloured when some of the wavelengths are absorbed and the complementary colour of the absorbed wavelengths is observed.

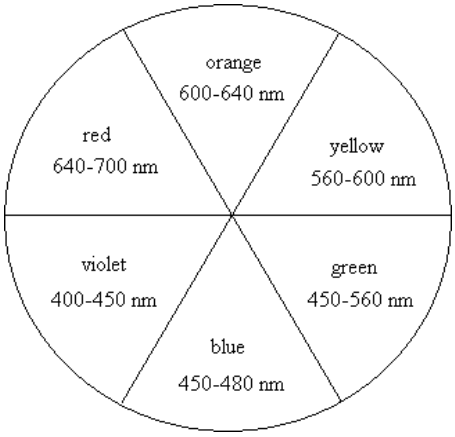
- Many transition metal compounds are coloured in both the solid and aqueous states.

- When white light strikes on a solution of $[Cu(H_2O)_6]^{2+}$,



Solution of $[Cu(H_2O)_6]^{2+}$ in glass cell absorbs some wavelengths of white light

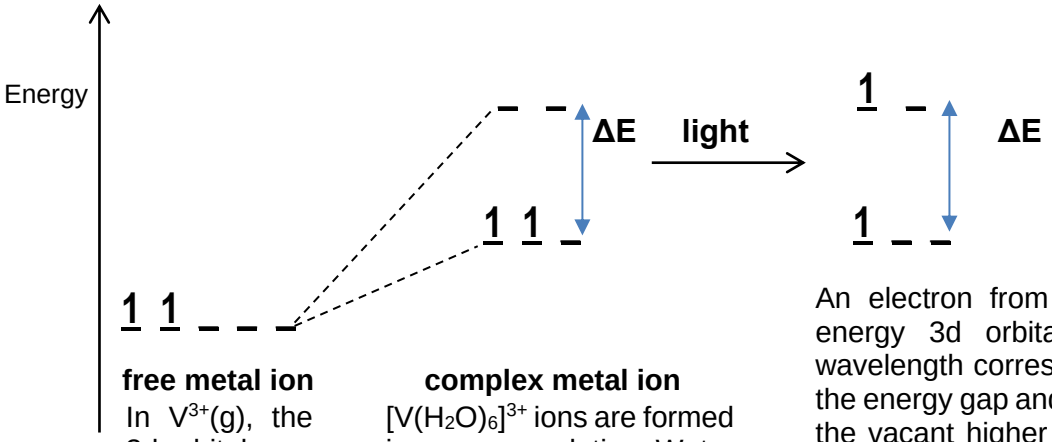
- The colour wheel can be used to predict the colour that will be observed. Colours directly opposite on this wheel are the complementary colours.



Explanation of Coloured Transition Metal Complexes

- In the presence of ligands, the partially filled 3d orbitals split into two energy levels, with a small energy gap, ΔE.
- An electron in the lower energy d orbital absorbs energy in the visible spectrum corresponding to ΔE and becomes excited to a vacant d orbital at the higher energy level (d-d transition).
- Unabsorbed wavelengths are transmitted and the colour observed is complementary to the colour absorbed.

Using $V^{3+}(aq)$ as example,



free metal ion
In $V^{3+}(g)$, the 3d orbitals are degenerate.

complex metal ion
$[V(H_2O)_6]^{3+}$ ions are formed in aqueous solution. Water ligands causes the 3d orbitals to split into 2 energy levels with an energy gap, ΔE.

An electron from the lower energy 3d orbital absorbs wavelength corresponding to the energy gap and excites to the vacant higher energy 3d orbital.

Note that once excitation of electron occur, relaxation of electrons from an excited state back to the ground state occurs.

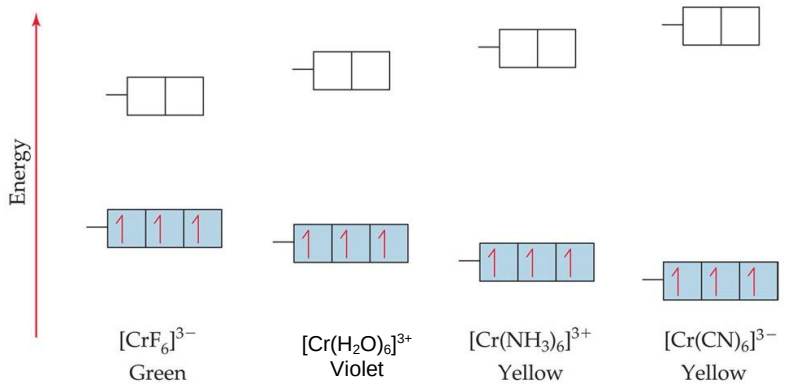
3.4.3 Factors Affecting Colour of Transition Metal Complexes

(a) Type of ligands

- **Different ligands** have different effects on the splitting of d orbitals, resulting in different energy gaps (ΔE). Wavelengths of light absorbed by the 3d electrons during d-d transition will hence be different and a different complementary colour is observed.

- The following is a list of common ligands arranged in order of increasing ΔE:

$$Cl^- < OH^- < H_2O < NH_3 < en < CN^- < EDTA^{4-}$$



Crystal-field splitting in a series of octahedral chromium(III) complexes

This list is the spectrochemical series**.** Ligands on the left end of the spectrochemical series are weak field ligands; those on the right end are strong field ligands.

❖ The energy gap, $\Delta E = \frac{h\,c}{\lambda}$

ΔE = energy in Joules (J)
h = Planck constant (6.63×10^{-34} J s)
c = speed of light (3.00×10^{8} m s^{-1})
λ = wavelength of visible light (m)

❖ From the equation above,
- if the ΔE is small, a longer wavelength of visible light is absorbed. Hence, the complementary colours of light with shorter wavelengths will be transmitted.

- if the ΔE is large, a shorter wavelength of visible light is absorbed. Hence, the complementary colours of light with longer wavelengths will be transmitted.

(b) Nature of transition metal ion

Different oxidation states of transition metal ions will result in different interactions with the electrons from the ligands. This have a different effect on the splitting of the d orbitals, resulting in different energy gaps (ΔE). Wavelengths of light absorbed by the 3d electrons during d-d transition will also be different and hence a different colour is observed.

3.4.4 Why are some transition (d-block) metal complexes not coloured?

- No electrons in the d orbitals

  Compounds with no d electrons (d^0) such as Sc^{3+} are colourless as d−d transition is not possible. There are no electrons in the d orbitals to absorb energy in the visible spectrum corresponding to ΔE.

- Fully occupied d orbitals

  Compounds with d orbitals fully occupied (d^{10}) such as Zn^{2+} are colourless as d−d transition is not possible. There are no vacant d orbitals at the higher energy level for the excitation of electrons from the lower energy level.

Example 16

Explain why an aqueous solution of copper(II) sulfate is blue while a solution of sodium sulfate is colourless.

Answer:

In the presence of H_2O ligands, the partially filled 3d orbitals split into two energy levels, with a small energy gap, ΔE. An electron in the lower energy d orbital absorbs energy in the visible spectrum corresponding to ΔE and becomes excited to a vacant d orbital at the higher energy level (d-d transition). Unabsorbed wavelengths are transmitted and the colour observed (blue) is complementary to the colour absorbed (orange).

Electronic configuration of Na^+: $1s^2 2s^2 2p^6$
For 2p electron to be excited to the 3s orbitals, the energy gap between the 2 energy levels is **very large**. The wavelength absorbed will **fall outside the visible region**. Hence, a solution of $Na^+(aq)$ appears colourless.

Example 17

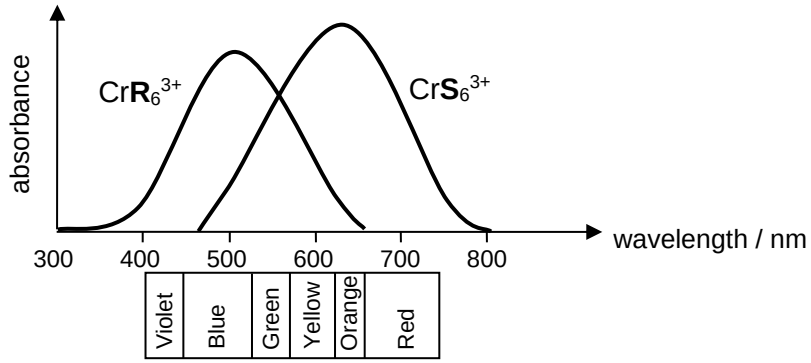
Explain why CuI is a white precipitate even though copper is a transition metal.

Answer:

Electronic configuration of Cu^+: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$
The 3d subshell is **fully filled**. There are no vacant d orbitals at the higher energy level for the excitation of electrons from the lower energy level. Hence, d-d transition is not possible and CuI appears white.

Example 18

The diagram below shows the visible spectra of two chromium (III) complexes, CrR_6^{3+} and CrS_6^{3+}. The various colours corresponding to the approximate wavelengths in the visible light region are shown below the axis.



For CrR_6^{3+}:
Blue/green is absorbed
⇒ complementary colour of orange/red is observed

For CrS_6^{3+}:
Orange/yellow is absorbed
⇒ complementary colour of blue/violet is observed

Using $\Delta E = hc / \lambda$,

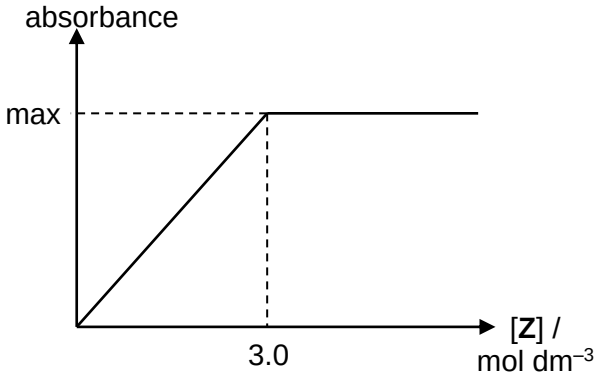
A smaller wavelength is absorbed for CrR_6^{3+}
⇒ R causes a larger d orbital splitting

What is the colour of each complex and which ligand caused a larger d orbital splitting?

	colour of CrR_6^{3+}	colour of CrS_6^{3+}	ligand which causes a larger d-orbital splitting
A	blue	yellow orange	R
B	blue	yellow orange	S
C	red	violet	R
D	red	violet	S

Example 19

100 cm^3 of 1.0 mol dm^{-3} $Cu^{2+}(aq)$ is added to 100 cm^3 of ligand **Z** of different concentrations to form an octahedral complex. The absorbance due to the complex in each mixture is measured with a colourimeter, using an appropriate filter. The graph of absorbance against concentration of ligand **Z** is obtained. Explain why ligand **Z** is a bidentate ligand.



Answer:

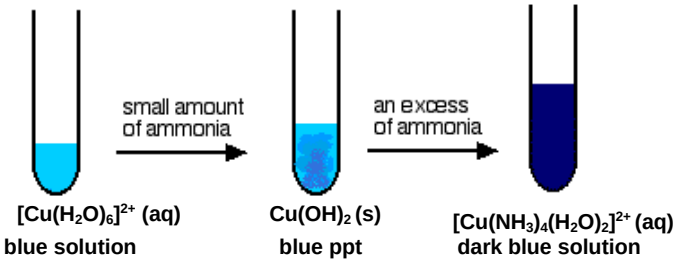
Amount of Cu^{2+} = 0.10 mol
Amount of **Z** = 0.30 mol
Amount of Cu^{2+} : amount of **Z** = 1 : 3

Since the complex formed is octahedral (coordination number = 6), each ligand **Z** forms two dative bonds. Thus, ligand **Z** is a bidentate ligand.

4. REACTIONS INVOLVING TRANSITION METAL COMPLEXES

4.1 Reactions of Copper Ions

4.1.1 Aqueous Copper(II) Ions and Aqueous Ammonia



- Copper(II) salts dissolve in water to give a blue solution, which is due to the complex ion $[Cu(H_2O)_6]^{2+}$. Note: $[Cu(H_2O)_6]^{2+}$ (aq) ≡ Cu^{2+}(aq).

$$CuSO_4\ (s) + 6H_2O\ (l) \rightarrow [Cu(H_2O)_6]^{2+}\ (aq) + SO_4^{2-}\ (aq)$$

- As NH_3 is a weak base, it dissociates partially in water to produce OH^-.

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

When **dilute NH_3 is added gradually**, deprotonation of $[Cu(H_2O)_6]^{2+}$ occurs and a blue precipitate of $[Cu(OH)_2(H_2O)_4]$ or $Cu(OH)_2$ is formed in the precipitation reaction (not ligand exchange reaction). Note: $[Cu(OH)_2(H_2O)_4] \equiv Cu(OH)_2$.

$$[Cu(H_2O)_6]^{2+}\ (aq) + 2OH^-\ (aq) \rightleftharpoons [Cu(OH)_2(H_2O)_4]\ (s) + 2H_2O\ (l) \qquad \text{eqm (1)}$$

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

- When **excess aqueous NH_3 is added**, the precipitate dissolves to give a dark blue solution, due to the formation of complex ion, $[Cu(NH_3)_4(H_2O)_2]^{2+}$. Note: $[Cu(NH_3)_4(H_2O)_2]^{2+} \equiv [Cu(NH_3)_4]^{2+}$.

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

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

NH_3 is a stronger ligand than H_2O and will displace the H_2O ligands in $[Cu(H_2O)_6]^{2+}$ in a ligand exchange reaction to form $[Cu(NH_3)_4(H_2O)_2]^{2+}$. By Le Chatelier's Principle, as the concentration of $[Cu(H_2O)_6]^{2+}$ decreases, the position of equilibrium (1) shifts to the left to increase the concentration of $[Cu(H_2O)_6]^{2+}$ and the $Cu(OH)_2$ precipitate dissolves.

(FYI)
When the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion is formed, concentration of $[Cu(H_2O)_6]^{2+}$ decreases, leading to a decrease in the ionic product of $Cu(OH)_2$ to the extent that ionic product of $Cu(OH)_2$ < K_{sp} of $Cu(OH)_2$. Hence, the $Cu(OH)_2$(s) precipitate dissolves.

The overall equation for the blue precipitate dissolving to give a deep blue solution:

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

4.1.2 Aqueous Copper(II) Ions and Concentrated HCl

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

- When concentrated HCl is added, $[Cl^-]$ increases. By Le Chatelier's Principle, the position of equilibrium shifts to the right to reduce the added Cl^-. Hence, the blue solution will turn green (mixture of blue and yellow), and then yellow.

- This is a **ligand exchange reaction**.
  Note that Cl^- is a weaker ligand than H_2O. Concentrated HCl is used because it provides a very high concentration of Cl^- which pushes the position of the equilibrium to the right.

- When water is added, the concentration of all aqueous ions decrease. There is a greater extent of decrease in concentration of aqueous ions at the reactant side. By Le Chatelier's Principle, position of equilibrium shifts to the left to increase the concentration of reactant ions. Hence, the yellow solution turns blue.

4.1.3 Reduction of Aqueous Copper(II) to Copper(I) Iodide

- $Cu^{2+}(aq)$ is reduced to CuI using aqueous potassium iodide, and I^- is oxidised to I_2. The white precipitate of CuI appears cream in the brown solution.

$$\underset{\text{blue}}{2Cu^{2+}(aq)} + \underset{\text{colourless}}{4I^-(aq)} \rightleftharpoons \underset{\text{white ppt}}{2\,CuI(s)} + \underset{\text{brown}}{I_2(aq)}$$

  Observation: Cream precipitate in brown solution.

- Upon addition of sodium thiosulfate (reducing agent) to the mixture, the brown solution of I_2 is reduced and becomes colourless. The white precipitate can now be observed clearly.

$$2S_2O_3^{2-}(aq) + \underset{\text{brown}}{I_2(aq)} \rightarrow S_4O_6^{2-}(aq) + \underset{\text{colourless}}{2I^-(aq)}$$

  Observation: White precipitate in colourless solution.

4.1.4 Disproportionation of Cu(I) Compounds

Cu(I) is unstable and it disproportionates into Cu(II) (pale blue solution) and Cu metal (reddish-brown solid).

$Cu^{2+} + e^- \rightleftharpoons Cu^+$ +0.15 V
$Cu^+ + e^- \rightleftharpoons Cu$ +0.52 V

$E^\theta_{cell} = (+0.52) - (+0.15) = +0.37$ V (> 0, feasible)

Overall equation: $2Cu^+ \rightarrow Cu^{2+} + Cu$

4.2 Reactions of Iron Ions

4.2.1 Reaction of Aqueous Iron(III) Ions and Thiocyanate Ion

- A solution of iron(III) chloride appears yellow. When a solution of KSCN is added, the solution turns blood red.

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

- $[Fe(H_2O)_6]^{3+}(aq)$ undergoes a **ligand exchange reaction**, where one of the H_2O ligands is substituted with a SCN^- ligand.

- The $[Fe(SCN)(H_2O)_5]^{2+}$ complex is more stable than $[Fe(H_2O)_6]^{3+}$.

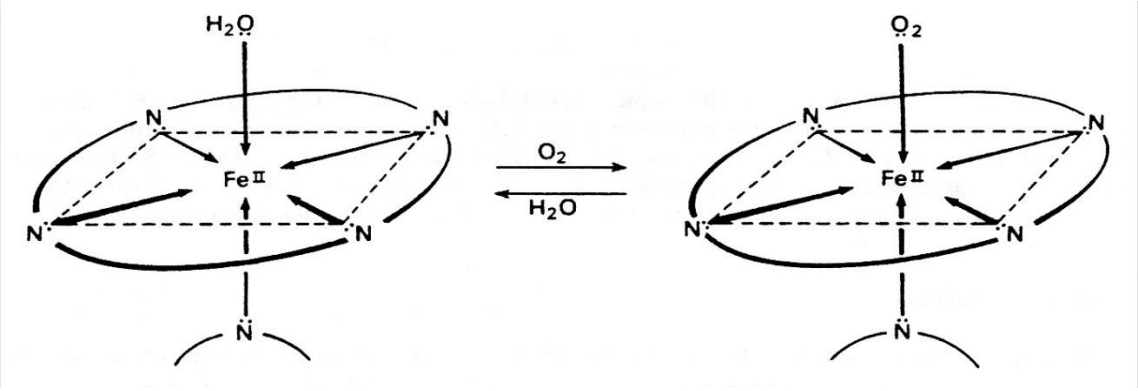
4.2.2 Ligand Exchange of CO / O_2 in Haemoglobin

- Haemoglobin is a protein found in the red blood cells that carries oxygen in the body and gives blood its red colour.

- Haemoglobin contains Fe^{2+} ion, which is hexa-coordinated (i.e. it forms six coordinate bonds).

- The Fe^{2+} ion is part of a complex called a haem group. The haem group contains four nitrogen atoms that act as ligands bonding to four of the sites of the Fe^{2+} ion. The fifth site is occupied by a nitrogen ligand from a protein.

- In the lungs where oxygen concentration is high, O_2 occupies the last site on the Fe^{2+} ion to form oxyhaemoglobin. O_2 bonds reversibly to the Fe^{2+} ion.



- In body tissues where O_2 is used up and the O_2 concentration becomes low, O_2 in the form of oxyhaemoglobin is transported to the tissues. The sixth site on the Fe^{2+} ion previously occupied by O_2 is then substituted by the H_2O ligand. In this way, haemoglobin acts as oxygen carrier.

- Ligands such as cyanide (CN^-) and carbon monoxide (CO) **bond strongly and irreversibly** to the Fe^{2+} ion by forming strong coordinate bonds (or dative bonds). They are not easily released and hence haemoglobin is less available to function as oxygen carrier.

  This accounts for the toxic nature of cyanide and carbon monoxide in causing suffocation.

4.3 Reactions of Chromium Ions

4.3.1 The chromate(VI)-dichromate(VI) equilibrium

- The two chromium complexes can be interconverted through addition of acid, alkali or water. This is an **acid−base reaction**.

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

- In acidic medium, the colour of the solution is orange ($Cr_2O_7^{2-}$). When an acid is added, $[H^+]$ increases. By Le Chatelier's Principle, the position of equilibrium shifts to the right to reduce the added H^+. Hence, the solution changes from yellow to orange.

- In alkaline medium, the colour of the solution is yellow (CrO_4^{2-}). When an alkali is added, OH^- reacts with H^+ causing $[H^+]$ to decrease. By Le Chatelier's Principle, the position of equilibrium shifts to the left to produce more H^+. Hence, the solution changes from orange to yellow.

4.3.2 Acidity of Transition Metal Ions

- Transition metal ions with high charge (i.e. 3+) hydrolyse in water to give an acidic solution.

- The M^{3+} ion has a high charge density and hence a high polarising power. Therefore, it can polarise the electron cloud of the water ligand, causing the O–H bond to weaken.

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

- Since an aqueous solution of M^{3+} is acidic, the following reaction takes place when aqueous carbonate solution is added.

$$2M^{3+}(aq) + 3CO_3^{2-}(aq) + 3H_2O(l) \rightarrow 2M(OH)_3(s) + 3CO_2(g)$$

  Effervescence due to the CO_2 evolved will be observed. The identity of the gas can be determined if a white precipitate is formed when the gas is bubbled into limewater.

4.3.3 Aqueous Chromium(III) Ions and Hydroxide Ions

- When **aqueous NaOH is added gradually**, deprotonation of $[Cr(H_2O)_6]^{3+}$ occurs and a grey-green precipitate of $[Cr(OH)_3(H_2O)_3]$ or $Cr(OH)_3$ is formed (**not** ligand exchange reaction). Note: $[Cr(OH)_3(H_2O)_3] \equiv Cr(OH)_3$.

$$[Cr(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \rightleftharpoons [Cr(OH)_3(H_2O)_3](s) + 3H_2O(l)$$
OR
$$[Cr(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Cr(OH)_3(s) + 6H_2O(l)$$

- When **excess aqueous NaOH is added**, the precipitate dissolves to give a dark green solution, due to the formation of complex ion, $[Cr(OH)_6]^{3-}$, in an acid-base reaction.

$$[Cr(OH)_3(H_2O)_3](s) + 3OH^-(aq) \rightleftharpoons [Cr(OH)_6]^{3-}(aq) + 3H_2O(l)$$

5. COMMON TRANSITION METAL IONS AND THEIR COLOURS

Transition Metal	Oxidation number of central metal ion	Formula	Colour
Chromium	+3	$[Cr(H_2O)_6]^{3+}$	green
	+6	CrO_4^{2-}	yellow
	+6	$Cr_2O_7^{2-}$	orange
Manganese	+2	$[Mn(H_2O)_6]^{2+}$	pale pink (colourless if dilute)
	+4	MnO_2	brown ppt
	+7	MnO_4^-	purple
Iron	+2	$[Fe(H_2O)_6]^{2+}$	pale green
	+2	$Fe(OH)_2$	green ppt
	+3	$[Fe(H_2O)_6]^{3+}$	yellow
	+3	$[Fe(SCN)(H_2O)_5]^{2+}$	blood red
	+3	$Fe(OH)_3$	red-brown ppt
Copper	+2	$[Cu(H_2O)_6]^{2+}$	pale blue
	+2	$[Cu(NH_3)_4(H_2O)_2]^{2+}$	dark blue
	+2	$CuCl_4^{2-}$	yellow
	+2	$Cu(OH)_2$	blue ppt
	+1	CuCl, CuI	white ppt

6. COMMON TRANSITION METALS IONS AND THEIR REACTIONS

6.1 Copper (II) Ions

NaOH(aq)	$[Cu(H_2O)_6]^{2+}(aq) \underset{H^+(aq)}{\overset{OH^-(aq)}{\rightleftharpoons}} Cu(OH)_2(s)$ pale blue solution → pale blue ppt insoluble in excess NaOH(aq)
	$[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons [Cu(OH)_2(H_2O)_4](s) + 2H_2O(l)$ *OR* $[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s) + 6H_2O(l)$
NH_3(aq) *refer to pg 27	$[Cu(H_2O)_6]^{2+}(aq) \underset{H^+(aq)}{\overset{NH_3(aq)}{\rightleftharpoons}} Cu(OH)_2(s) \underset{H^+(aq)}{\overset{\text{excess } NH_3}{\rightleftharpoons}} [Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$ pale blue solution → blue ppt → deep blue solution
	$[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons [Cu(OH)_2(H_2O)_4](s) + 2H_2O(l)$ *OR* $[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s) + 6H_2O(l)$ $[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$
Na_2CO_3(aq)	$[Cu(H_2O)_6]^{2+}(aq) \underset{H^+(aq)}{\overset{CO_3^{2-}(aq)}{\rightleftharpoons}} CuCO_3(s)$ pale blue solution → green ppt
	$[Cu(H_2O)_6]^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CuCO_3(s) + 6H_2O(l)$

6.2 Iron(II) Ions

NaOH(aq)	$[Fe(H_2O)_6]^{2+}(aq) \underset{H^+(aq)}{\overset{OH^-(aq)}{\rightleftharpoons}} Fe(OH)_2(s) \xrightarrow{O_2 \text{ in air}} Fe(OH)_3(s)$ pale green solution → green ppt insoluble in excess NaOH(aq) → red-brown ppt
	$[Fe(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons [Fe(OH)_2(H_2O)_4](s) + 2H_2O(l)$ *OR* $[Fe(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Fe(OH)_2(s) + 6H_2O(l)$ $4Fe(OH)_2(s) + O_2(g) + 2H_2O(l) \rightarrow 4Fe(OH)_3(s)$
NH_3(aq)	$[Fe(H_2O)_6]^{2+}(aq) \underset{H^+(aq)}{\overset{NH_3(aq)}{\rightleftharpoons}} Fe(OH)_2(s) \xrightarrow{O_2 \text{ in air}} Fe(OH)_3(s)$ pale green solution → green ppt insoluble in excess NH_3(aq) → red-brown ppt
	$[Fe(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons [Fe(OH)_2(H_2O)_4](s) + 2H_2O(l)$ *OR* $[Fe(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Fe(OH)_2(s) + 6H_2O(l)$ $4Fe(OH)_2(s) + O_2(g) + 2H_2O(l) \rightarrow 4Fe(OH)_3(s)$
Na_2CO_3(aq)	$[Fe(H_2O)_6]^{2+}(aq) \underset{H^+(aq)}{\overset{CO_3^{2-}(aq)}{\rightleftharpoons}} FeCO_3(s)$ pale green solution → green ppt
	$[Fe(H_2O)_6]^{2+}(aq) + CO_3^{2-}(aq) \rightarrow FeCO_3(s) + 6H_2O(l)$
$K_3[Fe(CN)_6]$	$[Fe(H_2O)_6]^{2+}(aq) \xrightarrow{[Fe^{III}(CN)_6]^{3-}(aq)} Fe_3^{II}[Fe^{III}(CN)_6]_2(s)$ pale green solution → dark blue ppt (Turnbull's blue ppt)
	$3Fe^{2+}(aq) + 2[Fe(CN)_6]^{3-}(aq) \rightarrow Fe_3[Fe(CN)_6]_2(s)$

6.3 Iron(III) Ions

NaOH(aq)	$[Fe(H_2O)_6]^{3+}(aq)$ (yellow solution) $\underset{H^+(aq)}{\overset{OH^-(aq)}{\rightleftharpoons}}$ $Fe(OH)_3(s)$ (red-brown ppt, insoluble in excess NaOH(aq))
	$[Fe(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \rightleftharpoons [Fe(OH)_3(H_2O)_3](s) + 3H_2O(l)$ *OR* $[Fe(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Fe(OH)_3(s) + 6H_2O(l)$
NH_3(aq)	$[Fe(H_2O)_6]^{3+}(aq)$ (yellow solution) $\underset{H^+(aq)}{\overset{NH_3(aq)}{\rightleftharpoons}}$ $Fe(OH)_3(s)$ (red-brown ppt, insoluble in excess NH_3(aq))
	$[Fe(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \rightleftharpoons [Fe(OH)_3(H_2O)_3](s) + 3H_2O(l)$ *OR* $[Fe(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Fe(OH)_3(s) + 6H_2O(l)$
Na_2CO_3(aq) *refer to pg 30	$[Fe(H_2O)_6]^{3+}(aq)$ (yellow solution) $\underset{H^+(aq)}{\overset{CO_3^{2-}(aq)}{\rightleftharpoons}}$ $Fe(OH)_3(s)$ (red-brown ppt)
	$2Fe^{3+}(aq) + 3CO_3^{2-}(aq) + 3H_2O(l) \rightarrow 2Fe(OH)_3(s) + 3CO_2(g)$
$K_4[Fe(CN)_6]$	$[Fe(H_2O)_6]^{3+}(aq)$ (yellow solution) $\xrightarrow{[Fe^{II}(CN)_6]^{4-}(aq)}$ $Fe_4^{III}[Fe^{II}(CN)_6]_3(s)$ (dark blue ppt, (Prussian blue ppt))
	$4Fe^{3+}(aq) + 3[Fe(CN)_6]^{4-}(aq) \rightarrow Fe_4[Fe(CN)_6]_3(s)$
NaSCN(aq) / NH_4SCN(aq) *refer to pg 29	$[Fe(H_2O)_6]^{3+}(aq)$ (yellow solution) $\xrightarrow{SCN^-(aq)}$ $[Fe(SCN)(H_2O)_5]^{2+}(aq)$ (blood red solution)
	$[Fe(H_2O)_6]^{3+}(aq) + SCN^-(aq) \rightleftharpoons [Fe(SCN)(H_2O)_5]^{2+}(aq) + H_2O(l)$

6.4 Chromium(III) Ions

NaOH(aq) *refer to pg 30	$[Cr(H_2O)_6]^{3+}(aq)$ (green solution) $\underset{H^+(aq)}{\overset{OH^-(aq)}{\rightleftharpoons}}$ $Cr(OH)_3(s)$ (grey-green ppt) $\underset{H^+(aq)}{\overset{\text{excess } OH^-}{\rightleftharpoons}}$ $[Cr(OH)_6]^{3-}(aq)$ (dark green solution)
	$[Cr(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \rightleftharpoons [Cr(OH)_3(H_2O)_3](s) + 3H_2O(l)$ *OR* $[Cr(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Cr(OH)_3(s) + 6H_2O(l)$ $[Cr(OH)_3(H_2O)_3](s) + 3OH^-(aq) \rightleftharpoons [Cr(OH)_6]^{3-}(aq) + 3H_2O(l)$
NH_3(aq)	$[Cr(H_2O)_6]^{3+}(aq)$ (green solution) $\underset{H^+(aq)}{\overset{NH_3(aq)}{\rightleftharpoons}}$ $Cr(OH)_3(s)$ (grey-green ppt, insoluble in excess NH_3(aq))
	$[Cr(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \rightleftharpoons [Cr(OH)_3(H_2O)_3](s) + 3H_2O(l)$ *OR* $[Cr(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Cr(OH)_3(s) + 6H_2O(l)$
Na_2CO_3(aq) *refer to pg 30	$[Cr(H_2O)_6]^{3+}(aq)$ (green solution) $\underset{H^+(aq)}{\overset{CO_3^{2-}(aq)}{\rightleftharpoons}}$ $Cr(OH)_3(s)$ (grey-green ppt)
	$2Cr^{3+}(aq) + 3CO_3^{2-}(aq) + 3H_2O(l) \rightarrow 2Cr(OH)_3(s) + 3CO_2(g)$

6.5 Manganese(II) Ions

NaOH(aq)	$[Mn(H_2O)_6]^{2+}(aq)$ (pale pink / colourless solution) $\underset{H^+(aq)}{\overset{OH^-(aq)}{\rightleftharpoons}}$ $Mn(OH)_2(s)$ (off-white ppt insoluble in excess NaOH(aq)) $\xrightarrow{O_2 \text{ in air}}$ $Mn(OH)_3(s)$ (brown ppt)
	$[Mn(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons [Mn(OH)_2(H_2O)_4](s) + 2H_2O(l)$ *OR* $[Mn(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Mn(OH)_2(s) + 6H_2O(l)$ $4Mn(OH)_2(s) + O_2(g) + 2H_2O(l) \rightarrow 4Mn(OH)_3(s)$
NH_3(aq)	$[Mn(H_2O)_6]^{2+}(aq)$ (pale pink / colourless solution) $\underset{H^+(aq)}{\overset{NH_3(aq)}{\rightleftharpoons}}$ $Mn(OH)_2(s)$ (off-white ppt insoluble in excess NH_3(aq)) $\xrightarrow{O_2 \text{ in air}}$ $Mn(OH)_3(s)$ (brown ppt)
	$[Mn(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons [Mn(OH)_2(H_2O)_4](s) + 2H_2O(l)$ *OR* $[Mn(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Mn(OH)_2(s) + 6H_2O(l)$ $4Mn(OH)_2(s) + O_2(g) + 2H_2O(l) \rightarrow 4Mn(OH)_3(s)$
Na_2CO_3(aq)	$[Mn(H_2O)_6]^{2+}(aq)$ (pale pink / colourless solution) $\underset{H^+(aq)}{\overset{CO_3^{2-}(aq)}{\rightleftharpoons}}$ $MnCO_3(s)$ (white ppt)
	$[Mn(H_2O)_6]^{2+}(aq) + CO_3^{2-}(aq) \rightarrow MnCO_3(s) + 6H_2O(l)$

Example 20

The reaction scheme starting from a solution containing chromium(III) ions is shown below. Both **M** and **N** are chromium-containing species.

$$Cr^{3+}(aq) \xrightarrow[\textbf{I}]{NaOH(aq)} \underset{\text{(green ppt)}}{\textbf{M}} \xrightarrow[\textbf{II}]{\text{excess NaOH(aq)}} \textbf{N} \xrightarrow[\textbf{III}]{H_2O_2(aq)} CrO_4^{2-}(aq)$$

Which of the following statements is correct?

A Hydroxide ions act as ligands in Step **I**.

B A redox reaction has occurred in Step **II**.

C **N** is a dark green solution containing $[Cr(OH)_6]^{3-}$.

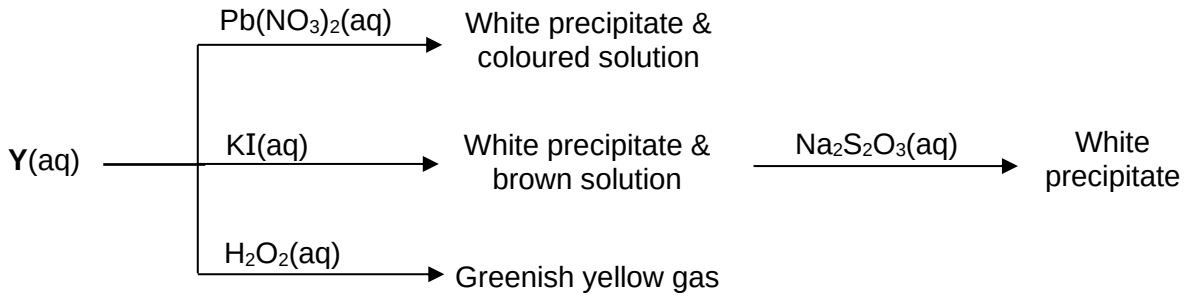
D An acidic medium is required for the formation of CrO_4^{2-}.

M is $Cr(OH)_3$; **N** is $[Cr(OH)_6]^{3-}$.

Steps **I** and **II** are acid-base reactions, where hydroxide ions act as bases.

An alkaline medium is required for the formation of CrO_4^{2-} (see pg 30).

Example 21



The compound **Y** in the above reaction scheme is

A $FeCl_3$ **B** $CuCl_2$ **C** $CuSO_4$ **D** $Fe_2(SO_4)_3$

Compound **Y** contains Cu^{2+}, which reacts with KI(aq) to give a white precipitate and brown solution.

$$\underset{\text{blue}}{2Cu^{2+}(aq)} + \underset{\text{colourless}}{4I^-(aq)} \rightarrow \underset{\text{white ppt}}{2CuI(s)} + \underset{\text{brown}}{I_2(aq)}$$

Compound **Y** contains Cl^-, which forms a white $PbCl_2$ precipitate with $Pb^{2+}(aq)$. Blue solution of $Cu^{2+}(aq)$ remains.

$$Pb^{2+}(aq) + Cl^-(aq) \rightarrow PbCl_2(s)$$

The Cl^- present is oxidised by $H_2O_2(aq)$ to form a greenish yellow Cl_2 gas.

$$H_2O_2(aq) + 2\,Cl^-(aq) + 2\,H^+(aq) \rightarrow Cl_2(g) + 2\,H_2O(l)$$

Example 22

When Na metal is added to a green solution of $Cr(NO_3)_3$ (aq), effervescence of H_2 gas is evolved. When drops of NaOH (aq) were added to a green solution of $Cr(NO_3)_3$ (aq), a grey-green precipitate was formed. The precipitate dissolved when excess NaOH (aq) was added, forming a dark green solution. Subsequent additions of liquid ammonia caused the solution to turn violet.

According to the information given above, which of the following statements are correct?

1 The grey-green precipitate is $Cr(OH)_3$ (aq).

2 When ammonia is added, it is a ligand exchange reaction.

3 The green solution of $Cr(NO_3)_3$ (aq) is acidic due to the high charge density of Cr^{3+}.

The green solution of $Cr(NO_3)_3$ (aq) is acidic (see pg 30), and the $H_3O^+(aq)$ produced reacts with Na to give $H_2(g)$.

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

When drops of NaOH (aq) were added to $Cr^{3+}(aq)$, a grey-green precipitate of $Cr(OH)_3$ was formed. The precipitate dissolved in excess NaOH(aq) to give a dark green solution of $[Cr(OH)_6]^{3-}$ (aq).

$$[Cr(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \rightleftharpoons [Cr(OH)_3(H_2O)_3](s) + 3H_2O(l)$$
$$[Cr(OH)_3(H_2O)_3](s) + 3OH^-(aq) \rightleftharpoons [Cr(OH)_6]^{3-}(aq) + 3H_2O(l)$$

A ligand exchange reaction occurred when liquid ammonia was added.

$$[Cr(H_2O)_6]^{3+}(aq) + 6\,NH_3(l) \rightleftharpoons [Cr(NH_3)_6]^{3+}(aq) + 6\,H_2O(l)$$

7. APPENDIX

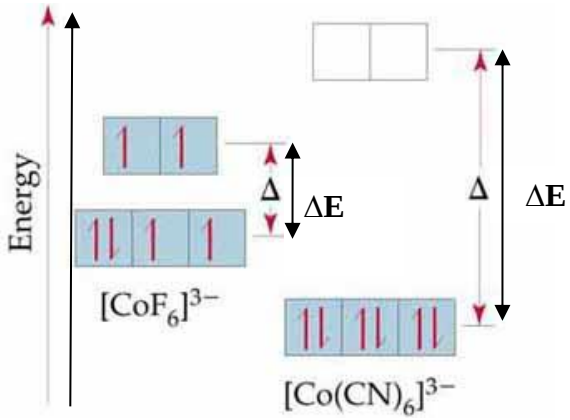
7.1 Magnetic Properties of a Complex Ion

The crystal field model also helps us understand the magnetic properties

Paramagnetic substances are those that contain net unpaired spins and are attracted by a magnet. It happens when two electrons have the same, or parallel spins (e.g. ↑↑ or ↓↓)

Diamagnetic substances do not contain net unpaired spins and are slightly repelled by a magnet (e.g. ↓↑ or ↑↓, where the magnetic effects cancel out)

For complex ions, the magnitude of the field splitting (ΔE) also determines the magnetic properties.



F^- is a **weak-field ligand**, and the energy gap, ΔE, between the d orbitals is not as large. Hence, the five d electrons occupy five separate d orbitals with parallel spins to create a high-spin complex.	**CN^-** is a **strong-field ligand**, causing the d orbitals to split with a larger energy gap between them. It is more energetically favourable for the five d electrons to be in the lower orbitals than in the higher energy orbitals, as the spin-pairing energy is smaller than ΔE. Hence the electrons are paired in the lower energy orbitals forming a low-spin complex.
The $[CoF_6]^{3-}$ complex is referred to as a **high-spin complex**. The electrons are arranged so that they remain unpaired as much as possible. On the other hand, the $[Co(CN)_6]^{3-}$ ion is referred to as a **low-spin complex.** High-spin complexes are more *paramagnetic* than low-spin complexes.	