

# 22 An Introduction to the Chemistry of Transition Elements

## GUIDING QUESTIONS

- What are transition elements?
- What are the characteristic properties of transition elements? How are these properties similar or different from a typical s-block element?
- Are there any trends/patterns in the properties of transition elements?
- What are some examples/applications of transition elements/their compounds?

## LEARNING OUTCOMES

Students should be able to:

*For the first set of transition elements, titanium to copper*

- 13 (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
- 13 (b) state the electronic configuration of a first row transition element and its ion (Refer to Topic 1 Atomic Structure and Physical Periodicity)
- 13 (c) explain why atomic radii and first ionisation energies of the transition elements are relatively invariant (Refer to Topic 1 Atomic Structure and Physical Periodicity)
- 13 (d) contrast, qualitatively, the melting point and density of the transition elements with those of calcium as a typical s-block element
- 13 (e) describe the tendency of transition elements to have variable oxidation states
- 13 (f) predict from a given electronic configuration, the likely oxidation states of a transition element
- 13 (g) describe and explain the use of  $\text{Fe}^{3+}/\text{Fe}^{2+}$ ,  $\text{MnO}_4^-/\text{Mn}^{2+}$  and  $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$  as examples of redox systems (Refer to Topic 20 Electrochemistry)
- 13 (h) predict, using  $E^\ominus$  values, the likelihood of redox reactions (Refer to Topic 20 Electrochemistry)
- 13 (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)
- 13 (j) explain qualitatively that ligand exchange may occur, as exemplified by the formation of the complexes in (i), including the colour changes involved, and  $\text{CO}/\text{O}_2$  exchange in haemoglobin
- 13 (k) describe, using the shape and orientation of the d orbitals, the splitting of degenerate d orbitals into two energy levels in octahedral complexes
- 13 (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]
- 13 (m) explain how some transition elements and/or their compounds can act as catalysts (Refer to Topic 6 Reaction Kinetics)

## REFERENCES

1. P. Cann & P. Hughes, *Chemistry*, 2<sup>nd</sup> Edition, Hodder Education, Chapter 24.
2. P. W. Atkins, M. T. Weller, T. L. Overton, J. P. Rourke & F. A. Armstrong, *Inorganic Chemistry*, 6<sup>th</sup> Edition, Oxford University Press, Chapter 7, 20 and 21.
3. P. Amateis & M. Silberberg, *Chemistry: the molecular nature of matter and change*, 7<sup>th</sup> Edition, McGraw-Hill Education, Chapter 23.

**LOOKING BACK**

In this topic, you will learn about the chemical and physical properties of the first row transition elements and compare them with the main group metals, applying knowledge from earlier topics such as Atomic Structure, Chemical Bonding, Physical Periodicity, Equilibria and Electrochemistry.

**1 INTRODUCTION****1.1 Definition of Transition Elements**

LO 13(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

**Transition elements** are d-block elements that form one or more stable ions with partially filled d subshell.

By this definition, both scandium and zinc will be **excluded** from the class of transition elements, even though they are part of d-block elements. This is because:

- Scandium forms only  $\text{Sc}^{3+}$  ion which has no electron in the 3d subshell ( $3d^0$ ).
- Zinc forms only  $\text{Zn}^{2+}$  ion which has 10 electrons in the 3d subshell ( $3d^{10}$ ).

**1.2 Electronic Configurations of First Row Transition Elements and its ions (covered in Topic 1 Atomic Structure and Physical Periodicity)**

LO 13(b): state the electronic configuration of a first row transition element and its ion

Atom	No. of electrons	Full electronic configuration	Electron-in-box representation					
			3d					4s
Sc Scandium ^	21	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$	[Ar]	↑				↑↓
Ti Titanium	22	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$	[Ar]	↑	↑			↑↓
V Vanadium	23	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$	[Ar]	↑	↑	↑		↑↓
Cr Chromium*	24	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$	[Ar]	↑	↑	↑	↑	↑
Mn Manganese	25	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$	[Ar]	↑	↑	↑	↑	↑↓
Fe Iron	26	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$	[Ar]	↑↓	↑	↑	↑	↑↓
Co Cobalt	27	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$	[Ar]	↑↓	↑↓	↑	↑	↑↓
Ni Nickel	28	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$	[Ar]	↑↓	↑↓	↑↓	↑	↑↓
Cu Copper*	29	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$	[Ar]	↑↓	↑↓	↑↓	↑↓	↑
Zn Zinc ^	30	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓

Table 1. Electronic configuration of first row elements from d-block.

^ Sc and Zn are not part of transition elements.

\* Cr and Cu are two exceptions to the general pattern of electronic configurations.



Ion	No. of electrons	Full electronic configuration	Electron-in-box representation					
				3d				
Sc <sup>3+</sup>	18	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>0</sup>	[Ar]					
Ti <sup>2+</sup>	20	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>2</sup>	[Ar]	↑	↑			
V <sup>3+</sup>	20	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>2</sup>	[Ar]	↑	↑			
Cr <sup>3+</sup>	21	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>3</sup>	[Ar]	↑	↑	↑		
Mn <sup>2+</sup>	23	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>5</sup>	[Ar]	↑	↑	↑	↑	↑
Fe <sup>2+</sup>	24	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>6</sup>	[Ar]	↑↓	↑	↑	↑	↑
Co <sup>2+</sup>	25	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>7</sup>	[Ar]	↑↓	↑↓	↑	↑	↑
Ni <sup>2+</sup>	26	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>8</sup>	[Ar]	↑↓	↑↓	↑↓	↑	↑
Cu <sup>2+</sup>	27	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>9</sup>	[Ar]	↑↓	↑↓	↑↓	↑↓	↑
Zn <sup>2+</sup>	28	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup>	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓

Table 2. Electronic configuration of selected ions of first row d-block elements.

### 1.3 Physical Properties of Transition Elements

LO 13(c): explain why atomic radii and first ionisation energies of the transition elements are relatively invariant (Refer to Topic 1 Atomic Structure and Physical Periodicity)

LO 13(d): contrast, qualitatively, the melting point and density of the transition elements with those of calcium as a typical s-block element

The atomic radii and first ionisation energies of the transition elements are relatively invariant. These concepts have been covered in Topic 1 Atomic Structure and Physical Periodicity.

The melting points of transition elements are higher than s-block elements, as both 3d and 4s electrons are involved in the metallic bonding in transition element.

The densities of transition elements are higher than s-block elements because the atomic radii of transition elements are smaller than s-block elements.

#### Lecture Exercise 1.1

Calcium is a fairly soft, silvery-grey metal which quickly tarnishes in air. Vanadium is a hard grey metal which is resistant to corrosion at ordinary temperatures. Metallic calcium has no commercial uses; vanadium is widely used as an alloying element in steels. Data about calcium and vanadium are given below.

	calcium	vanadium
electronic configuration	[Ar] 4s <sup>2</sup>	[Ar] 3d <sup>3</sup> 4s <sup>2</sup>
atomic radius/nm	0.197	0.135
melting point/°C	843	1710
density/g cm <sup>-3</sup>	1.54	6.07

- a) The melting point of vanadium is significantly higher than that of calcium. Explain this in terms of the type and strength of bonding in each metal.
- b) Explain why the density of vanadium is significantly higher than that of calcium.

#### 1.4 Chemical Properties of Transition Elements

The transition elements and their compounds display the following chemical properties that are different from s-block elements and their compounds.

Properties	Examples
Tendency to have variable oxidation states	<ul style="list-style-type: none"> <li>Manganese: +2 in <math>\text{Mn}^{2+}</math>, +4 in <math>\text{MnO}_2</math>, +7 in <math>\text{MnO}_4^-</math></li> <li>Iron: +2 in <math>\text{Fe}^{2+}</math>; +3 in <math>\text{Fe}^{3+}</math></li> </ul>
Catalytic properties	<ul style="list-style-type: none"> <li>Iron, Fe, in the Haber process (manufacturing of ammonia)</li> <li>Nickel, Ni, in hydrogenation of alkene</li> <li>Vanadium(V) oxide, <math>\text{V}_2\text{O}_5</math>, in the Contact process (manufacturing of sulfuric acid)</li> <li><math>\text{Fe}^{2+}</math> ion in <math>\text{I}^-/\text{S}_2\text{O}_8^{2-}</math> reaction</li> </ul>
Formation of complex ions	<ul style="list-style-type: none"> <li><math>[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}</math>, <math>[\text{Fe}(\text{CN})_6]^{3-}</math>, <math>[\text{Ag}(\text{NH}_3)_2]^+</math></li> </ul>
Formation of coloured ions	<ul style="list-style-type: none"> <li><math>\text{Cu}^{2+}(\text{aq})</math>: pale blue, <math>\text{Cr}_2\text{O}_7^{2-}(\text{aq})</math>: orange</li> <li><math>\text{Fe}^{3+}(\text{aq})</math>: yellow</li> </ul>

Table 3. Chemical properties of transition elements.



## 2 VARIABLE OXIDATION STATES

LO 13(e): describe the tendency of transition elements to have variable oxidation states

The transition elements show variable oxidation states due to the close similarity in energy of the 4s and 3d electrons. Hence, once the 4s electrons are removed, some or all the 3d electrons may also be removed without requiring much more energy.

In contrast, the s-block elements are limited to form compounds with oxidation states of +1 (Group 1) or +2 (Group 2). This is because once the outermost electrons in the s orbital are removed, subsequent removal of electrons would be from the inner quantum shell which requires too much energy.

				+7					
			+6	+6	+6				
		+5	+5	+5	+5	+5			
	+4	+4	+4	+4	+4	+4	+4		
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+2	+2	+2	+2	+2	+2	+2	+2	+2
	+1	+1	+1	+1	+1	+1	+1	+1	
Sc scandium	Ti titanium	V vanadium	Cr chromium	Mn manganese	Fe iron	Co cobalt	Ni nickel	Cu copper	Zn zinc

Table 4. Known oxidation states of d-block metals. The more familiar oxidation states are shaded. Other oxidation states can only be stabilised under special conditions.

Scandium and zinc, which are not part of transition elements, can only form one oxidation state, as shown in Table 4 above.

### General trends in oxidation states of transition elements

LO 13(f): predict from a given electronic configuration, the likely oxidation states of a transition element

- In their elemental states, the elements are assigned an oxidation number of zero.
- The value of the maximum oxidation number for the elements suggests that in each element, all the **available 3d and 4s electrons** may be used for bonding to form various compounds (either ionic bond by losing electrons or covalent bond by sharing electrons).
- The lower oxidation state metals are usually found in ionic compounds, e.g.  $\text{FeSO}_4$  and  $\text{MnCl}_2$ .
- The higher oxidation state metals tend not to exist as free ions, e.g.  $\text{Mn}^{7+}$  or  $\text{Cr}^{6+}$  do not exist. However, they are involved in covalent bonds, such as  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Mn}_2\text{O}_7$  and oxo-anions (e.g.  $\text{VO}_3^-$ ,  $\text{CrO}_4^{2-}$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{MnO}_4^-$ ).
- The number of available oxidation states of the elements increases from Ti to Mn and decreases from Mn to Cu. After Mn ( $3d^5$ ), **pairing of d-electrons occurs** such that there is a decrease in the number of electrons available for bond formation. This results in the decrease in the number of oxidation states exhibited by the elements with more than five d-electrons (from Fe to Cu).

**Lecture Exercise 2.1**

1. The table shows the possible oxidation states of five d-block elements in the Periodic Table. (The elements are represented by letters which are not their symbols.)

element	possible oxidation numbers						
P	–	–	3	–	–	–	–
Q	–	2	3	4	–	–	–
R	1	2	3	4	5	–	–
S	–	–	3	4	5	6	–
T	–	2	–	4	5	6	7

Which of the following ions is likely to exist?

- A**  $\text{PO}^{2+}$       **B**  $\text{QO}_3^-$       **C**  $\text{RO}_4^{2-}$       **D**  $\text{TO}_2^{2+}$

2. Titanium has the electronic structure  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$ . Which of the following compounds does **not** exist?

- A**  $\text{K}_2\text{TiO}_4$       **B**  $\text{K}_3\text{TiF}_6$       **C**  $\text{TiCl}_3$       **D**  $\text{TiO}$

3. The electronic configuration of vanadium is  $[\text{Ar}] 3d^3 4s^2$ . Which of the following ions does **not** exist?

- A**  $\text{VO}^{2+}$       **B**  $\text{VO}_2^+$       **C**  $\text{VO}_3^{2-}$       **D**  $\text{VO}_4^{2-}$

**Redox reactions involving transition elements**

LO 13(g): describe and explain the use of  $\text{Fe}^{3+}/\text{Fe}^{2+}$ ,  $\text{MnO}_4^-/\text{Mn}^{2+}$  and  $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$  as examples of redox systems

One of the applications of transition metal compounds is in the field of redox chemistry. In general, ions that have the transition metal in a high oxidation state tend to be oxidising agents (e.g.  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{MnO}_4^-$ ) while transition metal in low oxidation state tends to be reducing agents (e.g.  $\text{Cr}^{2+}$ ,  $\text{V}^{2+}$ ). When transition metal ions undergo redox reactions, a colour change is usually observed.

Common redox systems involving transition elements include:

$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$ yellow      pale green	As a homogeneous catalyst in the redox reaction between iodide ions and peroxodisulfate ions.
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$ purple      colourless	As an oxidising agent for organic compounds such as oxidation of primary alcohols to carboxylic acids.
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$ orange      green	

To predict whether a redox reaction is feasible, or to explain colour changes due to redox reactions, we can make use of  $E^\ominus$  values of the relevant species to find overall  $E^\ominus_{\text{cell}}$ , as learnt in Topic 20 Electrochemistry.

**If  $E^\ominus_{\text{cell}} > 0$ , redox reaction is feasible.**



LO 13(h): predict, using  $E^\circ$  values, the likelihood of redox reactions

### Lecture Exercise 2.2

By quoting and using relevant  $E^\circ$  values from the *Data Booklet*, explain each of the following observations. Write balanced equations for the reactions.

- (i) The green precipitate obtained when aqueous sodium hydroxide is added to aqueous iron(II) sulfate rapidly turns brown on exposure to air.
- (ii) The blue solution, containing  $\text{Cr}^{2+}(\text{aq})$ , obtained by dissolving chromium metal in dilute sulfuric acid slowly turns green even in the absence of air.

### 3 CATALYTIC PROPERTIES

LO 13(m): explain how some transition elements and/or their compounds can act as catalysts

Transition elements, both in the elemental form and in their compounds, are important catalysts. We have learnt about catalysts and their mode of action in Topic 6 Reaction Kinetics. In this section, pay attention to the part played by transition elements and why they are able to act as catalysts. Also learn to apply your knowledge of  $E^\ominus$  values to explain the mechanism of homogeneous catalysis.

A **catalyst** is a substance that increases the rate of a reaction by providing an alternative reaction pathway that requires lower activation energy than the uncatalysed reaction. The catalyst does not undergo any permanent chemical change during the process.

Transition elements and their compounds can act as heterogeneous catalysts as well as homogeneous catalysts:

Type	Homogeneous Catalyst	Heterogeneous Catalyst
phase of catalyst vs. phase of reactants	Catalyst operates in the same phase as the reactants	Catalyst operates in a different phase as the reactants (most commonly the catalysts are solids, and the reactants are gases)
reason why the transition metal or its compound could act as this type of catalyst	Variable oxidation states of the transition metal in its ions	Availability of partially filled 3d orbitals to accept electron pairs from, or donate electrons pairs to reactant molecules, for adsorption of reactant molecules onto the surface of the catalyst.



### 3.1 Heterogeneous Catalysis

In heterogeneous catalysis, the catalyst and the reactants are in different physical phases.

- The catalyst is usually in the solid phase and it provides active sites at which the reaction can take place.
- The reactants are usually gases or liquids.

Example: Haber process (manufacturing of ammonia)

Reaction:  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

Catalyst: finely divided Fe(s) or  $\text{Fe}_2\text{O}_3(\text{s})$

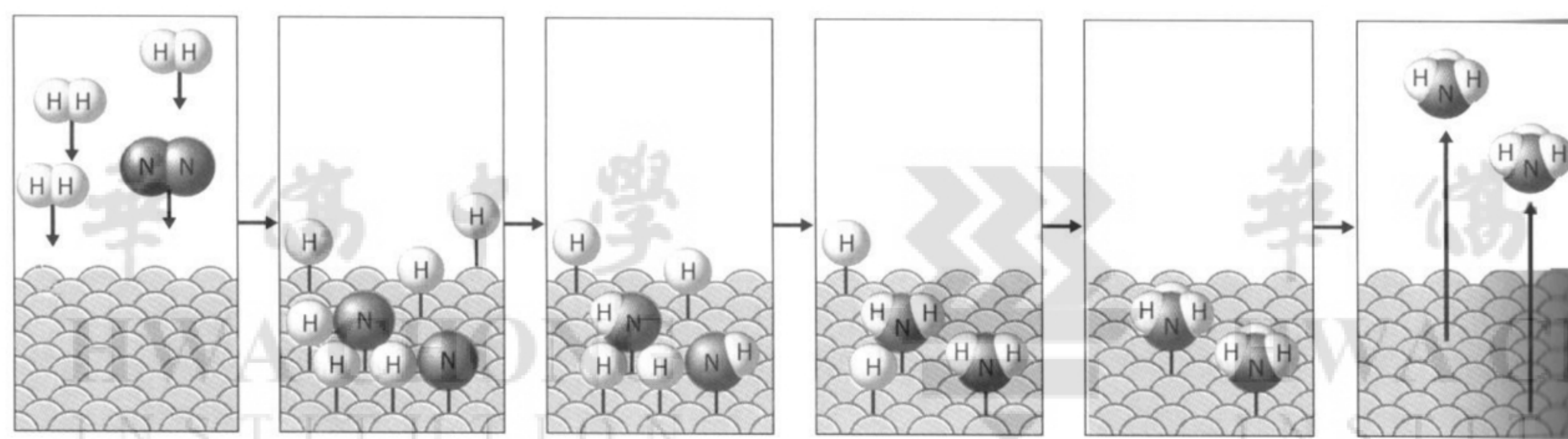


Figure 1. Heterogeneous catalysis in the Haber Process

#### Mode of action of the catalyst

- Adsorption: Gaseous reactant molecules,  $\text{N}_2$  and  $\text{H}_2$ , diffuse towards surface of the Fe catalyst.  $\text{N}_2$  and  $\text{H}_2$  adsorb onto the active sites of Fe catalyst by formation of weak attraction forces.
- The adsorption process brings reactant molecules closer together, thus increasing their surface concentration at the catalyst surface; weakens the  $\text{N}\equiv\text{N}$  and  $\text{H}-\text{H}$  bonds in them; and allows these molecules to be orientated in the right positions for reaction to form new bonds between N and H. All these lower the activation energy of the reaction.
- Desorption: Product molecule,  $\text{NH}_3$ , desorbs and diffuses away from catalyst surface so that active sites are exposed for further reaction.

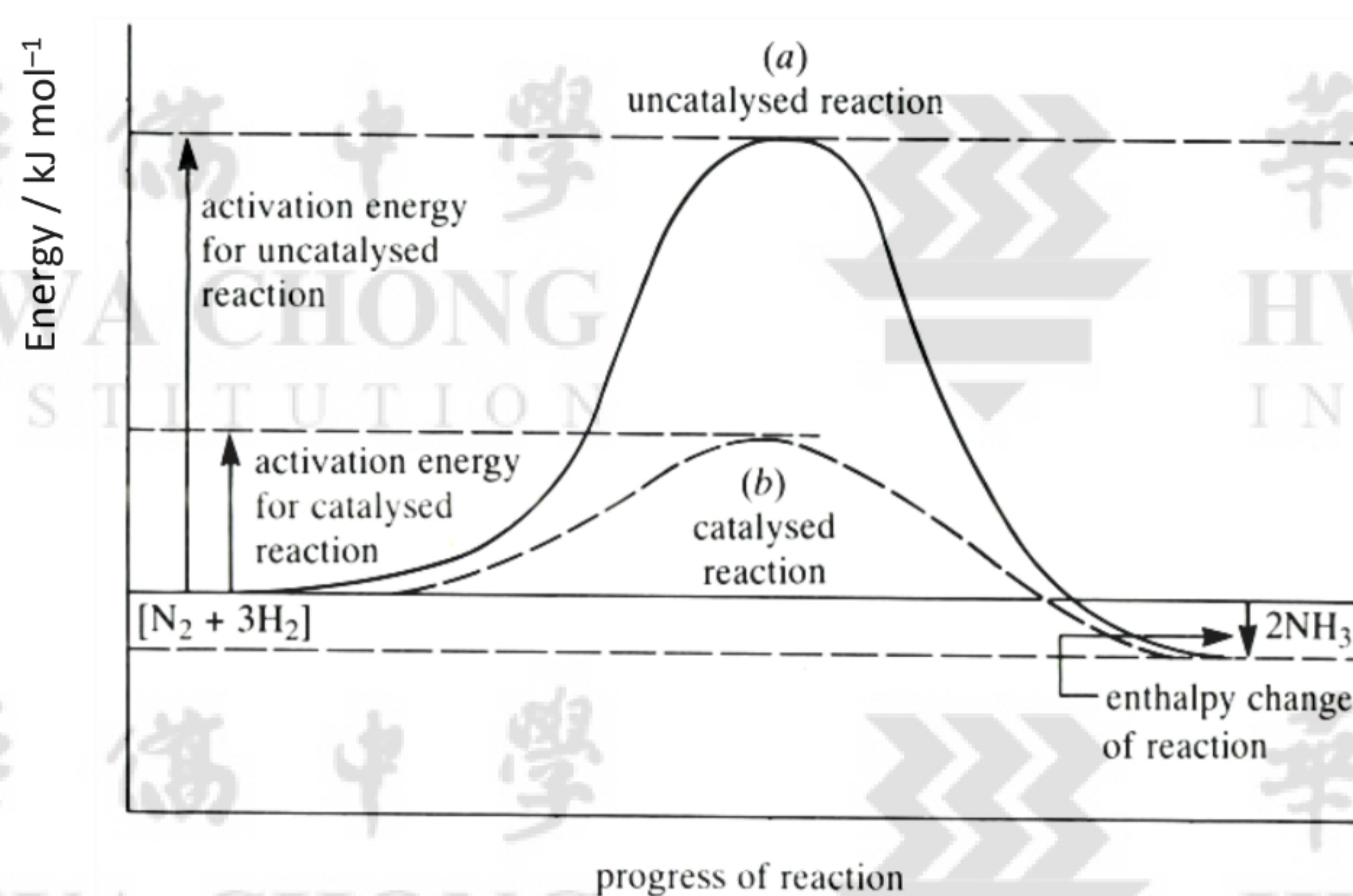


Figure 2. Energy profile diagrams for the catalysed and uncatalysed reactions.

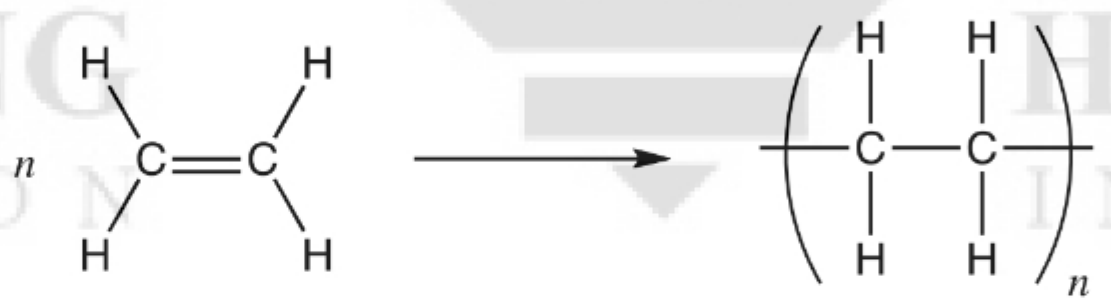


Figure 2 shows the energy profile diagram for the catalysed and uncatalysed reactions.

Important points to note:

- A catalyst speeds up the forward and the reverse reactions.
- A reaction with a catalyst does not yield more product than one without a catalyst, but it yields the product more quickly.
- A catalyst provides a different mechanism for the reaction, with a new, lower activation energy pathway.
- A catalyst does not alter the enthalpy change of reaction.

#### Other heterogeneous catalysts used in the chemical industry

Heterogeneous catalyst	Reaction catalysed
$V_2O_5$	Contact process $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
Ni	Hydrogenation of vegetable oils to make margarine $RCH=CH_2 + H_2(g) \rightarrow RCH_2CH_3$
$TiCl_3$ , $Al_2(C_2H_5)_6$ Ziegler-Natta catalyst	Polymerisation of ethene to poly(ethene) 

### 3.2 Homogeneous Catalysis

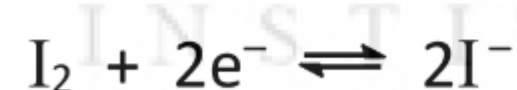
In homogeneous catalysis, the catalyst and the reactants are dispersed in the same phase (either liquid or gaseous).

The relative ease of inter-conversion between the different oxidation states of transition metals enables them to act as homogeneous catalysts.

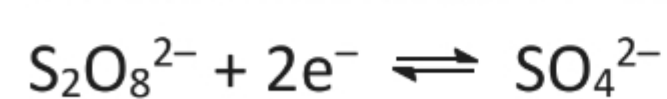
We shall use the same example of homogeneous catalyst given in Topic 6 Reaction Kinetics: the oxidation of iodide ion,  $I^-$ , by peroxodisulfate ion,  $S_2O_8^{2-}$ .

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

Catalyst: aqueous iron(III) ions



$$E^\ominus = +0.54 \text{ V}$$



$$E^\ominus = +2.01 \text{ V}$$

Based on the data above, the reaction is found to have  $E^\ominus_{\text{cell}} = +1.47 \text{ V}$ , which is expected to occur spontaneously. However, the rate of the reaction is found to be very slow. The electrostatic repulsion between the two negatively charged ions causes the reaction to have a high activation energy and hence to proceed very slowly.

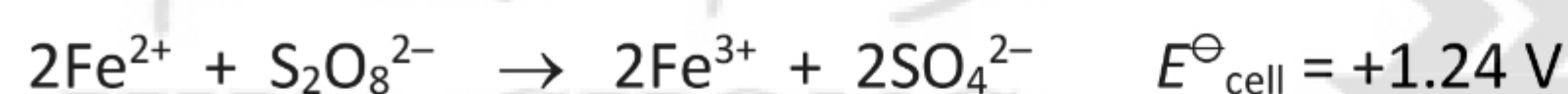


Aqueous iron(III) ions can catalyse this reaction via an alternative pathway involving 2 steps:

*Step 1:  $\text{Fe}^{3+}$  oxidises iodide, itself reduced to  $\text{Fe}^{2+}$*



*Step 2:  $\text{Fe}^{2+}$  reduces peroxodisulfate, itself oxidised to  $\text{Fe}^{3+}$ , thus  $\text{Fe}^{3+}$  is regenerated*



This 2-step alternative pathway requires a lower activation energy because both steps involve collision between two oppositely charged ions.  $\text{Fe}^{3+}$  is regenerated at the end of the reaction.

If  $\text{Fe}^{2+}$  were present at the start instead, the two steps above will take place in the reverse order and the net effect will still be the same.

Note that the  $E^{\ominus}_{\text{cell}}$  value for both steps are also positive, because:



Other redox couples of transition metal cations could also be used as catalysts in this reaction as long as their  $E^{\ominus}$  values were between +0.54 V and +2.01 V, such that each of the two steps in the alternative pathway are feasible.

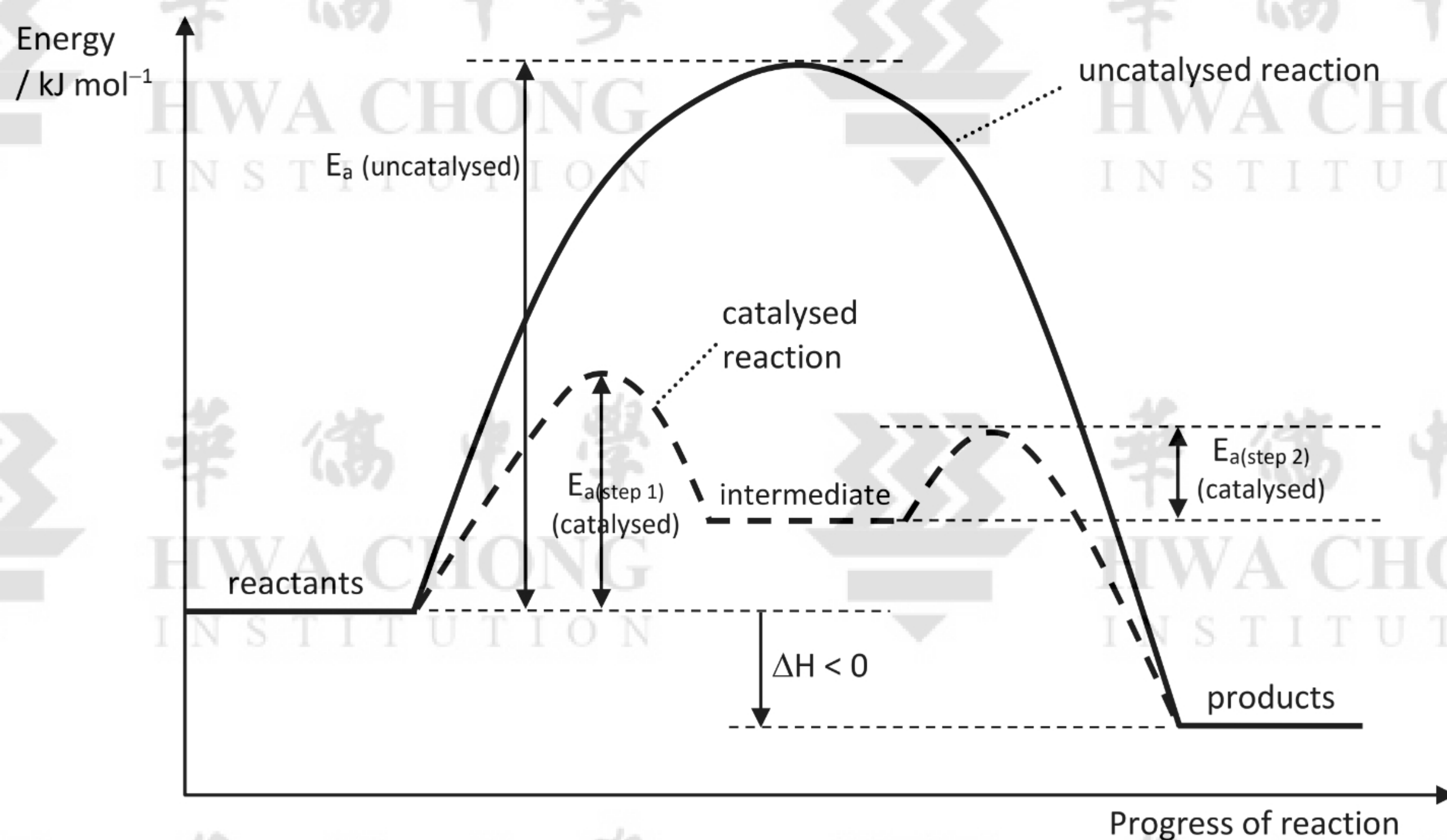
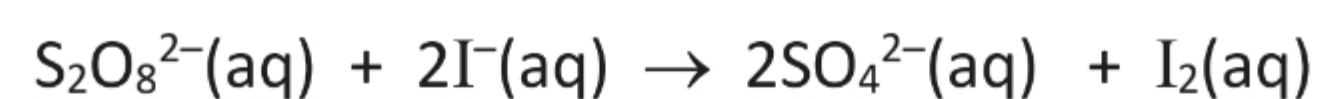


Figure 3. Energy profile diagrams for a catalysed and uncatalysed reaction

**Self-Practice 3.1**

The rate of the reaction between iodide and peroxodisulfate(VI) ions



is increased by the presence of small concentrations of  $\text{Co}^{2+}(\text{aq})$ . Suggest how  $\text{Co}^{2+}(\text{aq})$  ions are able to participate in this reaction.



## 4 TRANSITION METAL COMPLEXES

LO 13(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)

### 4.1 Introduction

Transition elements and their ions tend to form complexes.

A **complex** is a molecule or ion formed by a central metal atom or ion surrounded by one or more ligands.

When white anhydrous  $\text{CuSO}_4$  solid is dissolved in water, a pale blue solution is formed. In water,  $\text{Cu(II)}$  exists as the aqua complex, with formula  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ . When we write “ $\text{Cu}^{2+}(\text{aq})$ ”, it refers to  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ .

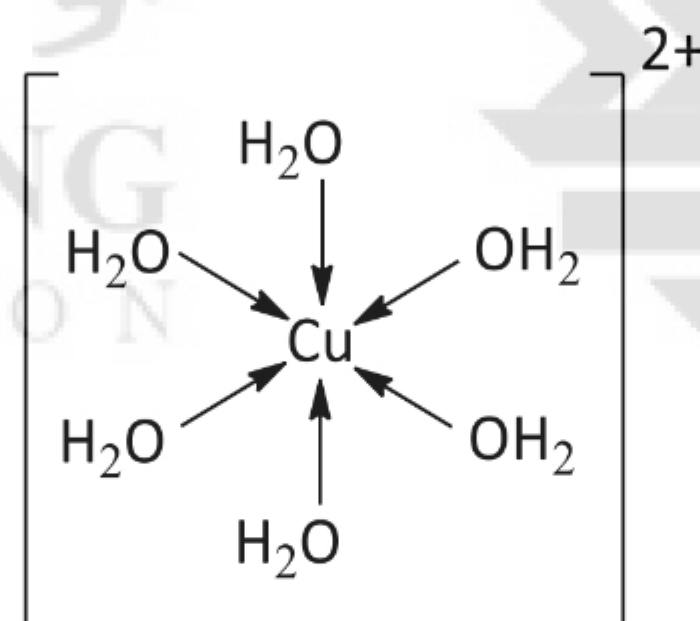
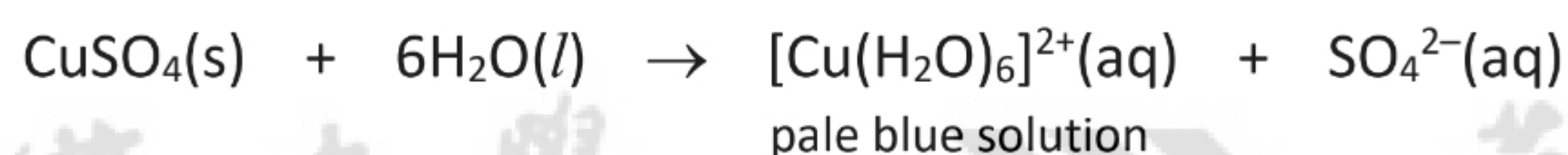


Figure 4. Copper(II) complex with water

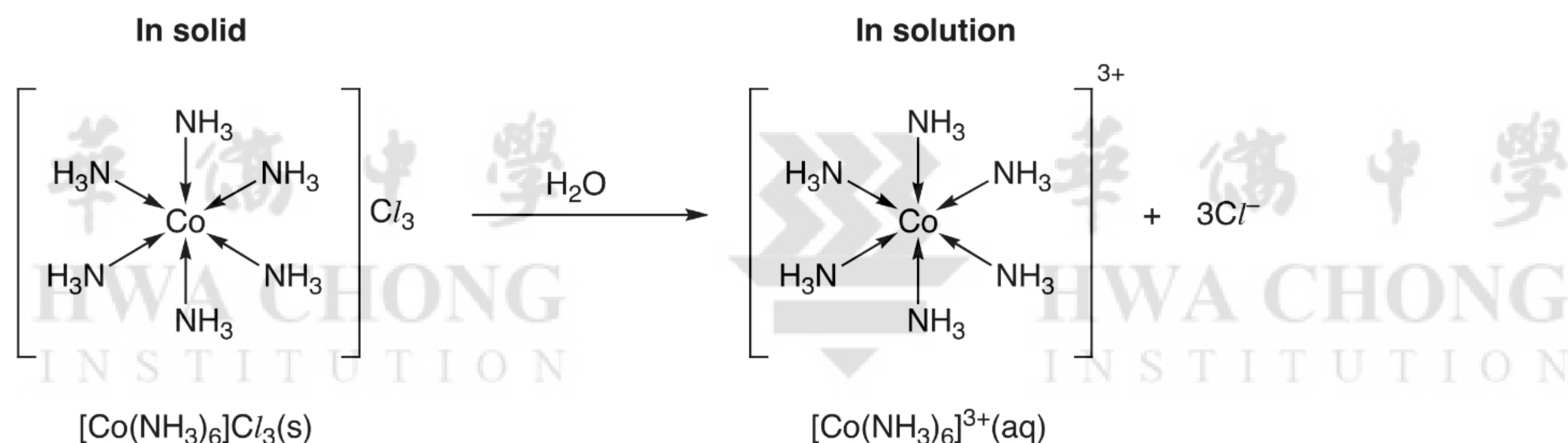
- In this complex, the central metal ion is  $\text{Cu}^{2+}$ , with six  $\text{H}_2\text{O}$  molecules acting as ligands.
- Each  $\text{H}_2\text{O}$  molecule bonds to the  $\text{Cu}^{2+}$  ion by forming a **coordinate (dative) bond**.
- Notice that the formula of a complex ion is usually written with a square bracket, the charge of the complex is indicated outside the square bracket.
- This complex is called the ‘aqua complex’ since its ligands are water.

A complex 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. The charge on the central metal is the oxidation number of the metal in that complex ion.

Type of complex	Central ion / atom	Ligands	Complex
Neutral	Ni	CO	$\text{Ni}(\text{CO})_4$
Cationic	$\text{Cu}^{2+}$	$\text{H}_2\text{O}$	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
Anionic	$\text{Fe}^{2+}$	$\text{CN}^-$	$[\text{Fe}(\text{CN})_6]^{4-}$

To maintain charge neutrality, complex ion is typically associated with **counter ions**, as in the case of the compound  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ , in which the complex ion is  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , the six  $\text{NH}_3$  molecules acting as ligands, and the three  $\text{Cl}^-$  ions are counter ions. So the whole compound is like a salt.

When  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  dissolves in water, the complex ion and counter ions separate from each other. The complex ion behaves like a polyatomic ion with **the ligands remaining attached to the central metal ion/atom**.



The tendency of transition metal ions to form complex ions rather than simple ions is due to two main factors:

- The “bare” cations of transition elements, with their incomplete 3d subshells are relatively small and highly charged. The resulting **high charge density** and hence **high polarising power** of the transition metal cations, produces a strong tendency towards covalent bond formation with ligands.
- The transition metal cations have **vacant 3d orbitals** (as well as 4s and 4p orbitals) which can be used to accommodate the lone pair of electrons from the ligands, resulting in dative bond formation.

## 4.2 Ligands

A **ligand** is an ion or molecule with one or more lone pairs of electrons available to be donated into the vacant orbitals of transition metal atom or ion.

Ligands can be classified according to the number of dative bonds that it forms with the central metal atom or ion.

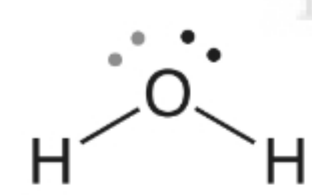
- Monodentate ligands bond using the electron pair of a single donor atom.
- Bidentate ligands bond using electron pairs on two donor atoms.
- Polydentate ligands bond using electron pairs on more than one donor atom (which includes bidentate ligand).

Polydentate ligands are sometimes called **chelating agents** (pronounced as *key-late-ting*) because of their ability to hold a metal ion like a claw. Chelating ligands form a stable complex ion with the central metal ion as the pincer-like grip of these polydentate ligands are able to hold the cation more securely. They typically form rings in the complex ion.

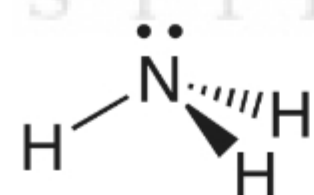


**Monodentate Ligands**

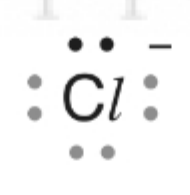
It is a ligand that forms one dative covalent bond to a central metal atom or ion.



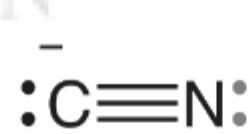
Water



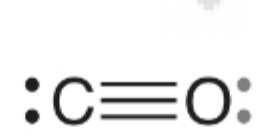
Ammonia



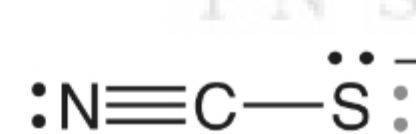
Chloride ion



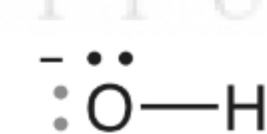
Cyanide ion



Carbon monoxide



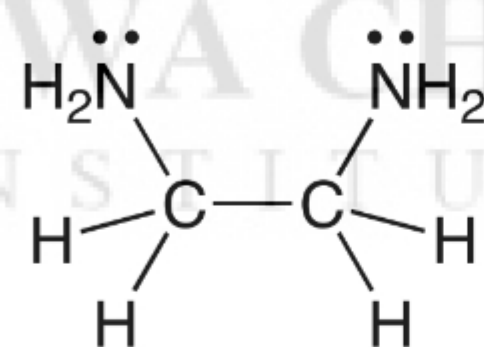
Thiocyanate ion



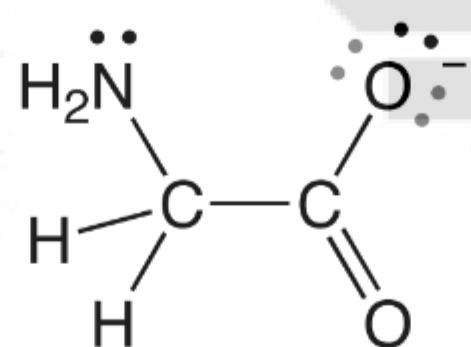
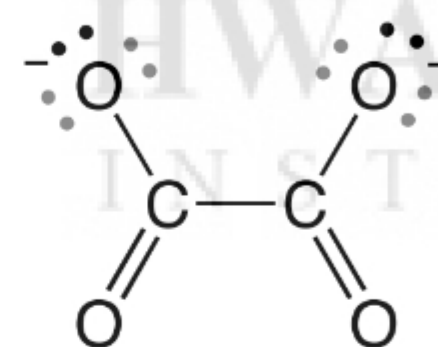
Hydroxide ion

**Bidentate Ligands**

It is a ligand that forms two dative bonds to a central metal atom or ion.



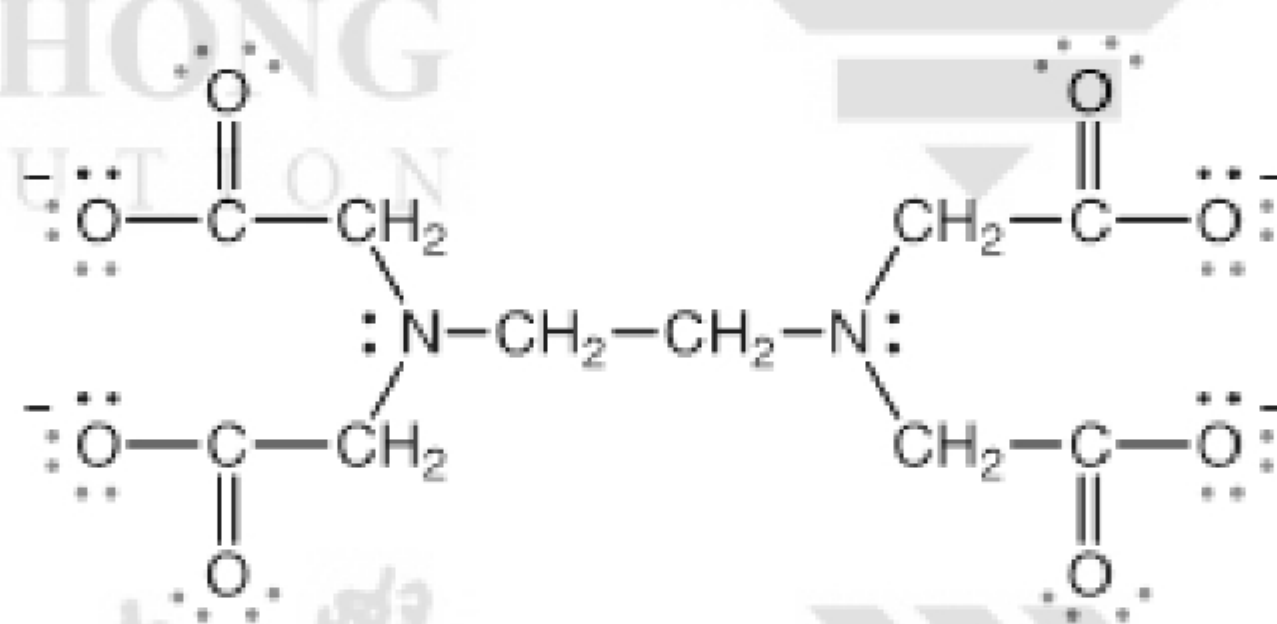
Ethane-1,2-diamine (en)

Glycinate ion (gly<sup>-</sup>)

Ethanedioate ion

**Hexadentate Ligands**

It is a ligand that forms six dative bonds to a central metal atom or ion.

Ethylenediaminetetraacetate ion (EDTA<sup>4-</sup>)

### 4.3 Coordination Number and Geometry

The **co-ordination number** indicates the **number of dative bonds** around the central atom or ion. The most common values are 4 and 6, but 2 is also observed and is particularly important in the chemistry of copper(I) and silver(I) compounds.


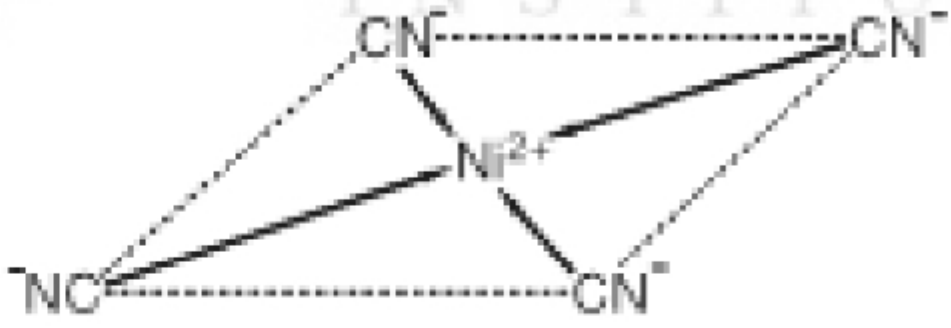
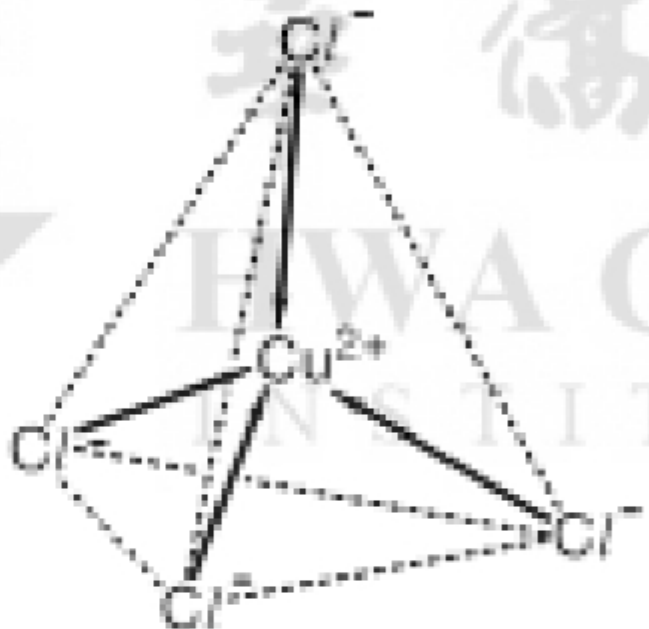
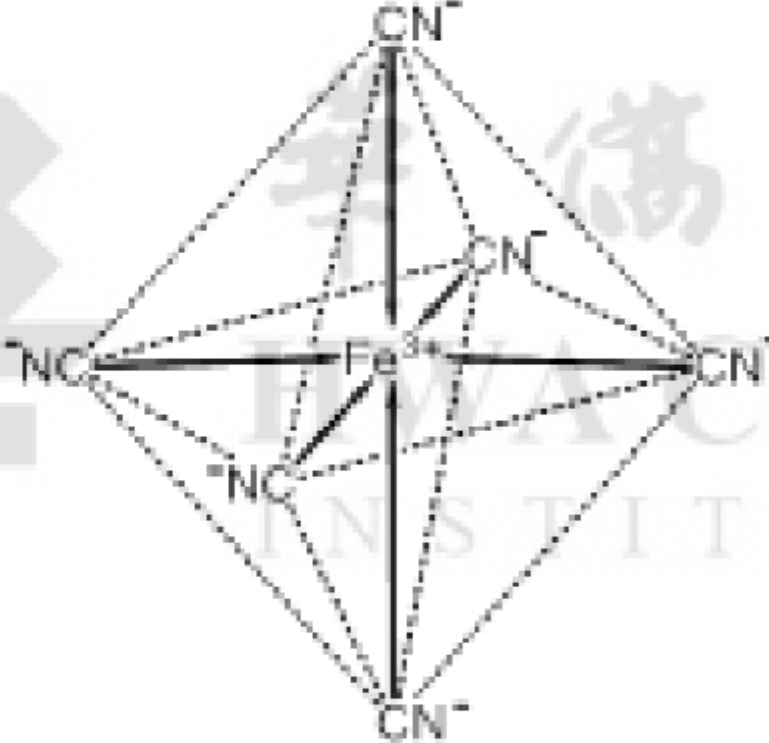
Formula	Coordination number	Geometry	Shape
$[\text{Ag}(\text{NH}_3)_2]^+$	2	linear	
$[\text{Ni}(\text{CN})_4]^{2-}$	4	square planar	
$[\text{CuCl}_4]^{2-}$	4	tetrahedral	
$[\text{Fe}(\text{CN})_6]^{3-}$	6	octahedral	

Table 5. Coordination number and shape of some complex ions

The shape (geometry) of the complex ion depends on the coordination number. For coordination number of 4, the geometry also depends on the electronic configuration of metal ions (not in syllabus).



**Lecture Exercise 4.1**

1. Complete the missing information in the table below.

Complex ion	Oxidation no. of central metal ion	No. of ligands per complex ion	Coordination number	Net charge
$[\text{Cr}(\text{CN})_6]^{3-}$		6		-3
$[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^x$		6	6	
$[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$	+3			-3
$[\text{Cu}(\text{EDTA})]^x$	+2		6	

2. A complex is obtained by reacting aqueous cobalt(III) chloride with ammonia. It is found that the co-ordination number of cobalt is 6 and that only one third of the total chloride is precipitated as AgCl when the complex is treated with an excess of aqueous silver nitrate. What is the formula of the compound?

A  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$

B  $\text{Co}(\text{NH}_3)_5\text{Cl}_3$

C  $\text{Co}(\text{NH}_3)_4\text{Cl}_3$

D  $\text{Co}(\text{NH}_3)_3\text{Cl}_3$

**4.4 Acidity of aqua complexes**

In aqueous solution, the transition metal ions exist as aqua complexes. Aqua complexes containing transition metal cations like  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$ , undergo **hydrolysis** in water to give a **mildly acidic solution**.



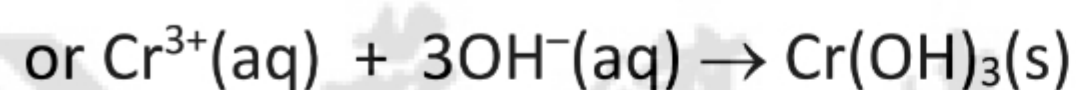
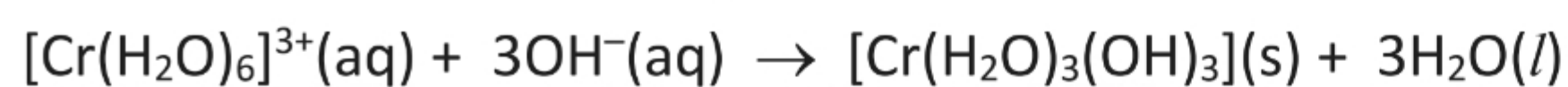
This is due to the **high charge density** on the central transition metal cation and these aqua complexes undergo appreciable hydrolysis in a similar fashion to the  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  ion (refer to salt hydrolysis in Topic 15 Acid-Base Equilibria).

However, for oxidation states higher than +3, the polarising power of the central metal cation is so great that the release of protons and loss of water molecules results in the **formation of oxoanions**.

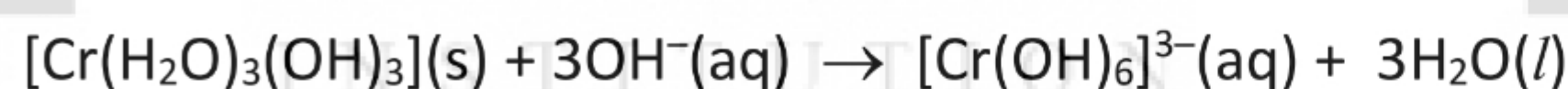
For instance,  $[\text{Cr}(\text{H}_2\text{O})_6]^{6+}$  ions do not exist in aqueous solution. Instead, Cr(VI), occurs in two well-known oxoanions, the chromate (VI) ion,  $\text{CrO}_4^{2-}$ , and the dichromate (VI) ion,  $\text{Cr}_2\text{O}_7^{2-}$ .

#### 4.4.1 Chromium complexes and oxoanions

When aqueous sodium hydroxide or aqueous ammonia is added dropwise to aqueous solution of chromium(III) ion, a grey-green ppt is formed. This is due to the formation of  $\text{Cr}(\text{OH})_3$ . This is an acid-base reaction as chromium(III) ion is acidic.

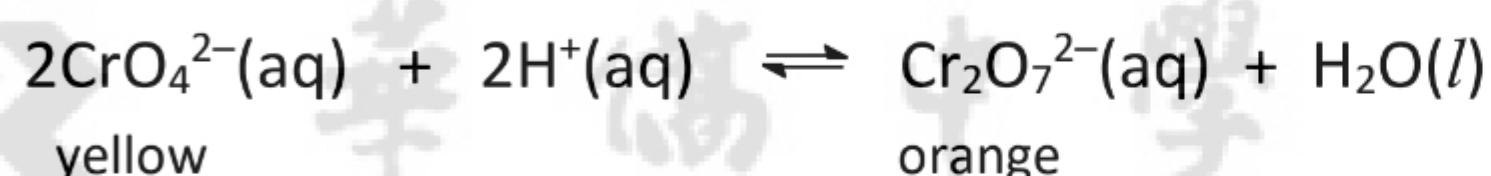


When aqueous sodium hydroxide is added in excess, a dark green solution is formed. This is due to the formation of  $[\text{Cr}(\text{OH})_6]^{3-}$  complex ion.



dark green solution

When acid is added to yellow solution of chromate(VI) ion, an orange solution of dichromate(VI) is formed. Notice that the oxidation state of the chromium ion remains the same.

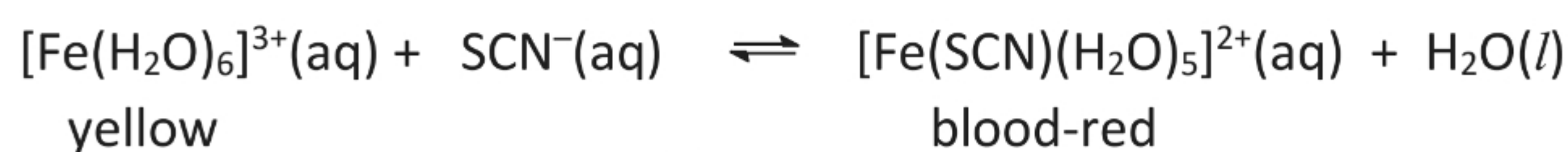


#### 4.5 Ligand exchange reaction

LO 13(j): explain qualitatively that ligand exchange may occur, as exemplified by the formation of the complexes in (i), including the colour changes involved, and  $\text{CO}/\text{O}_2$  exchange in haemoglobin

The ligands in a complex ion can be exchanged for other ligands. This reaction is known as **ligand exchange reaction**. This reaction will happen readily if the new complex formed is more stable than the original complex. A change in colour of the solution is usually observed.

Ligand exchange reactions are largely reversible reactions, and therefore, are represented by the equilibrium sign ' $\rightleftharpoons$ '. For example, the ligand exchange reaction between the water ligands in  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and  $\text{SCN}^{-}$  (thiocyanate) ions is represented by:



A colour change from yellow to blood-red will be observed in this ligand exchange reaction.

The equilibrium constant of this reaction is given by  $K_c = \frac{[\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}}{[\text{Fe}(\text{H}_2\text{O})_6]^{3+} [\text{SCN}^{-}]}$ .

Note that although water is a reacting species (in the reverse reaction), it is also a solvent. Hence,  $[\text{H}_2\text{O}]$  is almost constant and excluded from the  $K_c$  expression.

If the new complex formed is much more stable than the original complex,  $K_c$  would be large, the equilibrium position will lie very much to the right, and a single arrow may be used in the equation.





#### 4.5.1 Ligand exchange reactions involving copper complexes

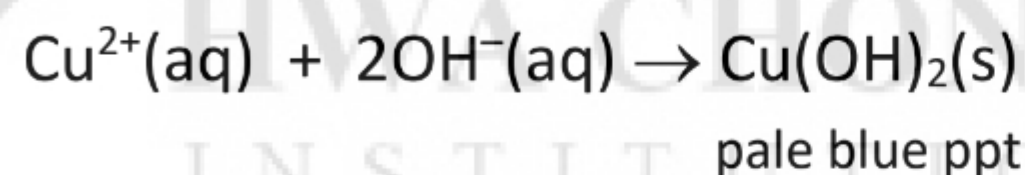
This section concerns some common complexes of Cu(II) and the reactions in which they can be formed (often seen in Inorganic QA tests).

- To a solution of  $\text{Cu}^{2+}(\text{aq})$ , add aqueous ammonia dropwise then in excess.

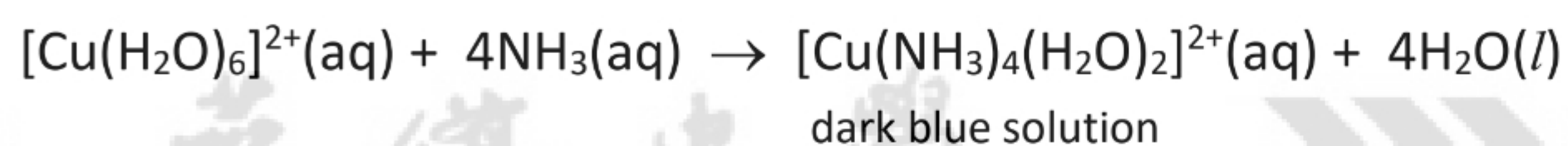
Observation: pale blue ppt formed, which dissolves in excess ammonia to give dark blue solution.

Explanation:

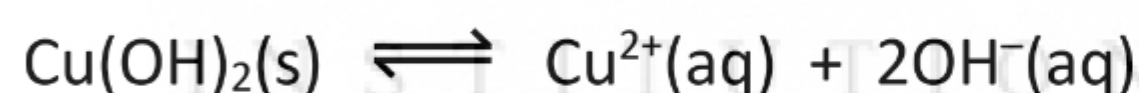
$\text{Cu}(\text{OH})_2$  is first precipitated when aqueous ammonia is added dropwise.



When excess ammonia is added, ligand exchange reaction takes place, with  $\text{NH}_3$  ligands replacing  $\text{H}_2\text{O}$  ligands.



This causes the concentration of  $\text{Cu}^{2+}(\text{aq})$  to drop, thus the equilibrium below will shift to the right. Thus the ppt will dissolve to give a dark blue solution.

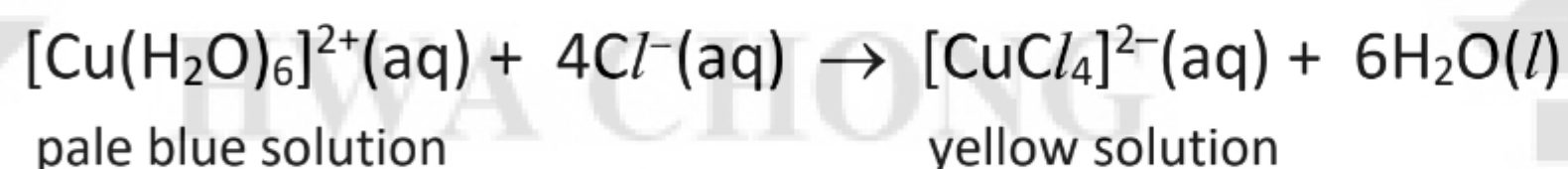


- To a solution of  $\text{Cu}^{2+}(\text{aq})$ , add concentrated hydrochloric acid dropwise.

Observation: solution turns from pale blue to green then yellow

Explanation:

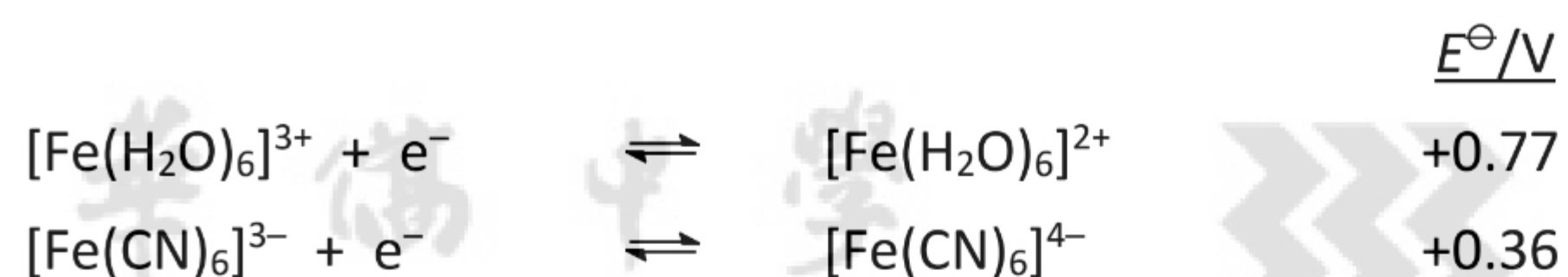
When conc.  $\text{HCl}$  is added, ligand exchange reaction takes place, with  $\text{Cl}^{-}$  ligands replacing  $\text{H}_2\text{O}$  ligands.



The green colour is observed due to the mixture of both the blue aqua complex and the yellow chloro complex present.

#### 4.5.2 Effects of ligand exchange on reduction potential (Application Example)

Ligands interact differently with the central metal ion, which will result in some change in reduction potential. For example, when water ( $\text{H}_2\text{O}$ ) ligands are replaced by cyanide ligands ( $\text{CN}^-$ ) for  $\text{Fe}^{3+}$ , we can see that there is a change in redox potential for the complex ions.



With the replacement of water ligands by cyanide ligands,  $E^\ominus$  for the reduction of Fe(III) to Fe(II) becomes less positive. This is significant in the reaction with iodide ions.



$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is able to oxidise  $\text{I}^-$  to  $\text{I}_2$  and a dark brown solution is obtained.



On the other hand,  $[\text{Fe}(\text{CN})_6]^{3-}$  is unable to oxidise  $\text{I}^-$  to  $\text{I}_2$ .

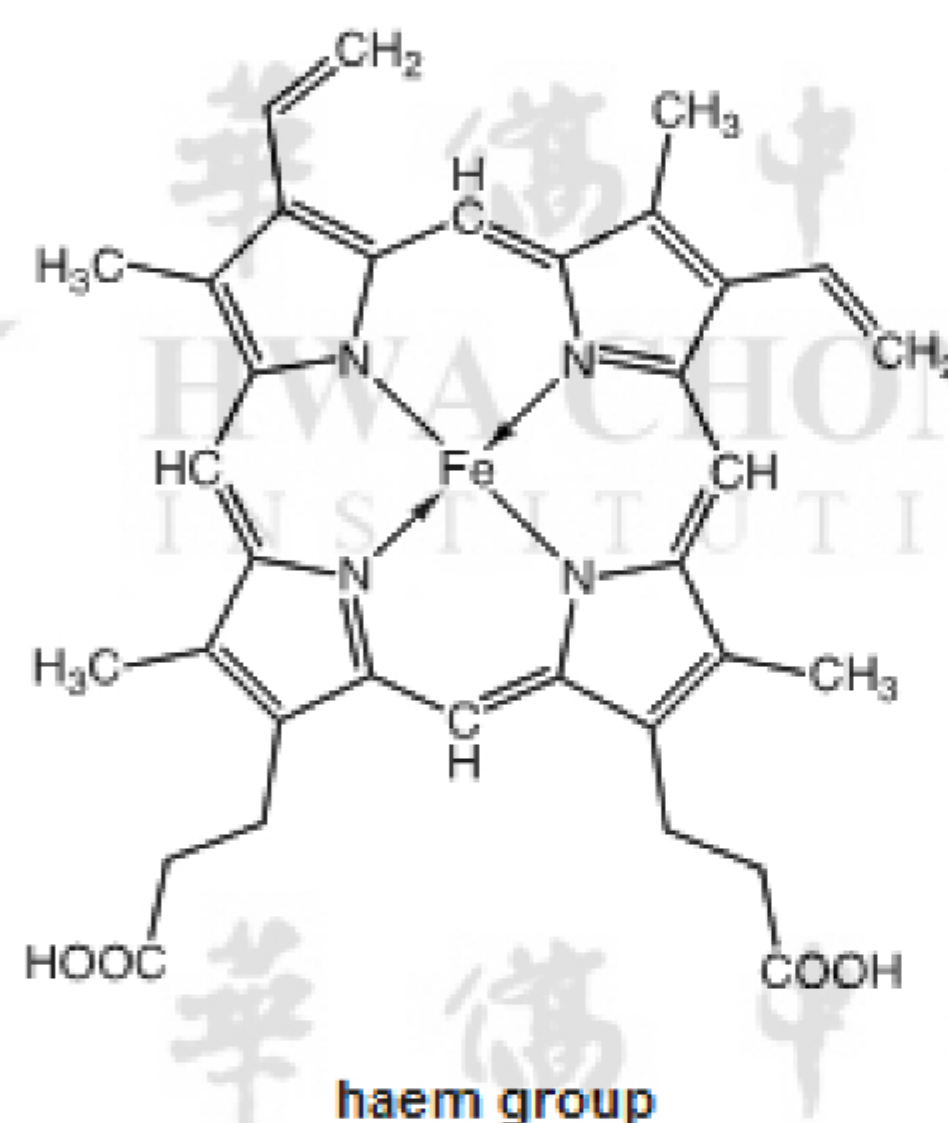
$$\begin{aligned}
 E^\ominus_{\text{cell}} &= E^\ominus_{\text{red}} - E^\ominus_{\text{ox}} \\
 &= +0.36 - 0.54 \\
 &= -0.18 \text{ V (not feasible)}
 \end{aligned}$$



### 4.5.3 Ligand exchange reaction in haemoglobin

Haemoglobin is the iron-containing protein in red blood cells that transports oxygen in blood. It consists of four protein chains loosely held together in a cluster. Each chain has a haem molecule within its folds. Iron (in the +2 oxidation state) is located in the centre of a plane of four nitrogen atoms. A haemoglobin molecule in the lungs picks up an  $O_2$  molecule, which forms a dative bond with the iron to form a species called *oxyhaemoglobin*. This binding is reversible and enables haemoglobin to carry oxygen around the body and release it where it is needed.

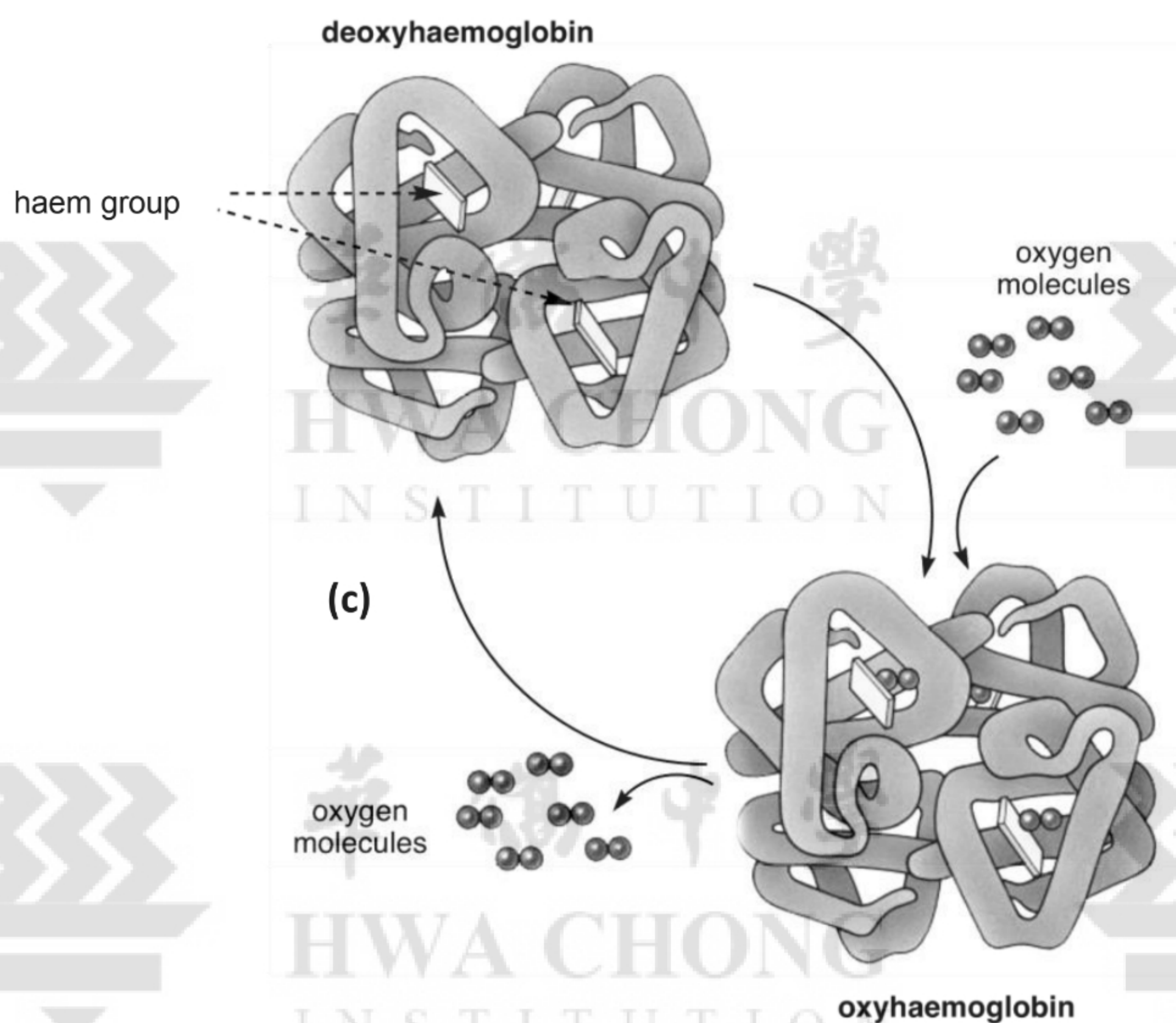
Carbon monoxide, CO, can replace  $O_2$  as the ligand attached to the iron(II). This is a **ligand exchange reaction**. The new complex is called *carboxyhaemoglobin*. The binding between CO and the iron(II) is irreversible, thus making carboxyhaemoglobin a very stable complex. The affinity of human haemoglobin for CO is about 210 times greater than that for  $O_2$ . As a result, a relatively small quantity of CO can inactivate a substantial fraction of the haemoglobin for oxygen transport. If the concentration of CO is high and the level of carboxyhaemoglobin becomes too high, oxygen transport is effectively shut down and death occurs.



(a)



(b)



(c)

Figure 5

**(a)** Structure of the haem group. **(b)** Haem, haemoglobin and oxygen transport. The central iron(II) exhibits hexa co-ordination. Four of the co-ordination sites are taken up by nitrogen from a ring system called a porphyrin that acts as a tetradentate ligand. Below the plane of this ring is a fifth nitrogen atom from a histidine side-chain on a protein molecule called globin. The  $O_2$  molecule may be reversibly bonded at the sixth site. **(c)**  $O_2$  molecules bind to the deoxyhaemoglobin, forming oxyhaemoglobin that is transported around the circulatory system in red blood cells. The  $O_2$  molecules bind reversibly with the iron, thus allowing easy release of  $O_2$  for cellular respiration



## 5 COLOURED COMPOUNDS AND COMPLEXES

Transition metal compounds are frequently coloured, both in the solid state and in solution. This is due to absorption of part of the visible spectrum by the solution. The reason behind the observed colour can be explained using crystal field theory.

### 5.1 Light and Colour

White light is an electromagnetic radiation consisting of all wavelengths in the visible range. It can be dispersed into a spectrum of colours, each of which has a narrower range of wavelengths. For example, it can be dispersed into seven colours commonly known as the rainbow by using a prism.

Each colour has a complementary colour. For example, green and red are complementary colours. This is shown as opposite wedges in the colour wheel diagram below.

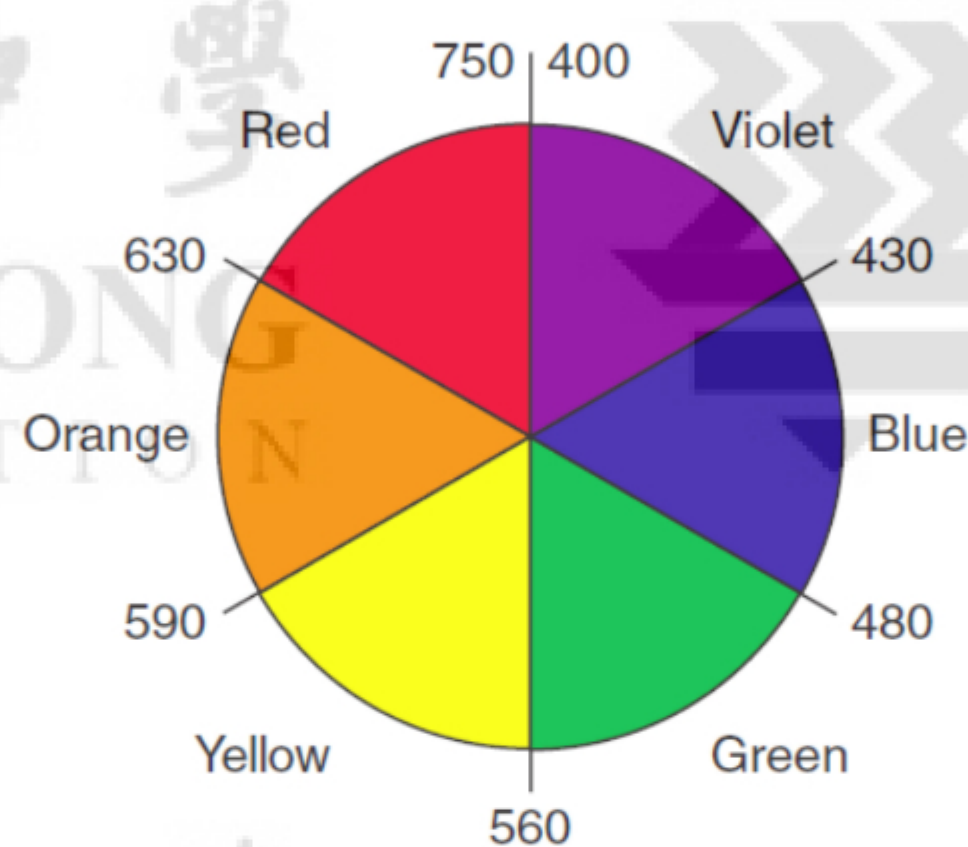


Figure 6. A diagram of the colour wheel, with approximate wavelength ranges (in nm), shown as wedges.

The energy of the light is inversely proportional to its wavelength. Therefore, red colour, with longer wavelength is lower in energy as compared to blue light, which is shorter in wavelength.

Objects appear coloured in white light because they absorb certain wavelengths and reflect or transmit others: an opaque object reflects light, whereas a clear one transmits it. The reflected or transmitted light enters the eye and the brain perceives a colour. If an object absorbs all visible wavelengths, it appears black; if it reflects all, it appears white.

### 5.2 Crystal Field Theory

The crystal field theory was first developed to account for the properties of transition metal ions in solids. In this theory, the lone pair on ligand is modelled as a point negative charge that attracts the positive central metal ion, which provides the stability to the complex. They also repel the electrons in the d orbitals of the metal ion.



Recall from Topic 1 Atomic Structure that the d orbitals have five different orientations and they are degenerate (same energy level).

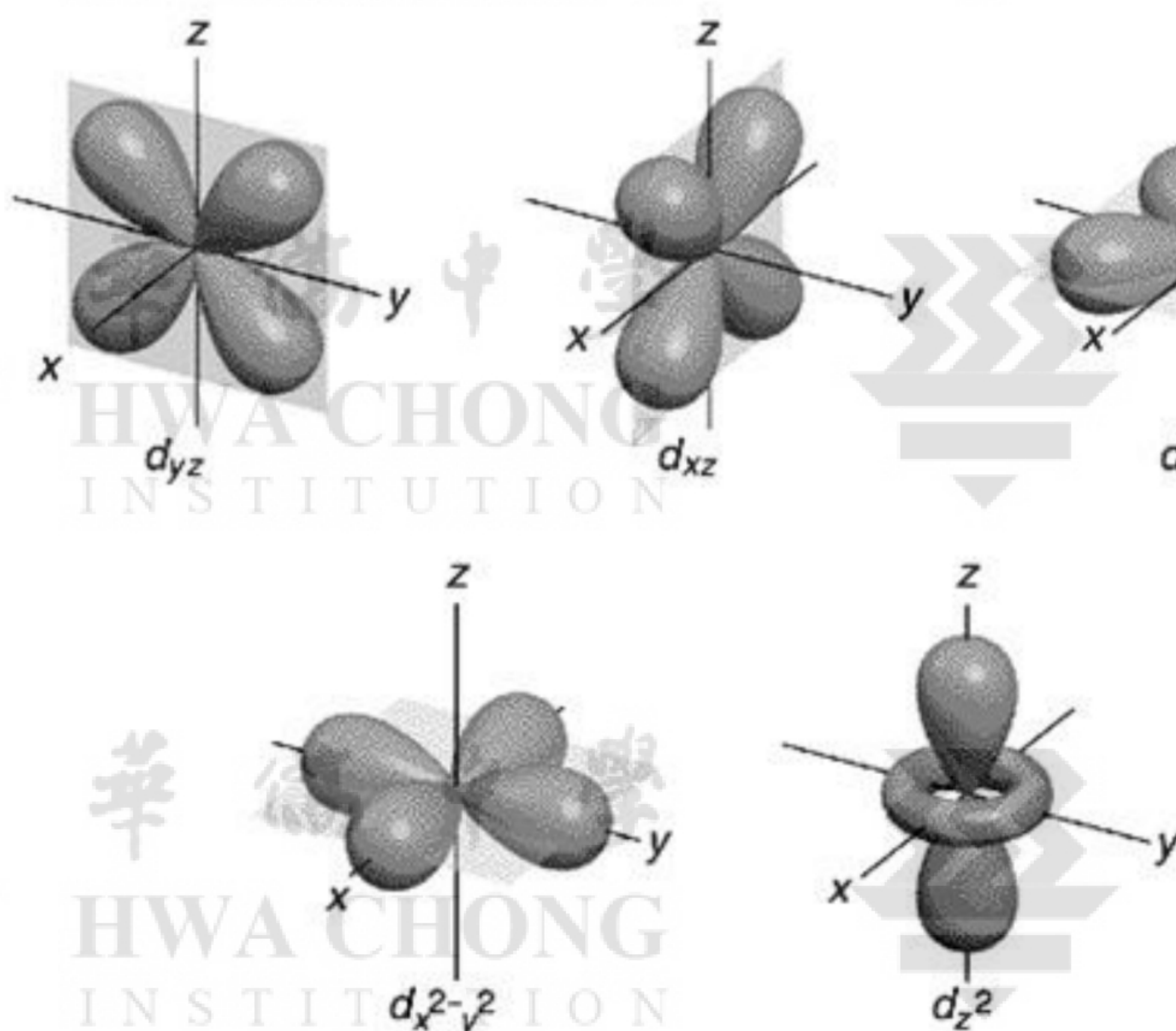


Figure 7. The shapes and orientations of the 3d orbitals

### Splitting of degenerate d orbitals in octahedral complex

LO 13(k): describe, using the shape and orientation of the d orbitals, the splitting of degenerate d orbitals into two energy levels in octahedral complexes

- In a free transition metal ion, all five orbitals are degenerate (have the same energy).
- In the presence of ligands in an octahedral field, the ligands approach the metal ion along the mutually perpendicular x, y, and z axes.

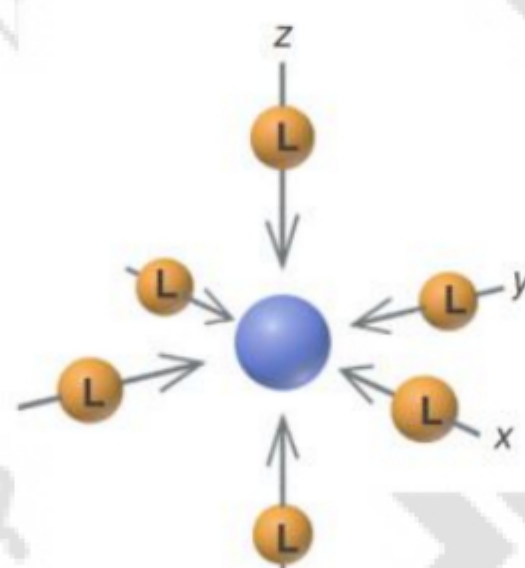


Figure 8. Ligands approach along the mutually perpendicular axes.

- As the ligands approach, their electron pairs repel electrons in the five d orbitals of metal ions, causing all five d orbitals to increase in energy.
- However, the d electrons are repelled unequally due to the different orientations of d orbitals. As the ligands move along the x, y and z axes, they approach directly toward the lobes of the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals but between the lobes of the  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  orbitals. Thus, the electrons in  $d_{x^2-y^2}$  and  $d_{z^2}$  orbital experienced stronger repulsion, which causes the energy of these orbitals to be higher than the  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  orbitals.
- The five d orbitals therefore are no longer degenerate, but are split into two groups with an energy gap ( $\Delta E$ ) between them.



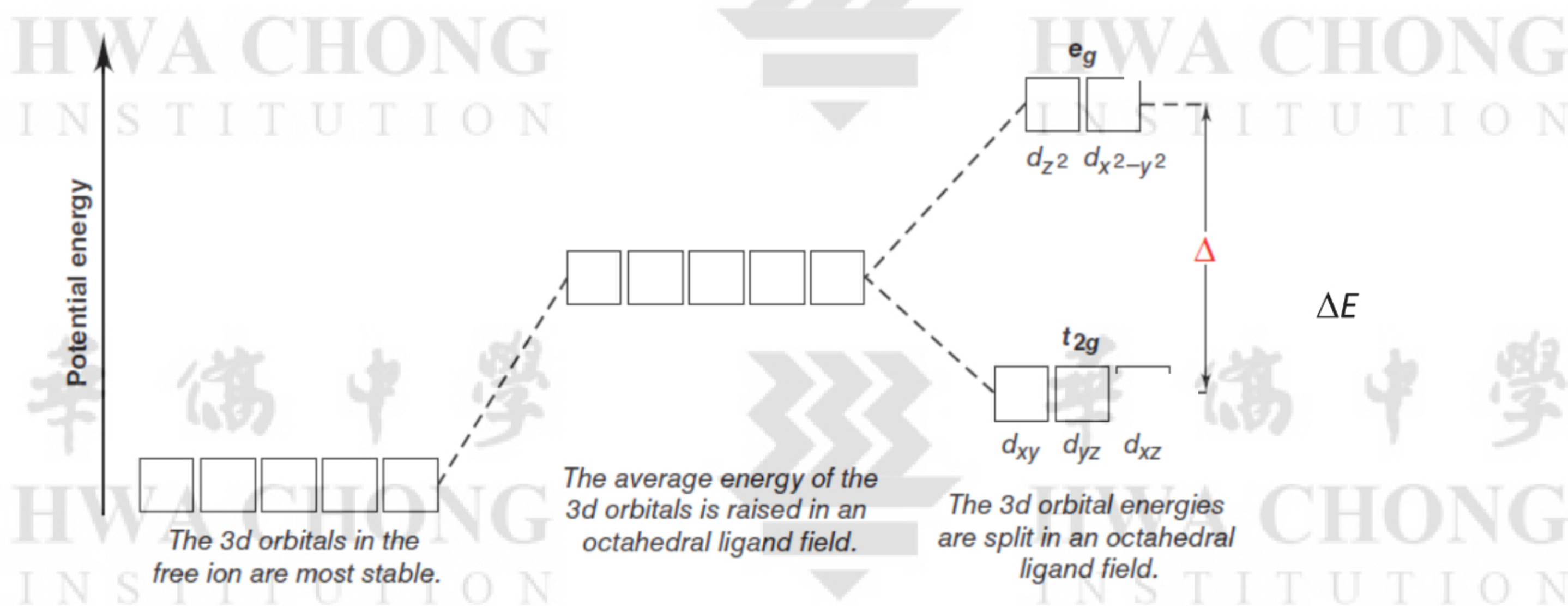


Figure 9. Splitting of d orbitals by an octahedral field of ligands.

### Electronic d-d transition

- Let us consider the  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  ion, which appears purple in aqueous solution.  $\text{Ti}^{3+}(\text{aq})$  is a  $d^1$  ion, with the  $d$  electron in one of the three lower energy orbitals.

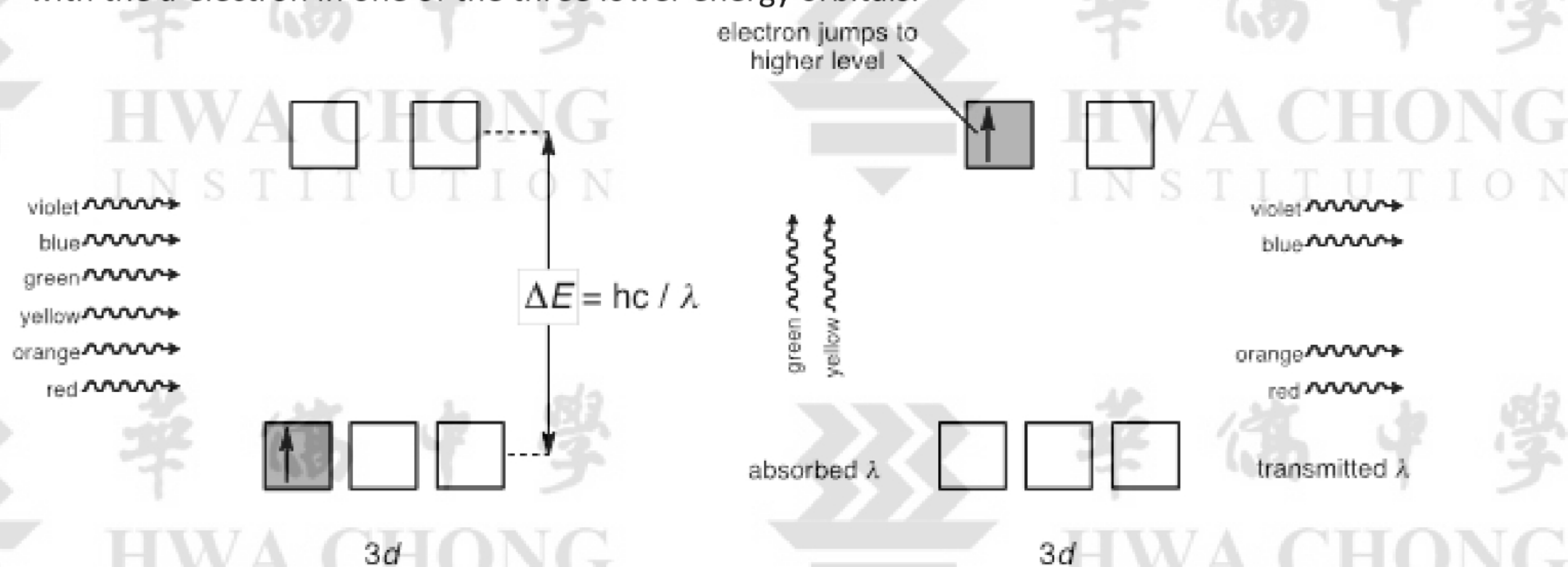


Figure 10. Orbital diagram depicting d-d electron transition.

- When white light shines on the solution, the electron at the lower energy level will absorb energy from the light and jump to one of the higher energy orbitals.
- The energy gap ( $\Delta E$ ) between the two levels corresponds to a range of wavelength in the visible spectrum. For  $\text{Ti}^{3+}(\text{aq})$ , it happens to be in the green and yellow range.
- The complementary colours red, orange, blue and violet lights are transmitted, thus the solution looks purple.

LO 13(I): 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]

In the presence of ligands, the partially filled degenerate 3d orbitals of a transition metal ion are split into two different energy levels with a small energy gap  $\Delta E$  between them. There are vacancies in the higher energy  $d$  orbitals. The promotion of an electron from the lower to the higher of these  $d$  orbitals requires the absorption of radiation in the visible spectrum with energy corresponding to the energy gap. Such a d-d transition is responsible for the colour of the complex ion. The colour observed is the complement of the colours absorbed.



### 5.3 Factors affecting the colour of complexes

#### 5.3.1 Oxidation state of the metal

Different number of electrons in the  $d$  orbitals of the transition metal ion will result in different interactions with the electrons from the ligands. This will give rise to different energy gap ( $\Delta E$ ) thus the wavelengths of light absorbed will also be different. The table below shows the example of vanadium complexes.

Formula of ion	$V^{3+}(aq)$	$V^{2+}(aq)$
Oxidation state of vanadium	+3	+2
Electronic configuration	$[Ar] 3d^2$	$[Ar] 3d^3$
Colour	green	violet

The absence of colour in  $Sc^{3+}$ ,  $Ti^{4+}$ ,  $Cu^+$  and  $Zn^{2+}$  is due to them having either no  $d$  electrons ( $3d^0$  for  $Sc^{3+}$  &  $Ti^{4+}$ ) or fully filled  $d$  orbitals ( $3d^{10}$  for  $Cu^+$  &  $Zn^{2+}$ ). In such cases, no  $d-d$  electronic transition is possible.

#### 5.3.2 Nature of ligand

Different ligands have different effects on the splitting of the  $d$  orbitals. The difference in magnitude of  $\Delta E$  will lead to different colours observed. The diagram below shows the example of nickel complexes.

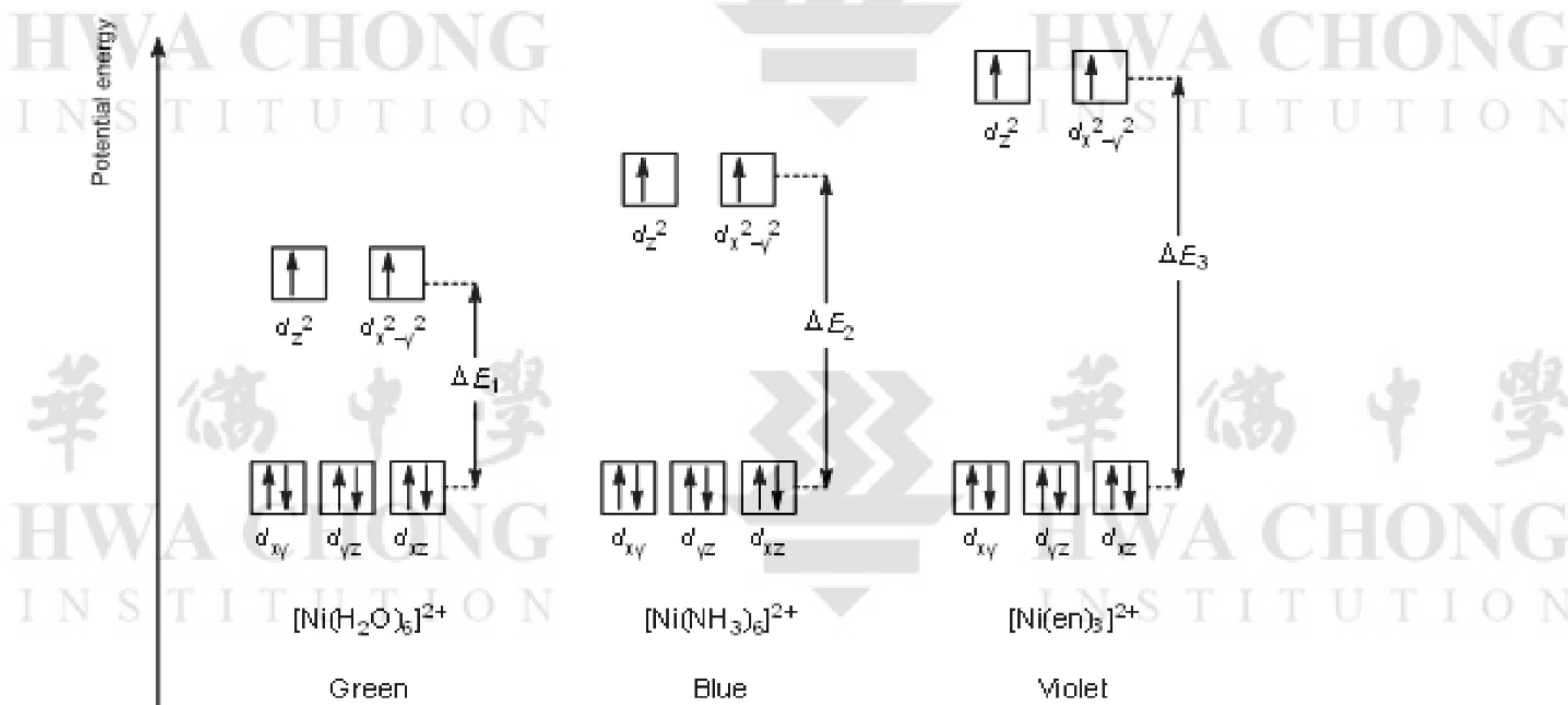


Figure 11. Size of  $d$  orbital splitting – the energy gap between the two groups of  $d$  orbitals depends on the ligand

## 5.4 Common transition metal ions/compounds and their corresponding colours

Transition metal	Oxidation number of transition metal	Formula	Colour
Chromium	+3	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	green
	+6	$\text{CrO}_4^{2-}$	yellow
	+6	$\text{Cr}_2\text{O}_7^{2-}$	orange
Manganese	+2	$\text{Mn}^{2+}$	faint pink / colourless if dilute
	+4	$\text{MnO}_2$	dark brown ppt
	+6	$\text{MnO}_4^{2-}$	dark green
	+7	$\text{MnO}_4^-$	purple
Iron	+2	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	pale green
	+2	$\text{Fe}(\text{OH})_2$	green ppt
	+3	$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	yellow
	+3	$[\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}$	blood red
	+3	$\text{Fe}(\text{OH})_3$	reddish brown ppt
Copper	+2	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	pale blue
	+2	$[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$	dark blue
	+2	$[\text{CuCl}_4]^{2-}$	yellow
	+2	$\text{Cu}(\text{OH})_2$	pale blue ppt

**Not all colours of transition metal compounds originate from d-d transition.** Some colours in the table above can be due to other electronic transitions which are not in the A Level syllabus (only d-d transition is required).



## 5.5 Using colorimetry in experiments

### 5.5.1 Determining the concentration of complex ions by colorimetry



#### To determine the concentration of a coloured complex using colorimetry

Example: N2013/P2/Q1 (Planning Question)

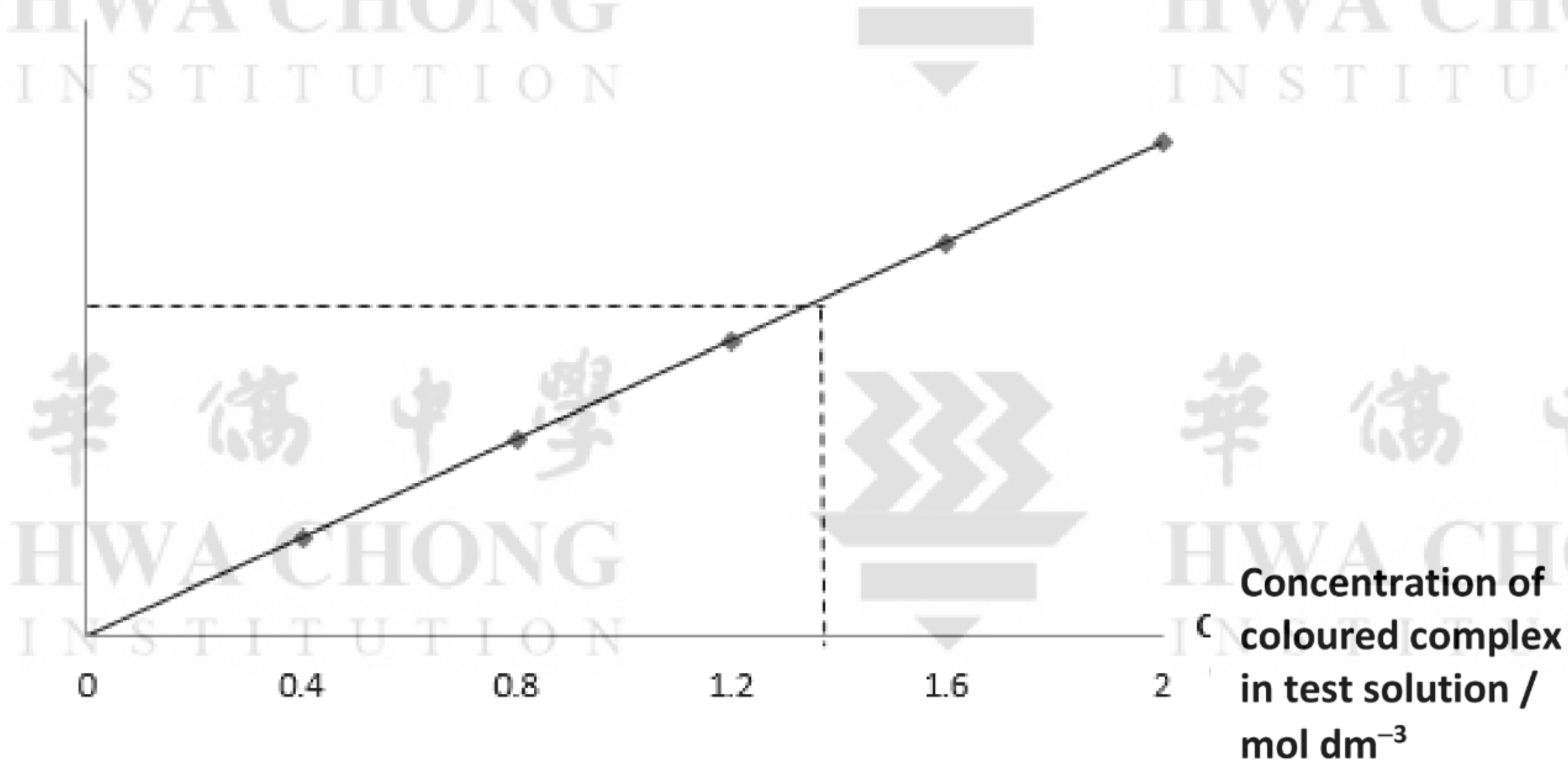
##### *Approach:*

A calibration graph is first obtained by measuring the absorbance of a series of solutions containing the coloured complex at various known concentrations. Then measure the absorbance of the unknown solution and read its concentration off the calibration graph.

##### Generic procedure

1. A suitable filter (of a complementary colour) is selected.
2. A 'blank' absorbance reading is taken using water as a reference.
3. A series of solutions of known concentrations of (the coloured complex) are made up (usually by dilution from a stock solution).
4. The absorbance of the solutions are measured in turn with the colorimeter.
5. A calibration graph of absorbance against concentration is plotted.
6. The absorbance of the test solution is now measured, and the calibration curve is used to determine the unknown concentration.

##### **Absorbance of test solution**



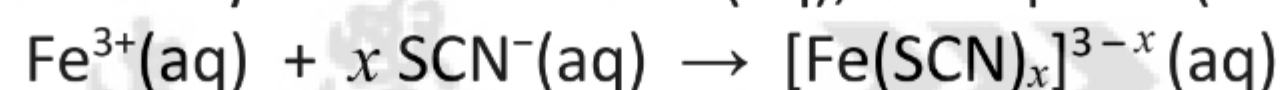
- If the UV-VIS spectrophotometer is used instead of the colorimeter, the absorbance readings are measured at a fixed wavelength (usually at the wavelength where absorbance is the greatest or the complementary colour), instead of using a filter in Step 1.



### 5.5.2 Investigating the stoichiometry of complex ions by colorimetry

The formula of a complex ion can be determined by measuring the colour intensity of the complex ion, provided the colour of the complex is quite different from the colours of the separate aqueous ions.

E.g. When  $\text{Fe}^{3+}(\text{aq})$  react with thiocyanate ions  $\text{SCN}^{-}(\text{aq})$ , a deep red (blood red) colour is produced:



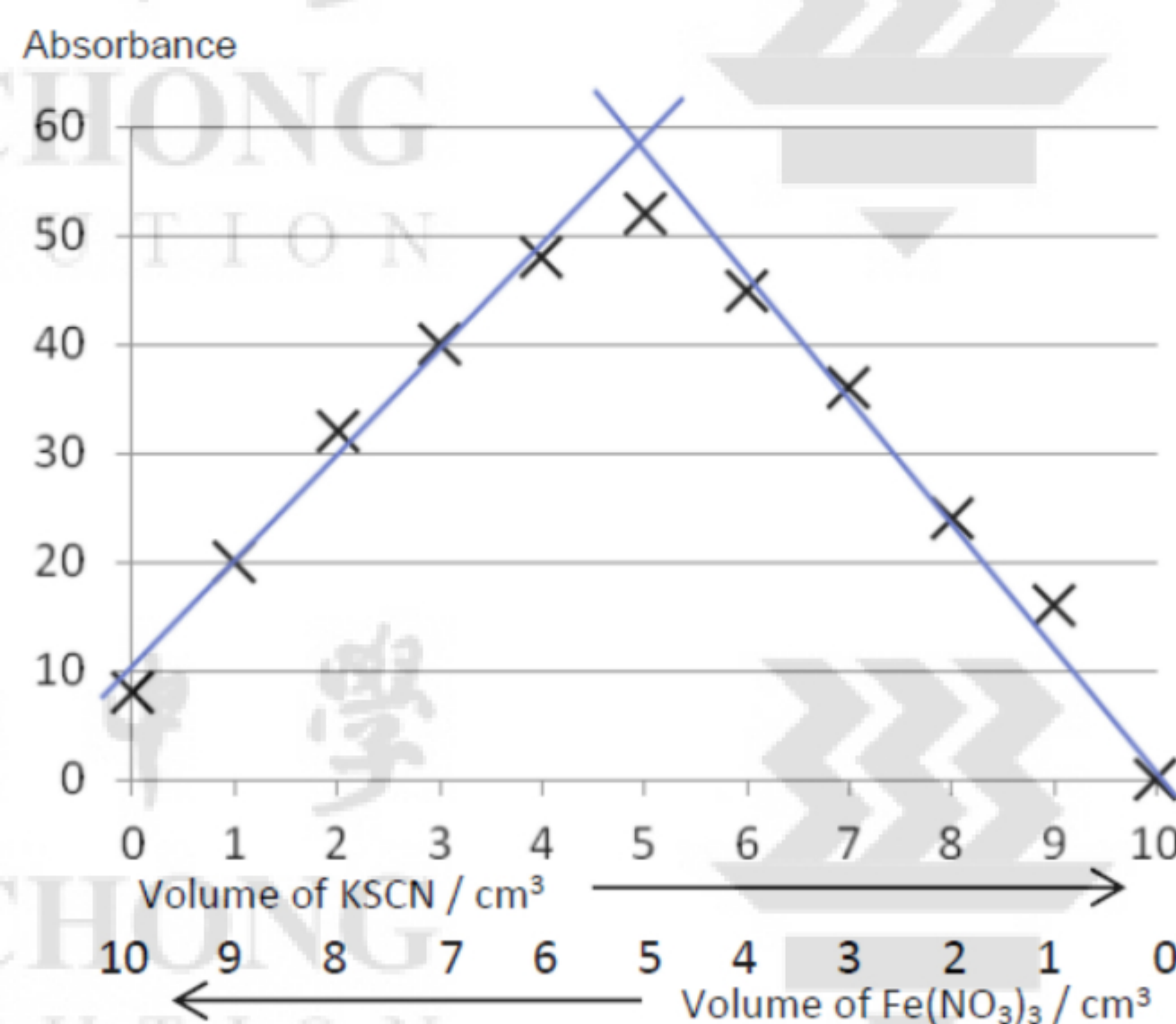
The stoichiometry of the complex can be determined by the **method of continuous variation**. Mixtures of  $\text{Fe}^{3+}$  and  $\text{SCN}^{-}$  with  $\text{Fe}^{3+} : \text{SCN}^{-}$  in molar proportions of 10:0, 9:1, 8:2, 7:3, 6:4, etc. is made. In other words, the relative proportions of  $\text{Fe}^{3+} : \text{SCN}^{-}$  are continuously varied from 10:0 to 0:10.

Clearly, the mixture with the most intense coloured solution corresponds to molar proportions of  $\text{Fe}^{3+}$  and  $\text{SCN}^{-}$  which just react completely leaving neither in excess. In some cases, it might be possible to tell by eye which mixture contains the darkest-coloured solution, but the judgment can be done much more reliably and accurately using a spectrophotometer. The spectrophotometer measures the absorbance of the test solution, which is proportional to the concentration of the complex.

The table below shows a typical set of results for the  $\text{Fe}^{3+} / \text{SCN}^{-}$  investigation.

Tube number	1	2	3	4	5	6	7	8	9	10	11
Volume of $5.00 \times 10^{-3} \text{ mol dm}^{-3} \text{Fe}(\text{NO}_3)_3 / \text{cm}^3$	10	9	8	7	6	5	4	3	2	1	0
Volume of $5.00 \times 10^{-3} \text{ mol dm}^{-3} \text{KSCN} / \text{cm}^3$	0	1	2	3	4	5	6	7	8	9	10
Absorbance	8	20	32	40	48	52	45	36	24	16	0

The results are represented graphically below.



Extrapolate the two straight lines to find the maximum absorbance (which corresponds to the highest concentration of the complex).

- In what molar proportions do  $\text{Fe}^{3+}$  and  $\text{SCN}^{-}$  react to form the blood red complex ion?
- Write the balanced equation for the formation of the complex ion by ligand exchange.



## 5.6 Procedure on Qualitative Analysis



## Planning an experiment involving qualitative analysis

You may be asked to propose a sequence of test-tube reactions to identify inorganic ions. This means you need to review your Inorganic Chemistry Qualitative Analysis notes. **Inorganic QA tests** are based on four main types of chemical reactions that produce precipitates, gases, and colour changes. Try to identify these four main types of inorganic reactions in your QA notes:

- Ionic precipitation reactions
- Acid-base reactions
- Redox reactions
- Complex forming reactions including ligand exchange

When planning a qualitative analysis experiment, you may be asked to:

- Present the sequence of tests. You may use a flowchart or table.
- Write the procedure with essential details of quantities and conditions for each test.
- State the expected observations for both positive and negative tests.
- Explain the chemistry underlying each test e.g. type of reaction, identity of species responsible for precipitate / gas / colour change.

The unknown ions might be present in a mixture, and you might be required to plan a filtration to separate the ions or precipitates. For example, **FA1** contains **two cations** ( $\text{Fe}^{2+}$  and  $\text{Zn}^{2+}$ ).  $\text{NaOH(aq)}$  and  $\text{NH}_3(\text{aq})$  are common test reagents for cations:  $\text{Fe}^{2+}$  forms an insoluble basic hydroxide while  $\text{Zn}^{2+}$  forms a soluble amphoteric hydroxide, which can be separated by filtration. A sample plan is shown below.

Test	Observations	Location of ions
To 1 cm <sup>3</sup> of <b>FA1</b> in a test tube, add excess $\text{NaOH(aq)}$ .	Green ppt insoluble in excess $\text{NaOH}$	$\text{Fe}^{2+}$ – $\text{Fe(OH)}_2$ ppt
Filter the mixture and collect the filtrate in a separate test tube.	Colourless filtrate Green residue turns reddish brown on contact with air	$\text{Zn}^{2+}$ – in the filtrate as $[\text{Zn(OH)}_4]^{2-}$ $\text{Fe(OH)}_2$ oxidised to $\text{Fe(OH)}_3$

You may also present your plan as a flowchart.

**LOOKING AHEAD**

*You have completed the last topic in 9729 H2 Chemistry. Do spend some time to consolidate all that you have learned and be able to see how basic chemistry principles are applied in different topics throughout the syllabus. All the best!*

