

Raffles Institution Year 6 Chemistry 2025 Lecture Notes 22 – An Introduction to the Chemistry of Transition Elements

Learning Outcomes

Candidates should be able to:

- (a) explain what is meant by a transition element, in terms of d-block elements forming one or more stable ions with partially filled d subshells
- (b) state the electronic configuration of a first row transition element and of its ions
- (c) explain why atomic radii and first ionisation energies of the transition elements are relatively invariant
- (d) contrast, qualitatively, the melting point and density of the transition elements with those of calcium as a typical s-block element
- (e) describe the tendency of transition elements to have variable oxidation states
- (f) predict from a given electronic configuration, the likely oxidation states of a transition element
- (g) describe and explain the use of Fe^{3+}/Fe^{2+} , MnO_4^-/Mn^{2+} and $Cr_2O_7^{2-}/Cr^{3+}$ as examples of redox systems
- (h) predict, using E^{\ominus} values, the likelihood of redox reactions (see Electrochemistry I)
- (i) define the terms *ligand* and *complex* as exemplified by the complexes of copper(II) ions with water, ammonia and chloride ions as ligands
- (including the transition metal complexes found in the Qualitative Analysis Notes)
- (j) explain qualitatively that ligand exchange may occur, as exemplified by the formation of the complexes in (i), including the colour changes involved, and CO/O₂ 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
- (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]

(m) explain how some transition metals and/or their compounds can act as catalysts (see Reaction Kinetics)

1. INTRODUCTION

1.1 The d-block elements

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

Period number				
1	1s			1s
2	2s		2р	
3	3s		Зр	
4	4s	3d	4p	
5	5s	4d	5p	
6	6s	5d	6р	
7	7s	6d		
			-	

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

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

- The 3d row contains **ten elements**, because the **3d subshell** contains **five orbitals**, each able to accommodate up to two electrons. These elements involve the filling of the 3d orbitals.
- They are all metals and tend to be hard metals compared with the s-block metals.

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

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$d_{x^2-y^2}$	z v dz ²
 These three orbitals have a similar 4–lobed shape. These orbitals have their lobes pointing between the axes. 	 This orbital also has a 4–lobed shape but it has its lobes aligned along the x and y axes. 	 This orbital consists of a dumb-bell surrounded by a small doughnut shaped ring at its waist This orbital is aligned along the z axis.

1.3 Electronic Configurations of the Elements

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

The Aufbau (building-up) Principle

Electrons fill orbitals from the lowest energy orbital upwards. •

The Pauli Exclusion Principle

No more than two electrons may occupy a single orbital and, if two ٠ electrons do occupy a single orbital, their spins must be opposite.

Hund's Rule

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



Recall from Atomic Structure: •

Electrons occupy the 4s subshell before the 3d subshell. 0

Electronic configuration of the first-row d-block elements

Element	'Electrons-in-boxes' diagram	Electronic configuration
	3d4	ls
21 SC	[Ar] 1 1	$\begin{array}{c c} & 1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ \mathbf{3d^1} \ \mathbf{4s^2} \end{array}$
₂₂ Ti	[Ar] 1 1 1	$\int 1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
₂₃ V	[Ar] 1 1 1 1	$\int 1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$
₂₄ Cr	[Ar] 1 1 1 1 1	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ⁵ 4s ¹
₂₅ Mn	[Ar] 1 1 1 1 1	$\downarrow 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$
₂₆ Fe	[Ar] 1 1 1 1	$\downarrow 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
27 Co	[Ar] 1111 1 1	$\downarrow 1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
₂₈ Ni	[Ar] 11 11 1	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$
29 Cu	[Ar] 11111111	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ¹⁰ 4s ¹
₃₀ Zn	[Ar] 11 11 11 11 11 1	$\downarrow \qquad 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$

Two exceptions:

Electronic configuration of chromium: 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁵ 4s¹
 For Cr, the configuration [Ar] 3d⁵ 4s¹ is more stable than [Ar] 3d⁴ 4s².

[Ar]	1 1 1 1 1	1		[Ar]	1 1 1 1	11	4.0
	3d	4s	✓		3d	4s	×
	more stabl	е		less stabl	е		

Electronic configuration of copper: 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s¹
 For Cu, the configuration [Ar] 3d¹⁰ 4s¹ is more stable than [Ar] 3d⁹ 4s².



1.4 Electronic Configurations of the lons

- In the formation of cations, the 4s electrons, which are at a higher energy level than the 3d electrons, are removed first.
- To write the electronic configuration of ions,
 - Step 1: Write out the electronic configuration of <u>element</u>, filling the **4s orbital first** before the 3d orbitals.
 - Step 2: Remove the **4s electrons first before the 3d electrons.**

Example:

	Electronic configuration
Cr	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ⁵ 4s ¹
Cr⁺	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ⁵
Cr ²⁺	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ⁴
Cr ³⁺	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ³

	Electronic configuration
Fe	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ⁶ 4s ²
Fe⁺	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ⁶ 4s ¹
Fe ²⁺	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ⁶
Fe ³⁺	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ⁵

Exercise 1

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

- A chromium
- B cobalt
- **C** iron
- **D** manganese

Exercise 2

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

- **A** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2$
- **B** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^1$
- C 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ 4s¹
- **D** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

1.5 The Transition Elements

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

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

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

 The element copper forms Cu⁺ ion (electronic configuration: 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰) which has a fully filled d subshell. Is copper a transition element?

Copper is still regarded as a transition element because it can form Cu²⁺ ion with a partially filled d subshell.

Cu $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ Cu²⁺ $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$

transition elements

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	-								

d-block elements

2. GENERAL PHYSICAL PROPERTIES

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

2.1 Atomic Radius

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

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

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

2.2 Ionisation Energies

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



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

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

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

2.3 Melting Points and Boiling Points

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

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

Reason:

• The valence 3d and 4s electrons are close in energy (see Atomic Structure notes).

s-block elements

- Thus, both 3d and 4s electrons are available for delocalisation into the sea of electrons.
- With a greater number of delocalised electrons and higher charge density of the cations, the metallic bonding is stronger in the transition elements.



transition elements

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

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

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

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

Transition elements have

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

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

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

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

3. CHARACTERISTIC CHEMICAL PROPERTIES

- Some important characteristic chemical properties of transition elements are listed below and contrasted against those of s-block elements.
- 1. The transition elements form compounds in which the transition element shows a variety of oxidation states.

Examples: +2 +3 +6 $FeCl_2$ $FeCl_3$ K_2FeO_4

2. The transition elements form coloured compounds and ions.

Examples:	
$[CuCl_4]^{2-}(aq)$	yellow
[Cu(NH ₃) ₄] ²⁺ (aq)	dark blue
[Cr(H ₂ O) ₆] ³⁺ (aq)	green
[Cr(OH) ₆] ^{3–} (aq)	dark green
[Cu(H ₂ O) ₆] ²⁺ (aq)	blue
[Fe(SCN)(H ₂ O) ₅] ²⁺ (aq)	blood-red

- 3. The transition elements and their compounds often show catalytic activity. Examples: Fe/Fe₂O₃ N₂(g) + 3H₂(g) → 2NH₃(g)
- 4. The transition elements show a great tendency to form stable complexes.

Examples:

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

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

> Examples: +1 +1 KC*l* K₂SO₄

- 2. The s-block elements form compounds that are usually white in the solid state and colourless in aqueous solution. Examples: CaSO₄(s) white CaCl₂(aq) colourless
- 3. The s-block elements and their compounds show little or no catalytic activity.
- 4. The s-block elements show much less tendency to form stable complexes.

Examples: [Be(OH)₄]^{2–}(aq), [Ca(edta)]^{2–}(aq)

4. VARIABLE OXIDATION STATES

4.1 Transition elements and variable oxidation states

Compound	CrSO ₄	CrCl ₃	K ₂ CrO ₄
Oxidation state of Cr	+2	+3	+6

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

• Lower oxidation states

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

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

- The successive IEs of chromium increase gradually (due to similarity in energy of the 3d and 4s electrons). Hence, Cr ([Ar]3d⁵4s¹) can form cations of variable oxidation states by losing two electrons to form Cr²⁺ ([Ar]3d⁴) or three electrons to form Cr³⁺ ([Ar]3d³).
- This is in contrast to calcium which has a large increase between the 2nd and 3rd IE. The third electron of calcium is from an inner shell and experiences much stronger attraction, requiring more energy to be removed. Hence, calcium forms only one cation, Ca²⁺ with a fixed oxidation state of +2.

• Higher oxidation states

- The higher oxidation states are usually found in species where the transition element is covalently bonded to other more electronegative atoms.
- For example, chromium can exist in a high oxidation state of +6 in CrO₄²⁻ where it utilises all its 3d electrons and 4s electrons (a total of six electrons) in covalent bond formation. This is possible due to the close similarity in the energies of the 3d and 4s electrons.

4.2 Common Oxidation Numbers

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

К	Са	Sc	Ti	v	Cr	Mn	Fe	Co	Ni	Cu	Zn
4s ¹	4s ²	3d ¹ 4s ²	3d ² 4s ²	3d ³ 4s ²	3d ⁵ 4s ¹	3d ⁵ 4s ²	3d ⁶ 4s ²	3d ⁷ 4s ²	3d ⁸ 4s ²	3d ¹⁰ 4s ¹	3d ¹⁰ 4s ²
+1			+1	+1	+1	+1	+1	+1	+1	+1	
	+2		+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					

• Highest possible oxidation state

An observation can be made that in general,

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



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

Some generalisations

- (a) From Sc to Mn, the number of available oxidation states for the element increases. The value of the highest oxidation number for Sc to Mn suggests that in each element all the available 3d and 4s electrons may be used for bonding.
- (b) From Mn to Zn, there is a decrease in the number of oxidation states exhibited by the elements.
- (c) The common oxidation states for each element include +2 or +3 or both.
- (d) Oxides of elements in low oxidation states tend to be basic as they are ionic while oxides of elements in high oxidation states tend to be acidic as they are covalent. Using compounds of manganese as an example,

MnO	+2	basic	$(MnO + H_2SO_4 \longrightarrow MnSO_4 + H_2O)$			
Mn ₂ O ₃	+3	basic				
MnO ₂	+4	amphoteric				
MnO ₃	+6	acidic				
Mn ₂ O ₇	+7	acidic	$(Mn_2O_7 + 2NaOH \longrightarrow 2NaMnO_4 + H_2O)$			
Exerc	ise 3					
N92/4/20 and J99/3/18 Titanium has the electronic structure 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ² 4s ² . Which titanium compound is unlikely to exist?						

A $K_2 TiO_4$ **B** $K_3 TiF_6$ **C** $TiCl_3$ **D** TiO

4.3 Redox systems involving transition metal ions

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

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

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

Cr ³⁺ + e ⁻	<i>E</i> [⇔] = −0.41 V		Electronic c	configurations
Mn ³⁺ + e⁻ ⊂ Mn ²⁺	<i>E</i> [⇔] = +1.54 V	Cr	M ³⁺ [Ar] 3d ³	M ²⁺ [Ar] 3d ⁴
Fe ³⁺ + e ⁻	<i>E</i> [⊖] = +0.77 V	Mn Fe	[Ar] 3d⁴ [Ar] 3d⁵	[Ar] 3d⁵ [Ar] 3d ⁶
Co ³⁺ + e [−] ⊂ Co ²⁺	$E^{\ominus} = +1.82 \text{ V}$	Co	[Ar] 3d ⁶	[Ar] 3d ⁷

(i) Going across the transition elements, there is a **general** increase in E° value.

- (ii) There is a decrease in E^{\ominus} from Mn³⁺/Mn²⁺ to Fe³⁺/Fe²⁺.
 - Addition of an electron to Fe³⁺ results in a 3d⁶ configuration, where there is inter-electronic repulsion between the paired electrons in the same 3d orbital. Thus, reduction of Fe³⁺ to Fe²⁺ is less favoured.

(b) Aqueous KMnO₄ acidified with dilute H₂SO₄ and aqueous K₂Cr₂O₇ acidified with dilute H₂SO₄ are common oxidising agents used in laboratories.

MnO₄⁻ + 8H⁺ + 5e⁻ \Rightarrow Mn²⁺ $4H_2O$ *E*[⊕] = +1.52 V + very light pink purple / colourless \rightleftharpoons 2Cr³⁺ $E^{\ominus} = +1.33 \text{ V}$ $Cr_2O_7^{2-} + 14H^+ + 6e^-$ + 7H2O orange green

5. CATALYTIC ACTIVITY

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

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

• How does a catalyst increase the rate of a reaction?

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

• What are the two types of catalysis?

- 1. heterogeneous catalysis catalyst and the reactants are in different physical phases
- 2. homogeneous catalysis catalyst and the reactants are in the same phase
- Transition elements and their compounds are useful in both heterogeneous catalysis and homogeneous catalysis.

Transition element or their compounds used as catalyst.	Reaction catal	Type of catalysis	
V_2O_5	$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$	Contact process	Heterogeneous
MnO ₂	$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$		Heterogeneous
Fe/Fe ₂ O ₃	$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$	Haber process	Heterogeneous
Ni	$RCH=CH_2+H_2\longrightarrowRCH_2CH_3$	Hardening of vegetable oils (e.g. manufacture of margarine)	Heterogeneous
FeC <i>l</i> ₃	$C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl$	Electrophilic substitution of benzene	Homogeneous
Mn ²⁺	$2MnO_{4^{-}} + 5C_{2}O_{4^{2-}} + 16H^{+}$ $\longrightarrow 2Mn^{2+} + 10CO_{2} + 8H_{2}O$	An example of autocatalysis	Homogeneous

5.1 Heterogeneous Catalysis

- In heterogeneous catalysis, the catalyst and the reactants are in different phases.
 - The catalyst is usually in the solid phase and it provides active sites at which the reaction can take place and the reactants are usually liquids or gases.
- For heterogeneous catalysis to occur, the reactant molecules need to be readily <u>adsorbed</u> onto the catalyst surface. Such type of catalysis is a surface effect which involves the <u>formation of</u> weak attractive forces between reactant molecules and the atoms of the surface of the catalyst.
- What are the important features of first row transition elements (and their compounds) that enable them to function effectively as heterogeneous catalysts?

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

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

1. Diffusion

Reactant molecules diffuse towards catalyst surface.

2. Adsorption

Reactant molecules become **adsorbed** onto the **active sites** of the catalyst surface through attractive forces. This adsorption leads to an **increase in reaction rate** since

- the **bonds** within the reactant molecules are weakened, thereby **reducing the activation energy**
- the reactant molecules are brought into close contact with correct orientation for reaction

3. Chemical Reaction

This reaction has lower activation energy than the uncatalysed reaction





4. Desorption

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

5. Diffusion

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



5.2 Homogeneous Catalysis

- In homogeneous catalysis, the **catalyst and the reactants are in the same phase**, either liquid, aqueous or gaseous.
- Consider a reaction $A + B \longrightarrow D$ catalysed by Ct



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



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

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

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

• Example of homogeneous catalysis

The reaction between peroxodisulfate ions and iodide ions catalysed by Fe²⁺ or Fe³⁺.

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

(i) Uncatalysed reaction

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

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

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Relevant E^{\ominus} values:S_2O_8^{2^-} + 2e^- \Rightarrow 2SO_4^{2^-}E^{\ominus} = +2.01 VFe^{3+} + e^- \Rightarrow Fe^{2+}E^{\ominus} = +0.77 VI_2 + 2e^- \Rightarrow 2I^-E^{\ominus} = +0.54 V
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- Since E[⊕]_{cell} = 2.01 − 0.54 = +1.47 V > 0 V, the uncatalysed reaction is spontaneous (thermodynamically feasible) under standard conditions.
- However, the uncatalysed reaction involves the collision between negatively charged ions. The electrostatic repulsion between these negatively charged ions causes the reaction to have a high activation energy and hence proceeds slowly.

(ii) Reaction catalysed by Fe³⁺ or Fe²⁺

$ \begin{array}{l} \textcircled{\textbf{P}} \underline{\textbf{Exercise 4}} \\ \textbf{Q1} - Write equations to show how the reaction is catalysed by Fe3+ ion. \end{array} $				
Step 1: E [⊖] _{cell} =				
Step 2: E [⊕] _{cell} =				
 The catalysed reaction proceeds via two steps. For each step, E^o_{cell} > 0 V indicating that each step is spontaneous (thermodynamically feasible) under standard conditions. 				
 Each step involves a reaction between oppositely charged ions which have a natural tendency to attract each other. This lowers the activation energy and enhances the reaction rate. 				
Q2 – Write equations to show how the reaction is catalysed by Fe ²⁺ ion.				
Step 1:				
E⇔ _{cell} =				
Step 2:				
$E^{\ominus}_{\text{cell}} =$				

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

6. COMPLEXES

6.1 Introduction

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

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

• What is a **complex**?

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

• What is a **ligand**?

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

Examples of ligand: Cl⁻, OH⁻ CN⁻, H₂O, NH₃, CO, H₂N–CH₂CH₂–NH₂

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

• For complexes, the <u>number of bonds formed with the metal ion exceeds the oxidation state</u> of the <u>metal ion</u>. For example,

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

	Examples	Central atom/ion	Co-ordination number
noutral complexes	Ni(CO)4	Ni	4
	Fe(CO)₅	Fe	5
actionia complexes	[Fe(H ₂ O) ₆] ²⁺	Fe ²⁺	6
cationic complexes	[Ag(NH ₃) ₂]+	Ag⁺	2
anionic complexes	[Fe(CN) ₆] ^{4–} [CuC <i>l</i> 4] ^{2–}	Fe ²⁺ Cu ²⁺	6 4

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

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

[Ag(NH ₃) ₂]+	overall charge of complex ion = $(1)(1+) + (2)(0) = 1+$
[CuCl4] ²⁻	overall charge of complex ion = $(1)(2+) + (4)(1-) = 2-$
[Fe(CN) ₆] ^{4–}	overall charge of complex ion = $(1)(2+) + (6)(1-) = 4-$
[Fe(SCN)(H ₂ O) ₅] ²⁺	overall charge of complex ion = $(1)(3+)+(1)(1-) + 5(0) = 2+$

• Summary of terms applied to the [Fe(CN)₆]^{3–} complex



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

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

Complex salt	constituent cation	constituent anion
$[CoCl(NH_3)_5]Cl_2$	[CoC <i>l</i> (NH ₃) ₅] ²⁺	Cl⁻
pentaamminechlorocobalt(III) chloride	a complex cation	a simple anion
K4[Fe(CN)6]	K+	[Fe(CN) ₆] ^{4–}
potassium hexacyanoferrate(II)	a simple cation	a complex anion

Exercise 5 Q1 – Determine the oxidation nuises:	umber of the transition metal in	each of the following complex
(a) $[Fe(OH)_2(H_2O)_4]$	(b) K[Cu(CN) ₂]	(c) [CoCl ₄] ⁻
Q2 –Determine the overall char (a) [Fe(SCN)(H ₂ O) ₅] Fe(III)	ge of the following ions: (b) [Ni(NH ₃) ₆] Ni(II)	(c) [VO ₃ (OH)] V(V)

6.2 Types of Ligands

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

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



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

(a) Monodentate ligands

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

Examples of monodentate ligands: Cl⁻, OH⁻ CN⁻, H₂O, NH₃, C=O

Examples of complexes with monodentate ligands: [Fe(SCN)(H₂O)₅]²⁺, [CoCl₄]²⁻

(b) Bidentate ligands

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



(c) Hexadentate ligands

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



6.3 Transition Metal lons and Complex Formation

Complex formation

Ni ²⁺ +	6 H ₂ Ö	\downarrow	[Ni(H ₂ O) ₆] ²⁺	
metal ion	ligand		complex ion	
Lewis acid (electron pair acceptor)	Lewis base (electron pair (donor)		

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

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

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

6.4 Aqua Complexes

- In aqueous solution, the cations of Group 1 elements are surrounded by water molecules, with the negative ends of dipoles of these water molecules directed towards the cations. The cations are said to be **hydrated**.
- The type of interaction between the cations and the water molecules is that of **ion-dipole interaction**, i.e. electrostatic attraction between the positive ion and the negative ends of the dipoles.
- Due to their high charge density, transition metal ions exist as aqua complexes in aqueous solution. Each oxygen atom of a water molecule donates a lone pair of electrons into a low-lying vacant orbital of the transition metal ion and forms a coordinate bond. In general, aqua complexes are of the form [M(H₂O)₆]ⁿ⁺, where n = 2 or 3. (Note: Other cations with high charge density, e.g. Mg²⁺ and Al³⁺, also form aqua complexes.)

Solution	Cation	Complex ions
NaC <i>l</i> (aq)	Na⁺(aq)	-
MgSO₄(aq)	Mg ²⁺ (aq)	[Mg(H ₂ O) ₆] ²⁺ (aq)
AlCl₃(aq)	A <i>l</i> ³⁺ (aq)	[Al(H ₂ O) ₆] ³⁺ (aq)
Cr(NO ₃) ₃ (aq)	Cr ³⁺ (aq)	[Cr(H ₂ O) ₆] ³⁺ (aq)
FeCl ₃ (aq)	Fe ³⁺ (aq)	[Fe(H ₂ O) ₆] ³⁺ (aq)





6.5 Acidity of Aqua Complexes

• Why is an aqueous solution of FeCl₃ acidic?

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

Due to its high charge and small size, the Fe^{3+} ion has **high charge density** and is hence **strongly polarising**. It **distorts the electron cloud** of the H₂O molecules bonded to it, **weakening the O–H bonds** and enabling these H₂O molecules bonded to it to become proton donors. The free water molecules in the solution act as bases and the following equilibrium is established:



The Fe³⁺ ion is consequently said to undergo **appreciable hydrolysis** in aqueous solution. The slight excess of H_3O^+ ions in the solution causes the solution to be **acidic**.

- The aqueous solutions of most transition metal compounds such as CrCl₃(aq), FeCl₃(aq), CuSO₄(aq) and Co(NO₃)₂(aq) are acidic.
- An aqueous solution containing either Cr³⁺ or Fe³⁺ ions is acidic enough to react with sodium carbonate to produce carbon dioxide gas together with the formation of a hydroxide precipitate.
- What happens when Na₂CO₃ is added to an aqueous solution containing Fe³⁺ ions?

The following three equilibria are relevant to the Fe³⁺ ion in aqueous solution:

 $[Fe(H_2O)_6]^{3+}(aq) + H_2O(I) \Rightarrow [Fe(OH)(H_2O)_5]^{2+}(aq) + H_3O^{+}(aq) \qquad \dots \dots \dots \dots \dots (1)$

 $[Fe(OH)(H_2O)_5]^{2+}(aq) + H_2O(I) \Rightarrow [Fe(OH)_2(H_2O)_4]^{+}(aq) + H_3O^{+}(aq) \qquad \dots \dots \dots (2)$

 $[Fe(OH)_2(H_2O)_4]^+(aq) + H_2O(I) \Rightarrow [Fe(OH)_3(H_2O)_3](s) + H_3O^+(aq) \qquad \dots \dots \dots (3)$

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

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

The consumption of H_3O^+ ions causes the equilibrium position of reaction (1) to shift to the right. With more CO_3^{2-} ions added, and hence more H_3O^+ ions removed, the equilibrium position of reaction (2) and then subsequently that of reaction (3) are also forced to shift to the right. Consequently, **a red-brown precipitate** of [Fe(OH)₃(H₂O)₃] (usually written simply as **Fe(OH)**₃) is obtained *together* with the evolution of CO₂.

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

7. STEREOCHEMISTRY OF COMPLEXES

7.1 Shapes of complexes

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

Co-ordination number	Shape	Examples	
2	linear	[Ag(NH ₃) ₂]⁺ [Ag(CN) ₂]⁻ [CuC <i>l</i> ₂]⁻	$[H_{3}N \longrightarrow Ag \longleftarrow NH_{3}]^{+}$ $[Cl \longrightarrow Cu \longleftarrow Cl]^{-}$
	tetrahedral	Ni(CO) ₄ [Zn(NH ₃) ₄] ²⁺ [CoC <i>l</i> ₄] ²⁻ [Cu(CN) ₄] ³⁻ [CuC <i>l</i> ₄] ²⁻	$\begin{bmatrix} NH_3 \\ \downarrow \\ I_3N \\ NH_3 \end{bmatrix}^{2+}$
4	square planar	[Ni(CN)4] ^{2–} [Cu(NH ₃)4] ²⁺	NC NI NC NC CN
6	octahedral	[Fe(CN) ₆] ^{3−} [Fe(CN) ₆] ^{4−} [Ni(NH ₃) ₆] ²⁺	CN NC NC Fe CN CN CN

Note:

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

7.2 Isomerism in compounds of transition elements

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

 $\begin{array}{ccc} [Cr(H_2O)_4Cl_2]Cl \bullet 2H_2O \longrightarrow & [Cr(H_2O)_5Cl]Cl_2 \bullet H_2O \longrightarrow & [Cr(H_2O)_6]Cl_3 \\ green & blue-green & violet \end{array}$

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

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

7.3 Stereoisomerism in Complexes of Transition Elements

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

(a) Cis-Trans Isomerism

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



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

(b) Enantiomerism

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







Scan this QR code with your device's camera and point the camera at the 'Hiro' image to see the WebAR 3D models of the two non-superimposable images of (i) ML₃ and (ii) MA₂L₂.

☐ <u>Exercise 6</u> Q1 – N02/17

The anti-cancer drug, *cisplatin* has the formula PtC*l*₂(NH₃)₂. In the human body, one of the chloride ions of *cisplatin* is replaced by one water molecule.

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

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

Q2 – N05/1 Like other transition elements, platinum(IV) chloride combines with ammonia to form compounds. The co-ordination number of platinum in these compounds is 6. A formula unit of one of the compounds contains a cation and only two chloride ions.		Q3 Chi forr nur trea only pre	romium(III) chlorid n compound X nber of chromiur ated with an exce y two thirds of t cipitated as AgC <i>l</i> .	de con in w n is (ess of he to	nbines with ammonia to hich the co-ordination 6. When solution X is aqueous silver nitrate, tal chloride present is		
Wł	nat is the formula	a of th	nis compound?	Wh	at is the formula c	of com	pound X?
A	Pt(NH ₃) ₃ Cl ₄	В	Pt(NH ₃) ₄ Cl ₄	Α	Cr(NH ₃) ₃ Cl ₃	В	Cr(NH ₃) ₄ Cl ₃
С	Pt(NH ₃) ₆ Cl ₂	D	Pt(NH ₃) ₆ Cl ₄	С	Cr(NH₃)₅C <i>l</i> ₃	D	Cr(NH ₃) ₆ Cl ₃

8. COLOUR OF COMPLEXES

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

Aqua complex ion	Electronic configuration of the cation	Colour
[Sc(H ₂ O) ₆] ³⁺	[Ar] 3d ⁰	colourless
[Ti(H ₂ O) ₆] ³⁺	[Ar] 3d ¹	violet
[V(H ₂ O) ₆] ³⁺	[Ar] 3d ²	green
$[V(H_2O)_6]^{2+}$	[Ar] 3d ³	violet
[Cr(H ₂ O) ₆] ³⁺	[Ar] 3d ³	violet / green
[Cr(H ₂ O) ₆] ²⁺	[Ar] 3d ⁴	blue
[Mn(H ₂ O) ₆] ³⁺	[Ar] 3d ⁴	violet
[Mn(H ₂ O) ₆] ²⁺	[Ar] 3d⁵	faint pink
[Fe(H ₂ O) ₆] ³⁺	[Ar] 3d⁵	pale violet (lilac) / yellow
[Fe(H ₂ O) ₆] ²⁺	[Ar] 3d ⁶	pale green
[Co(H ₂ O) ₆] ²⁺	[Ar] 3d ⁷	pink
[Ni(H ₂ O) ₆] ³⁺	[Ar] 3d ⁸	green
[Cu(H ₂ O) ₆] ²⁺	[Ar] 3d ⁹	blue
[Zn(H ₂ O) ₆] ²⁺	[Ar] 3d ¹⁰	colourless

• Typical colours for common ions (i.e. with H₂O as the ligand) are summarised below.

Note:

- 1. Vacant or fully filled d sub-shell is associated with a lack of colour.
- 2. Aqueous solutions of Cr³⁺
 - [Cr(H₂O)₆]³⁺ is violet in cold aqueous solution.
 - The observed green colour of its solutions is due to the partial replacement of water ligands by other ligands, e.g. Cl⁻ or SO4²⁻.
 - For simplicity, the green solution is still commonly written as [Cr(H₂O)₆]³⁺.

3. Aqueous solutions of Fe³⁺

- [Fe(H₂O)₆]³⁺ is pale violet.
 - The observed yellow colour of its solutions is due to the partial loss of H⁺ by a water ligand to form [Fe(OH)(H₂O)₅]²⁺, which is yellow.
- For simplicity, the yellow solution is still commonly written as [Fe(H₂O)₆]³⁺.

8.1 Occurrence of colour



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

(b) Coloured objects

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

• What determines the observed colour of a coloured object?

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

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

(c) Complementary colours

			- 650 nm 580 nm
Wavelength range (nm)	Colour	Complementary colour	orange
400 - 430	violet	yellow	red
430 – 490	blue	orange	700 nm / 100 yenow
490 – 550	green	red	400 nm violet 550 hm
550 - 580	yellow	violet	green
580 - 650	orange	blue	blue
650 – 700	red	green	430 nm 490 nm

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

• Example: A green object

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



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

8.2 Absorption of Light Energy and Electronic Transition

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



8.3 Sodium chloride solution



8.4 Occurrence of Colour in Octahedral Complexes

(a) Crystal Field Theory

- **Crystal Field Theory** provides a way of determining, by simple electrostatic considerations, how the energies of the metal ion orbitals will be affected by the set of surrounding ligands.
- In an isolated metal ion in the gaseous phase, the five 3d orbitals all have the same energy and are said to be **degenerate**.
- In an octahedral complex, six ligands L approach the central metal ion M along the x, y and z axes. This results in electrostatic repulsion between the electrons in the 3d orbitals and the lone pairs on the ligands, and thus an increase in potential energy. Hence the energy of an electron in either of the 3d orbitals in a complex of M is higher than in an isolated M atom.
- **3d**_x²-y²**and 3d**_z²: These orbitals have their greatest electron density **along** the co-ordinate axes on which the ligands are situated. Hence electrons in these orbitals are pointing towards the lone pairs of ligands, and will be **repelled** by them.



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



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

Worked Example 1

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



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

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



- The resulting small energy gap (i.e. ΔE_o) between the two sets of d-orbitals turns out to correspond to energies of electromagnetic radiation in the visible region of the spectrum.
- Transition metal compounds are therefore coloured because radiation in the visible region
 of the spectrum is of the right quantity of energy to promote electrons from d-orbitals of
 lower energy to one of higher energy (i.e. d-d transitions). The colour observed is the
 complement of the colour absorbed.

• Why is an aqueous solution of NiCl₂ coloured?

In aqueous solution, Ni²⁺ exists as an octahedral complex [Ni(H₂O)₆]²⁺.

The presence of the H_2O ligands causes the <u>splitting</u> of the five originally degenerate 3d orbitals in the Ni²⁺ ion into two sets of slightly different energy levels.

Since the 3d subshell is <u>partially filled</u> (Ni²⁺: [Ar] 3d⁸), the <u>electrons</u> from the lower energy d orbitals can <u>absorb energy corresponding to certain wavelengths from the visible spectrum</u> and get <u>promoted to the higher energy d orbitals</u>.

Such d-d transitions are responsible for the colour observed in NiC $l_2(aq)$. The <u>colour observed</u> is the complement of the colour absorbed.

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

8.5 Factors affecting the Colour of Transition Metal Complexes

- The colour of a transition metal complex is dependent on the energy gap (ΔE) between the two groups of d orbitals. This in turn depends on the following factors.
 - 1. The identity of the metal and its oxidation state (which depends on the number of d electrons present).

[Cr(H ₂ O) ₆] ²⁺ (aq)	[Cr(H ₂ O) ₆] ³⁺ (aq)	[Fe(H ₂ O) ₆] ²⁺ (aq)	[Fe(H ₂ O) ₆] ³⁺ (aq)
[Ar] 3d ⁴	[Ar] 3d ³	[Ar] 3d ⁶	[Ar] 3d ⁵
blue	violet	pale green	lilac

- Compounds of the same element in different oxidation states show different colours.
- [Fe(H₂O)₆]²⁺ and [Fe(H₂O)₆]³⁺ have different no. of d-electrons and repel the electrons
 of the ligands to different extent, thus the energy gap between the split d-orbitals are
 different.

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

[Ni(H ₂ O) ₆] ²⁺ (aq)	green	[Cu(H ₂ O) ₆] ²⁺ (aq)	blue
[Ni(NH ₃) ₆] ²⁺ (aq)	blue	$[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$	dark blue

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

8.6 Splitting of d-orbitals in Tetrahedral Complexes

- In tetrahedral complexes, the situation is the reverse of that in octahedral complexes. The four ligands in tetrahedral complexes approach the central metal ion in between the x, y and z axes.
- Electrons in the 3d_{xy}, 3d_{yz} and 3d_{xz} orbitals now experience the greatest electrostatic repulsion from the ligand lone pairs, so have a higher energy than electrons in the 3d_x²-y² and the 3d_z² orbitals.



9. LIGAND EXCHANGE

9.1 Stability constant

- An aqueous solution of nickel(II) sulfate contains [Ni(H₂O)₆]²⁺ ions. When excess aqueous ammonia is added to this solution, there is a noticeable change of colour because some of the [Ni(H₂O)₆]²⁺ ions are converted into [Ni(NH₃)₆]²⁺ ions.
- A ligand exchange reaction occurs and the following equilibrium is established:

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

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

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

- K_{stab} is known as the stability constant for the [Ni(NH₃)₆]²⁺ ion. It is a measure of how stable the [Ni(NH₃)₆]²⁺ ion is as compared to the [Ni(H₂O)₆]²⁺ ion.
- Definition of K_{stab}

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

- The large value of K_{stab} means that:
 - The equilibrium position for the above reaction lies very much to the right.
 - The $[Ni(NH_3)_6]^{2+}$ ion is **relatively more stable** than the $[Ni(H_2O)_6]^{2+}$ ion.
 - \circ NH₃ is a **stronger ligand** than H₂O.
 - \circ NH₃ forms a stronger dative covalent bond with the Ni²⁺ ion.
 - There will be **replacement of the H₂O ligands by the NH₃ ligands** when excess NH₃ is added to NiSO₄(aq) (i.e. a ligand exchange reaction can occur).

9.2 Ligand exchange in terms of stability constants

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

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

K_{stab} of complexes of copper(II)

complex	[CuCl ₄] ²⁻	[Cu(NH ₃) ₄ (H ₂ O) ₂] ²⁺	[Cu(edta)] ²⁻
log K _{stab}	5.6	13.1	18.8
colour	yellow	dark blue	light blue

<u>Worked Example 2 (N93/2/1a)</u>

(i) Describe and explain what happens when dilute aqueous ammonia is gradually added to an aqueous solution containing Cu ²⁺ (aq).			
$ \begin{bmatrix} Cu(H_2O)_6 \end{bmatrix}^{2^+}(aq) & \xrightarrow{NH_3(aq)} Cu(OH)_2(s) \xrightarrow{NH_3(aq)} \begin{bmatrix} Cu(NH_3)_4(H_2O)_2 \end{bmatrix}^{2^+}(aq) \\ \hline \\ $			
Aqueous NH_3 is a weak base which ionises in water to form OH^- ions.			
$NH_3(aq) + H_2O(I) \Rightarrow NH_4^+(aq) + OH^-(aq)$			
An aqueous solution containing Cu^{2+} ions is blue due to the presence of $[Cu(H_2O)_6]^{2+}$ ions. When dilute NH ₃ (aq) is gradually added, a <u>pale blue precipitate</u> of Cu(OH) ₂ is first formed since ionic product of Cu(OH) ₂ exceeds the K_{sp} of Cu(OH) ₂ .			
$[Cu(H_2O)_6]^{2+}(aq) + 2OH^{-}(aq) \rightleftharpoons [Cu(OH)_2(H_2O)_4](s) + 2H_2O(I) \qquad \dots $			
or $Cu^{2+}(aq) + 2OH^{-}(aq) \rightleftharpoons Cu(OH)_2(s)$			
When excess NH_3 is added, a ligand exchange reaction occurs and the following equilibrium is established.			
$\begin{bmatrix} Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons \begin{bmatrix} Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(I) & \dots & \dots & (2) \\ blue \text{ solution} & dark \text{ blue solution} \end{bmatrix}$			

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

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

Note:

- In this case, there exist two competing equilibria, (1) and (2). Both NH₃ and OH⁻ compete to combine with Cu²⁺(aq). With a large excess of NH₃ (i.e. higher [NH₃]), the formation of [Cu(NH₃)₄(H₂O)₂]²⁺ is more favourable.
- 2. The following equation is sometimes used to represent the dissolution of the pale blue precipitate upon the addition of excess aqueous NH₃.

 $Cu(OH)_{2}(s) + 4NH_{3}(aq) + 2H_{2}O(I) \longrightarrow [Cu(NH_{3})_{4}(H_{2}O)_{2}]^{2+}(aq) + 2OH^{-}(aq)$

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

When aqueous edta is added to a <u>dark blue solution</u> containing the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ions, the colour of the solution lightens considerably as a ligand exchange reaction occurs. The hexadentate edta ligand replaces the NH₃ and H₂O ligands to form the more stable $[Cu(edta)]^{2-}$ ions leading to <u>the formation of a light blue solution</u>. The following equilibrium is established and the equilibrium position lies more to the right.

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

Worked Example 3

J91/4/1bii Describe and explain what is seen when concentrated hydrochloric acid is added to a solution of Cu²⁺ ions in water.

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

$$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^{-}(aq) \Rightarrow [CuCl_4]^{2-}(aq) + 6H_2O(I)$$

blue vellow

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

Addition of more concentrated HC*l* to the green solution increases the C*l*⁻ concentration, causing the equilibrium position of the above reaction to shift further right. The green solution turns yellow as more yellow [CuC*l*₄]²⁻ ions are formed.

(b) Complexes of Ag(I):

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

	Ligand	Colour and state of complex
$[Ag(H_2O)_2]^+(aq)$	H_2O	Colourless solution
\downarrow add NaCl(aq)		
AgC/(s)	C/⁻	White precipitate
\downarrow add NH $_3$ (aq)		
[Ag(NH ₃) ₂] ⁺ (aq)	NH_3	Colourless solution
\downarrow add KBr(aq)		
AgBr(s)	Br⁻	Cream precipitate
\downarrow add Na ₂ S ₂ O ₃ (aq)		
[Ag(S ₂ O ₃) ₂] ³⁻ (aq)	S ₂ O ₃ ²⁻	Colourless solution
↓ add KI(aq)		
AgI(s)	I_	Yellow precipitate
↓ add KCN(aq)		
[Ag(CN) ₂] ⁻ (aq)	CN ⁻	Colourless solution
\downarrow add Na ₂ S(aq)	a ² -	D
Ag ₂ S(s)	S²	Black precipitate
↓ add Na₂edta(aq)	14 - 2-	O davela a a a batian
[Ag(edta)] (aq)	edta ²	Colourless solution

Note:

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

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

Exercise 7: (J96/IV/22)

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

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

M^{m_+}	L-	n	$K_{ m stab}$
Fe ³⁺	SCN⁻	1	9 x 10 ²
Fe ³⁺	CN⁻	6	1 x 10 ³¹
Co ³⁺	CN⁻	6	1 x 10 ⁶⁴

- (i) Rewrite the above equation for the case of $M^{m_+} = Fe^{3+}$ and $L^- = CN^-$. Write the expression for the equilibrium constant, K_{stab} , and state its units.
- Use the data given in the table to predict what would be the predominant complex formed when

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

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

[5]

9.3 Exchange of ligands in haemoglobin

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

Structure:

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



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



9.4 Effect of Ligand Exchange on E^O values

- Replacement of H₂O ligands in an aqua-complex by other ligands can cause large changes in electrode potential values.
- (a) Effect of CN⁻ ligand on the relative stability of Fe(II) and Fe(III)

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

- Replacing the H₂O ligand by the CN⁻ ligand causes the E[⊕] value for the Fe(III)/Fe(II) system to become less positive i.e. Fe(III) becomes less easily reduced and hence less oxidising.
- Hence there is stabilisation of the +3 oxidation state of iron relative to the +2 oxidation state of iron by the CN⁻ ligand.
- The positively charged [Fe(H₂O)₆]³⁺ ion accepts an electron more readily since oppositely charged species attract each other naturally. The negatively charged [Fe(CN)₆]³⁻ ion does not accept an electron readily since there is naturally repulsion between similarly charged species.

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

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

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

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

Observation: Brown solution of I₂(aq) is not produced.

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

- The E[⊕] values show that there is stabilisation of Co(III) with respect to Co(II) by the NH₃ and the CN⁻ ligands.
- $[Co(H_2O)_6]^{3+}$ ions are so strongly oxidising that they react with water to produce oxygen.
- [Co(NH₃)₆]²⁺(aq) and [Co(CN)₆]⁴⁻(aq) are so strongly reducing that they are oxidised by air.

10. SUMMARY

10.1 Typical reactions undergone by transition metal ions

(a) Precipitation reactions

- Common reagents used: NH₃(aq), NaOH(aq)
- See the QA Notes for details
- Explanation is usually couched in terms of ionic product exceeding K_{sp}

 $Cu^{2+}(aq) + 2OH^{-}(aq) \xrightarrow{NH_{3}(aq)} Cu(OH)_{2}(s)$ blue solution pale blue precipitate

(b) Ligand exchange reactions

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

$$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \xrightarrow{excess NH_3(aq)} [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 2H_2O(l)$$
blue solution
$$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \xrightarrow{conc. HCl} [CuCl_4]^{2-} + 6H_2O(l)$$
blue solution
$$[Fe(H_2O)_6]^{3+}(aq) + SCN^-(aq) \xrightarrow{KSCN(aq)} [Fe(SCN)(H_2O)_5]^{2+}(aq) + H_2O(l)$$
blood red solution
$$[Fe(H_2O)_6]^{3+}(aq) + 3C_2O_4^{2-}(aq) \xrightarrow{Na_2C_2O_4(aq)} [Fe(C_2O_4)_3]^{3-}(aq) + 6H_2O(l)$$
blow solution
$$[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \xrightarrow{conc. HCl} [CoCl_4]^{2-}(aq) + 6H_2O(l)$$
blue solution
$$[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \xrightarrow{conc. HCl} [CoCl_4]^{2-}(aq) + 6H_2O(l)$$
blue solution
$$[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \xrightarrow{conc. HCl} [CoCl_4]^{2-}(aq) + 6H_2O(l)$$
blue solution
$$[Cocl_4]^{2-}(aq) + 6H_2O$$

(c) Redox reactions

• Justification of whether a redox reaction can occur is usually based on E^{\ominus} values

 $\begin{array}{cccc} 2\mathsf{F}e^{2+}(\mathsf{aq}) + \mathsf{C}l_2(\mathsf{aq}) & \longrightarrow 2\mathsf{F}e^{3+}(\mathsf{aq}) + 2\mathsf{C}l^-(\mathsf{aq}) \\ \text{pale green solution} & \text{yellow solution} \end{array}$ $2\mathsf{F}e^{3+}(\mathsf{aq}) + 2\mathsf{I}^-(\mathsf{aq}) & \longrightarrow 2\mathsf{F}e^{2+}(\mathsf{aq}) + \mathsf{I}_2(\mathsf{aq}) \\ 2\mathsf{C}u^{2+}(\mathsf{aq}) + 4\mathsf{I}^-(\mathsf{aq}) & \longrightarrow 2\mathsf{C}u(\mathsf{s}) + \mathsf{I}_2(\mathsf{aq}) \\ & & & \text{cream ppt. brown solution} \end{array}$ $\begin{array}{c} \mathsf{C}u^{2+}(\mathsf{aq}) + \mathsf{Z}n(\mathsf{s}) & \longrightarrow \mathsf{C}u(\mathsf{s}) + \mathsf{Z}n^{2+}(\mathsf{aq}) \\ & & & \text{pink solid} \end{array}$

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

An aqueous solution containing Fe³⁺ or Cr³⁺ is acidic due to hydrolysis.

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

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

APPENDIX

(I) Rules for Nomenclature of Complexes

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

(a) Formulae of Complexes

- The symbol for the central atom is written first, followed by anionic ligands and neutral ligands in that order. Example: [Fe(OH)(H₂O)₅]²⁺
- Within each ligand class, the order should be alphabetical in terms of the symbol for the donor atom of the ligand. Example: [Cu(NH₃)₄(H₂O)₂]²⁺
 - N is the donor atom in NH₃.
 - O is the donor atom in H₂O.
- Polyatomic ligands, but not monatomic ligands, are enclosed in curved brackets, and the formula of the whole complex is enclosed in square brackets. Example: [CrCl₂(NH₃)₄]⁺

(b) Naming of Complexes

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

(c) Steps to be taken

- 1. Identify the ligands (see **Box A**).
- 2. Identify the number of ligands (see **Box B**).
- 3. If several ligands are present, list them in alphabetical order. Note: prefixes do not alter order.
- 4. Name the central cation/atom and indicate its oxidation state using a Roman numeral in parentheses.

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

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

