Raffles Institution
Year 6 Chemistry 2018
Lecture Notes 21 – An Introduction to the
Chemistry of Transition Elements

Lecturers: Mrs Sze Lih Sin & Ms Chloe Lim

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

(i) define the terms *ligand* and *complex* as exemplified by the complexes of copper(II) ions with water, ammonia and chloride ions as ligands
(including the transition metal complexes found in the Qualitative Analysis Notes)

(j) explain qualitatively that ligand exchange may occur, as exemplified by the formation of the complexes in (i), including the colour changes involved, and CO/O_2 exchange in haemoglobin

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

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

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

---

1.   INTRODUCTION

1.1 The d-block elements

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

Period number			
1	1 s		1 s
2	2 s		2 p
3	3 s		3 p
4	4 s	3 d	4 p
5	5 s	4 d	5 p
6	6 s	5 d	6 p
7	7 s	6 d	
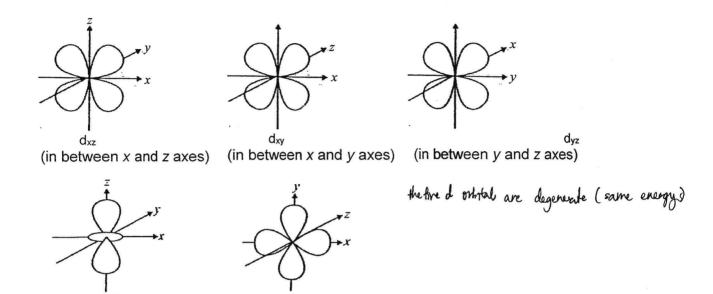
- We will focus on the **first row d-block elements**.

45.0	47.9	50.9	52.0	54.9	55.8	58.9	58.7	63.9	65.4
Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
scandium	titanium	vanadium	chromium	manganese	iron	cobalt	nickel	copper	zinc
21	22	23	24	25	26	27	28	29	30

- The 3d block contains **ten elements**, because the **3d subshell** contains **five orbitals**, each able to accommodate up to two electrons. All 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.

1.2 Shapes of the 3d orbitals

- There are a total of **five 3d orbitals**:

d_{xz}
(in between x and z axes)

d_{xy}
(in between x and y axes)

d_{yz}
(in between y and z axes)

d_{z^2}
(along z axis)

$d_{x^2-y^2}$
(along x and y axes)

the five d orbitals are degenerate (same energy)

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 electrons do occupy a single orbital, their spins must be paired.

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).

1s
2s 2p
3s 3p 3d
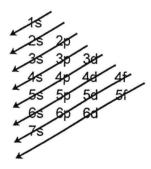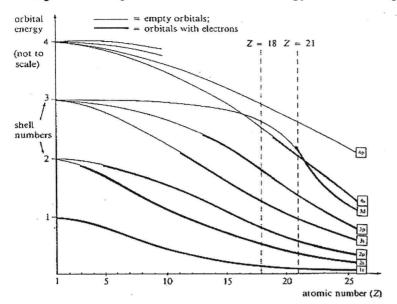4s 4p 4d 4f
5s 5p 5d 5f
6s 6p 6d
7s

Diagram showing the decrease in orbital energy with increasing atomic number:

Orbital energy decreases with Z from 1s to 4f

(Source: Advancing Chemistry by Lewis and Waller)

For z = 1 to 17 (H to Cl), energy level of 3d < 4s
For z = 18 to 20 (Ar to Ca), energy level of 3d > 4s
For z ≥ 21 (from Sc onwards), energy level of 3d < 4s

- As the nuclear charge increases, the energies of all the orbitals decrease. However because of their proximity to the nucleus, the spherically symmetrical s orbitals are affected to a greater degree than the more angular p and d orbitals, and so their energies decrease more rapidly than the other types of orbital.
- By the time the fourth shell is reached, there is, in fact **an overlap between the third and fourth shells.** As can be seen from the given graph, **the energy of the 4s orbital has already become less than that of the 3d orbital** at Z = 18 (argon).
- Thus the next two electrons enter the 4s orbital i.e. the electronic configurations of potassium (Z = 19) and calcium (Z = 20) are $[Ar]4s^1$ and $[Ar]4s^2$ respectively since the lower energy 4s orbital is filled before the 3d orbitals. This is because the energy of the empty 4s orbital is slightly lower than that of the empty 3d orbitals.
- Starting from scandium (Z = 21), electrons start to occupy the 3d orbitals Once electrons occupy the **inner** 3d orbitals, they (i.e. the 3d electrons) provide some shielding for the **outermost 4s electrons.** They repel the 4s electrons to a slightly higher energy level.

Element	'Electrons-in-boxes' diagram		Electronic configuration
	3d	4s	
$_{21}$Sc	[Ar] ↑ □ □ □ □	↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^1\ 4s^2}$
$_{22}$Ti	[Ar] ↑ ↑ □ □ □	↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^2\ 4s^2}$
$_{23}$V	[Ar] ↑ ↑ ↑ □ □	↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^3\ 4s^2}$
$_{24}$**Cr**	[Ar] ↑ ↑ ↑ ↑ ↑	↑	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^5\ 4s^1}$
$_{25}$Mn	[Ar] ↑ ↑ ↑ ↑ ↑	↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^5\ 4s^2}$
$_{26}$Fe	[Ar] ↑↓ ↑ ↑ ↑ ↑	↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^6\ 4s^2}$
$_{27}$Co	[Ar] ↑↓ ↑↓ ↑ ↑ ↑	↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^7\ 4s^2}$
$_{28}$Ni	[Ar] ↑↓ ↑↓ ↑↓ ↑ ↑	↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^8\ 4s^2}$
$_{29}$**Cu**	[Ar] ↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^{10}\ 4s^1}$
$_{30}$Zn	[Ar] ↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^{10}\ 4s^2}$

Two exceptions:

1. Electronic configuration of chromium: **$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$**

    For Cr, the configuration [Ar] $3d^5\ 4s^1$ is **more stable** than [Ar] $3d^4\ 4s^2$.

	3d	4s
[Ar]	⬆ ⬆ ⬆ ⬆ ⬆	⬆

    The electrons occupy the 3d and 4s orbitals singly so that interelectronic repulsion is minimised.

	3d	4s
[Ar]	⬆ ⬆ ⬆ ⬆	⬆⬇

    There is a repulsion between the two 4s electrons within the same orbital.

2. Electronic configuration of copper: **$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$**
    For Cu, the configuration [Ar] $3d^{10}\ 4s^1$ is **more stable** than [Ar] $3d^9\ 4s^2$.

1.4 Electronic Configurations of the Ions
- 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 **element** first, with electrons occupy 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+}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$

Ion	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: Electronic Structure of a d-Block Element (N98/III/1)**
The diagram shows the energy levels of various electronic subshells of an atom of a transition element in the fourth period of the Periodic Table.

What are subshells x and y?

A $x = 3d, y = 4s$
B $x = 4s, y = 3d$
C $x = 4s, y = 4p$
D $x = 4p, y = 3d$

A

```
— y
— x
— 3 p    ↑
— 3 s
— 2 p  energy
— 2 s
— 1 s
```

once 3d-subshell starts to fill, the inner 3d-electron repel 4s to a higher energy. 3d - lower in energy than 4s when z ≥ 21 (Sc)

📖 **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 $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$
D $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$

Summary: - most d-block elements have outer electronic configuration of [Ar]$3d^x\ 4s^2$
except Cr : [Ar]$3d^5\ 4s^1$ and Cu : [Ar]$3d^{10}\ 4s^1$.

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 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.
>
> | | | | |
> |---|---|---|---|
> | Sc | $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^1\,4s^2$ | Zn | $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2$ |
> | Sc^{3+} | $1s^2\,2s^2\,2p^6\,3s^2\,3p^6$ | Zn^{2+} | $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}$ |

- The element copper forms Cu^+ ion (electronic configuration: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}$) which has a fully filled d subshell. Is copper a transition element?

> Copper is still regarded as a transition element because it can form Cu^{2+} ion with a partially filled d subshell.
>
> | | | | |
> |---|---|---|---|
> | Cu | $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^1$ | Cu^{2+} | $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^9$ |

---

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 <u>good conductors of heat and electricity</u>

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**
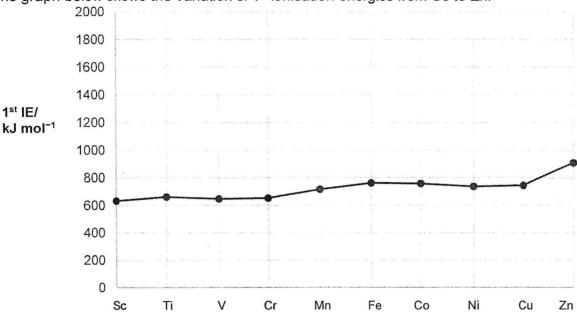
Element	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic radius/nm	0.197	0.144	0.132	0.122	0.117	0.117	0.116	0.116	0.115	0.117	0.125

- In traversing the first-row transition elements, the **number of protons increases**, and hence, the **nuclear charge increases**. (inner)
- The number of electrons also increases. Electrons are added to the penultimate 3d subshell. These **inner 3d electrons shield the outer 4s electrons** from the increasing nuclear charge.
- The **increase in shielding effect**, due to an **increase in the number of 3d electrons, offsets the increase in nuclear charge to a considerable extent.**
- There is only a **small increase in the effective nuclear charge** and attraction for valence electrons ~~increases slightly.~~ (is relatively constant.)
- The atomic radii ~~decreases slightly~~ and is often regarded as being **relatively constant**.
- 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 Sc to Cu is **almost constant.**

The graph below shows the variation of 1st ionisation energies from Sc to Zn.

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**.
- Electrons are added to the penultimate 3d sub-shell. These inner 3d electrons shield the outer 4s electrons from the increasing nuclear charge.
- The **increase in shielding effect**, due to an **increase in the number of 3d electrons, offsets the increase in nuclear charge to a considerable extent.** $\longrightarrow$ Z_{eff} α constant,
- Thus, energy required to remove the first electron is **almost constant.** attraction for outer electrons α constant.

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.

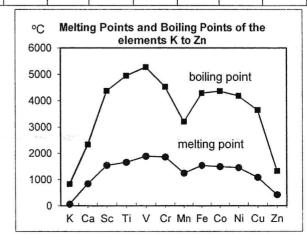|	s-block elements			transition elements								
Element	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Melting point / °C	64	839	1541	1660	1890	1857	1244	1535	1495	1455	1083	420
Boiling point / °C	760	1494	2831	3287	3380	2670	1962	2750	2870	2730	2567	907

Reason:
- The valence 3d and 4s electrons are close in energy.
- Thus, both **3d and 4s electrons are available for delocalisation** into the sea of electrons.
- Metallic bonding is stronger.

$\rightarrow$ better electrical conductivity for transition metals.
$\rightarrow$ more delocalised e^- to act as mobile charge carriers.

Melting Points and Boiling Points of the elements K to Zn

Example: The melting point of Ti is higher than that of Ca. Why is that so?

> Both Ti and Ca are metals. Ti has a higher melting point than Ca due to **stronger metallic bonding** in Ti which require more energy to break.
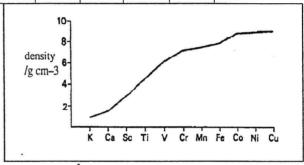> The stronger metallic bonding in Ti arises due to:
> - Ti cation has a higher charge density.
> - Both 3d and 4s electrons are available for delocalisation into the sea of electrons.

2.4 Density

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

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

- Transition elements have **smaller atomic size but larger atomic mass** as compared to s-block elements.

- There are more atoms packed per unit volume for the transition elements as compared to s-block elements.

$$\text{Density} = \frac{mass}{volume}$$

where volume $= \frac{4}{3}\pi r^3$ where r is atomic radius.

Comparing transition elements

> From Sc 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

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

   Examples:
   +1   +1
   KCl K_2SO_4

2. The transition elements form coloured compounds and ions.

Examples:
$[CuCl_4]^{2-}$ (aq)	yellow
$[Cu(NH_3)_4]^2$ (aq)	dark blue
$[Cr(H_2O)_6]^{3+}$(aq)	green
$[Cr(OH)_6]^{3-}$ (aq)	dark green
$[Cu(H_2O)_6]^{2+}$(aq)	blue
$[Fe(SCN)(H_2O)_5]^{2+}$(aq)	blood-red

2. The s-block elements form compounds that are usually white in the solid state and colourless in aqueous solution.

Examples:
$CaSO_4$(s)	white
$CaCl_2$(aq)	colourless

3. The transition elements and their compounds often show catalytic activity.
Examples: Fe/Fe_2O_3 homogeneous / heterogeneous catalysts.
$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

3. The s-block elements and their compounds show little or no catalytic activity.

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)

4. The s-block elements show much less tendency to form stable complexes.

Examples:
$[Be(OH)_4]^{2-}$(aq), $[Ca(edta)]^{2-}$(aq)
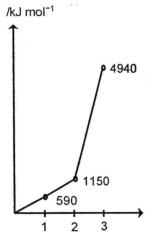
---

4. VARIABLE OXIDATION STATES

4.1 Transition elements and variable oxidation states

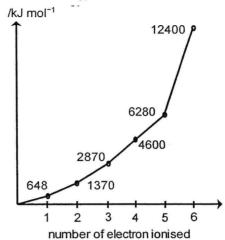| Compound	$MnSO_4$	$MnCl_3$	MnO_2	K_3MnO_4	K_2MnO_4	$KMnO_4$
Oxidation state of Mn	+2	+3	+4	+5	+6	+7

- **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).

- For example, Cr can form the Cr^{2+} ion (by losing one 4s electron and one 3d electron) in which it exists in a low oxidation state of +2. It can also exist in a high oxidation state of +6 in CrO_4^{2-} where it utilises all its 3d electrons and 4s electrons (a total of six electrons) in covalent bond formation.

- The close similarity in energy of the 3d and the 4s electrons of a first row transition element means that successive ionisation energies involving these electrons will **increase gradually**.

-8-

- Consider the ionisation energies of calcium and vanadium as shown below.

Ionisation energy of calcium
/kJ mol^{-1}

Ionisation energy of vanadium
/kJ mol^{-1}

12400

6280

4600

4940

2870

1150

648   1370

590

1   2   3
number of electron ionised

1   2   3   4   5   6
number of electron ionised

- The graph for vanadium shows that the first five successive ionisation energies of vanadium increase rather gradually with no distinct large increment. This is unlike the case of calcium (an s-block element).

- This is because the 3rd and 4th electrons of Ca, which are in an inner principal quantum shell nearer the nucleus, experience much greater nuclear attraction and require much more energy to be removed.

4.2 Common Oxidation Numbers
- The table below summarises the known oxidation numbers of the elements Sc to Zn.

K	Ca	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					

Observation: In general,
Highest possible oxidation state = No. of unpaired d-electrons + 4s electrons

Example:
Co: [Ar] | ↑↓ | ↑↓ | ↑ | ↑ | ↑ | | ↑↓ |

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

Some generalisations
(a) The number of available oxidation states for the element increases from Sc to Mn. The value of the maximum oxidation number for the elements from 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.

-9-

(d) The lower oxidation states are usually found in ionic compounds. Such compounds tend to be reducing agents as the d-block elements can be oxidised to a higher oxidation state.

(e) The higher oxidation states tend to involve covalency and electronegative atoms such as F and O (e.g. TiO_2, V_2O_5, Mn_2O_7) and can be found in polyatomic oxo-anions (e.g. VO_3^-, CrO_4^{2-}, MnO_4^-). Such compounds tend to be oxidising agents as the d-block elements can be reduced to a lower oxidation state.

(f) 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. *oxides with high ionic and covalent characters are amphoteric.*

low oxidation state → ionic, basic

MnO	+2	basic	($MnO + H_2SO_4 \longrightarrow MnSO_4 + H_2O$)
Mn_2O_3	+3	basic	
MnO_2	+4	amphoteric	
MnO_3	+6	acidic	
Mn_2O_7	+7	acidic	($Mn_2O_7 + 2NaOH \longrightarrow 2NaMnO_4 + H_2O$)

high oxidation state → covalent, acidic.

📖 **Exercise 2**

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_2TiO_4 B K_3TiF_6 C $TiCl_3$ D TiO
  +6   *+3*   *+3*   *+2*

4.3 Redox systems involving transition metal ions

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

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

- A more positive E^θ value $\Rightarrow$ equilibrium position tends to lie on the RHS, i.e. the +2 oxidation state is favoured over the +3 oxidation state.

$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	$E^\theta = -0.41$ V
$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$	$E^\theta = +1.49$ V
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	$E^\theta = +0.77$ V
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	$E^\theta = +1.82$ V

Electronic configurations		
	M^{3+}	M^{2+}
Cr	[Ar] $3d^3$	[Ar] $3d^4$
Mn	[Ar] $3d^4$	[Ar] $3d^5$
Fe	[Ar] $3d^5$	[Ar] $3d^6$
Co	[Ar] $3d^6$	[Ar] $3d^7$

- Going across the transition elements, there is a general increase in E^θ value for reduction of +3 oxidation state to +2 oxidation state.

- There is a dip in E^θ value for Fe^{3+}/Fe^{2+}.
  - ➤ Addition of electron to Fe^{3+} results in a $3d^6$ configuration, where there is inter-electronic repulsion between the paired electrons in the same 3d orbital. Thus, reduction of Fe^{3+} to Fe^{2+} is less favoured.(refer to section 1.3 page 4)
- Aqueous $KMnO_4$ acidified with dilute H_2SO_4 and aqueous $K_2Cr_2O_7$ acidified with dilute H_2SO_4 are common oxidising agents used in laboratories.

$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$ purple very light pink	$E^\theta = +1.52$ V
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$ orange green	$E^\theta = +1.33$ V *weaker oxidising agent.*

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?** *use Maxwell-Boltzmann distribution to illustrate.*

> 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 <u>different physical phases</u>
> 2. homogeneous catalysis – catalyst and the reactants are in the <u>same phase</u>

- Transition elements and their compounds are useful in both heterogeneous catalysis and homogeneous catalysis.

Transition element	Substance used as catalyst	Reaction catalysed	
V	V_2O_5	$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$	Contact process
Mn	MnO_2	$2KClO_3 \longrightarrow 2KCl + 3O_2$	-
Fe	Fe/Fe_2O_3	$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$	Haber process
Ni	Ni	$RCH=CH_2 + H_2 \longrightarrow RCH_2CH_3$	Hardening of vegetable oils (e.g. manufacture of margarine)
Fe	$FeCl_3$	$C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl$	Electrophilic substition of benzene
Mn	Mn^{2+}	$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$	An example of autocatalysis

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 sites (usually termed **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 weak attractive forces between reactant molecules and the atoms of the surface of the catalyst</u>.

- **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** which allows for the ready exchange of electrons to and from reactant molecules, thus facilitating the formation of weak bonds with the reactant molecules.
>
> -the availability of 3d electrons for bond formation with the reactant molecules or the availability of low lying vacant orbitals which can accept electron pairs from the reactant molecules.
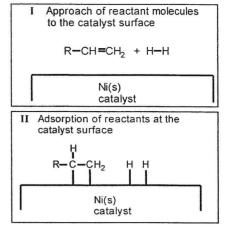
1. Approach

Reactant molecules diffuse towards the catalyst surface.
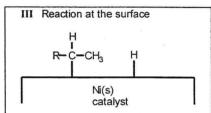
2. Adsorption

Reactant molecules become **adsorbed** onto the **active sites** of the catalyst surface by means of 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

I Approach of reactant molecules to the catalyst surface

$$R-CH=CH_2 \ + \ H-H$$

Ni(s) catalyst

II Adsorption of reactants at the catalyst surface

Ni(s) catalyst

3. Chemical Reaction

Adjacent reactant molecules are brought into close contact with proper orientation for reaction. This reaction has lower activation energy than the uncatalysed reaction

III Reaction at the surface

Ni(s) catalyst

4. Desorption

This is the reverse of adsorption. The product molecule eventually breaks free from the catalyst surface. The product molecule diffuses away from the surface. The vacant active sites are now available for adsorbing other reactant molecules.

IV Desorption of product

$$R-CH_2-CH_3$$

Ni(s) catalyst

- Examples of heterogeneous catalysis
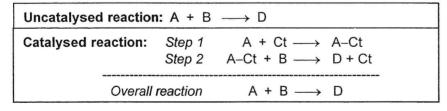
  1. nickel in the hydrogenation of alkenes

$$R-CH=CH_2(g) + H_2(g) \xrightarrow{\overset{(s)}{Ni}, \ heat} R-CH_2-CH_3(g)$$

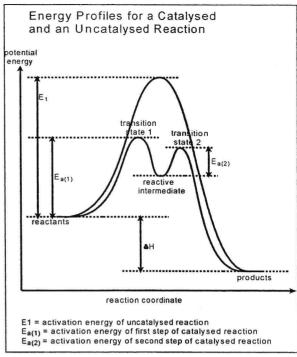 2. iron/iron(III) oxide in the Haber process
  3. vanadium(V) oxide in the Contact process

5.2 Homogeneous Catalysis

- In homogeneous catalysis, the **catalyst and the reactants are in the same phase**, either liquid or gaseous.

- Consider a reaction A + B $\longrightarrow$ D catalysed by Ct

Uncatalysed reaction: A + B $\longrightarrow$ D
Catalysed reaction: *Step 1* A + Ct $\longrightarrow$ A–Ct   *Step 2* A–Ct + B $\longrightarrow$ D + Ct   --   *Overall reaction* A + B $\longrightarrow$ D

- Typical features of homogeneous catalysis:

  1. The catalyst (Ct) takes part in the reaction by being converted into an intermediate compound (A–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.

  $E_{a(1)}$ and $E_{a(2)}$ are smaller than E_1.

  $\therefore \uparrow$ rate of reaction.

Energy Profiles for a Catalysed and an Uncatalysed Reaction

E1 = activation energy of uncatalysed reaction
$E_{a(1)}$ = activation energy of first step of catalysed reaction
$E_{a(2)}$ = activation energy of second step of 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 with which they can be converted from one oxidation state to another.

Reaction between peroxodisulfate ions and iodide ions **catalysed by Fe^{2+} or Fe^{3+}.**

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

Relevant $E^\ominus$ values:

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

Note:
Do not confuse the above reaction with the reaction between iodine and thiosulfate.

$$2S_2O_3{}^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6{}^{2-}(aq) + 2I^-(aq)$$

Uncatalysed reaction

$$S_2O_8{}^{2-}(aq) + 2I^-(aq) \longrightarrow 2SO_4{}^{2-}(aq) + I_2(aq) \qquad E^\ominus{}_{cell} = 2.01 - 0.54 = +1.47 \text{ V} > 0 \text{ V}$$

- Since $E^\ominus{}_{cell} > 0$ V, the uncatalysed reaction is thermodynamically feasible under standard conditions.

- However, in the uncatalysed reaction, there is a direct reaction between two similarly charged ions. The electrostatic repulsion between the two negatively charged ions partly causes the reaction to have a **high activation energy** and hence to proceed slowly.

Exercise 3

Q1 – Write equations to show how the reaction is catalysed by Fe^{3+} ion.

Step 1: $Fe^{3+}(aq) + I^-(aq) \longrightarrow Fe^{2+}(aq) + \frac{1}{2}I_2(aq)$

$$E^\ominus_{cell} = 0.77 - 0.54 = +0.23V > 0$$

Step 2: $Fe^{2+}(aq) + \frac{1}{2}S_2O_8^{2-}(aq) \longrightarrow Fe^{3+}(aq) + SO_4^{2-}(aq)$

$$E^\ominus_{cell} = 2.01 - 0.77 = +1.24V > 0$$

▪ The catalysed reaction proceeds via a 2-step route. For each step, $E^\ominus_{cell} > 0$ V indicating that each step is 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: $Fe^{2+}(aq) + \frac{1}{2}S_2O_8^{2-}(aq) \longrightarrow Fe^{3+}(aq) + SO_4^{2-}(aq)$

$$E^\ominus_{cell} = 2.01 - 0.77 = +1.24V > 0$$

Step 2: $Fe^{3+}(aq) + I^-(aq) \longrightarrow Fe^{2+}(aq) + \frac{1}{2}I_2(aq)$

$$E^\ominus_{cell} = 0.77 - 0.54 = +0.23V > 0$$

● In the above given example, it would be anticipated that other couples involving transition metal cations would also act as catalysts, as long as their $E^\ominus$ values were intermediate 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 complex ions.

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

● What is a **complex ion**?

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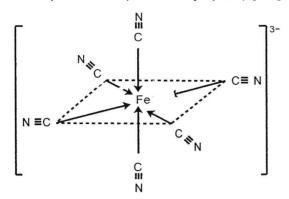> If the species carries an overall charge, it is called a **complex ion**.

● For complexes, the number of bonds formed with the metal ion exceeds the oxidation state of the metal ion.

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 of neutral complexes: $Ni(CO)_4$ and $Fe(CO)_5$

Examples of complex ions: $[Ni(H_2O)_6]^{2+}$, $[Co(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{3-}$ (shown below)

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 / dative covalent bond
Co-ordination number of Fe^{3+} in the complex ion	6
Co-ordination geometry	Octahedral

- 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)**, and resulting in the formation of a complex.

  Examples of ligand: Cl^-, OH^- CN^-, H_2O, NH_3, CO, $H_2N–CH_2CH_2–NH_2$

  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>. → electron pair acceptor   ↓ electron pair donor

- What is meant by **co-ordination number**?

  In a complex, 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) formed with ligands.

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

	Examples	Central atom/ion	Co-ordination number
neutral complexes	$Ni(CO)_4$	Ni	4
	$Fe(CO)_5$	Fe	5
cationic complexes	$[Fe(H_2O)_6]^{2+}$	Fe^{2+}	6
	$[Ag(NH_3)_2]^+$	Ag^+	2
anionic complexes	$[Fe(CN)_6]^{4-}$	Fe^{2+}	6
	$[CuCl_4]^{2-}$	Cu^{2+}	4

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

Complex salt	constituent cation	constituent anion
$[CoCl(NH_3)_5]Cl_2$ pentaamminechlorocobalt(III) chloride	$[CoCl(NH_3)_5]^{2+}$ a complex cation	Cl^- a simple anion
$K_4[Fe(CN)_6]$ potassium hexacyanoferrate(II)	K^+ a simple cation	$[Fe(CN)_6]^{4-}$ a complex anion

- 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 = $(1)(+1) + (2)(0) = +1$
$[CuCl_4]^{2-}$	overall charge of complex ion = $(1)(+2) + (4)(-1) = -2$
$[Fe(CN)_6]^{4-}$	overall charge of complex ion = $(1)(+2) + (6)(-1) = -4$
$[Fe(SCN)(H_2O)_5]^{2+}$	overall charge of complex ion = $(1)(+3)+(1)(-1) = +2$

📖 Exercise 4

Q1 – Determine the oxidation number of the transition metal in each of the following complex ions:

(a) $[Fe(OH)_2(H_2O)_4]$ *(+2, H, +1, -1)*

(b) $K[Cu(CN)_2]$

(c) $[CoCl_4]^-$ *(+3)*

+2

+1

+3

Q2 – Determine the overall charge of the following complex ions:

(a) $[Fe(SCN)(H_2O)_5]$

Fe(III) +2

2+

(b) $[Ni(NH_3)_6]$

Ni(II) +2

2+

(c) $[VO_3(OH)]$

$HO - \overset{O}{\underset{O^-\ \ O^-}{\overset{||}{V}}}$

V(V) +3

2−

not a complex since
no. of bonds = 5 = oxidation state.
complex only if no. of bonds > oxidation state.

6.2 Types of Ligands

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

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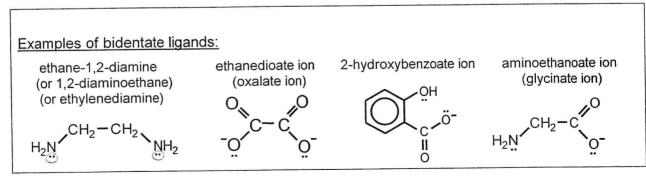
- A monodentate (or unidentate) ligand is one which can form **only one co-ordinate bond** with a central metal ion (or atom).

- Note: The word "dens" in Latin means tooth. A monodentate ligand is so called since it has only "one tooth" with which to attach itself to the central cation in a complex.

Examples of monodentate ligands: Cl^-, OH^- CN^-, H_2O, NH_3, $C\equiv O$
Examples of complexes with monodentate ligands: $[Fe(SCN)(H_2O)_5]^{2+}$, $[CoCl_4]^{2-}$

(b) bidentate ligands

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

Examples of bidentate ligands:

ethane-1,2-diamine (or 1,2-diaminoethane) (or ethylenediamine)	ethanedioate ion (oxalate ion)	2-hydroxybenzoate ion	aminoethanoate ion (glycinate ion)

Examples of complexes with bidentate ligands:

$[Co(H_2NCH_2CH_2NH_2)_3]^{3+}$

$[Cr(C_2O_4)_3]^{3-}$

coordinate bond on x and z axis.
→ need to be anthon dist. apart.

coordination no = no. of ligands × 2.

(c) hexadentate ligands

- A hexadentate ligand is one which can form **six co-ordinate bonds** simultaneously with the central metal ion.

•

Example of a hexadentate ligand:

ethylenediaminetetraacetate ion

- edta^{4-} ion or EDTA^{4-} ion

- or sometimes just represented by edta or EDTA

acetate {

ethylenediamine ——
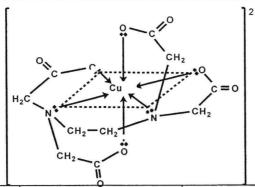
Note:
1. The edta^{4-} ion is formed from 1,2-bis[bis(carboxymethyl)amino]ethane (i.e. ethylenediaminetetraacetic acid), which may be written as H$_4$edta.

H$_4$edta
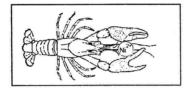
2. Edta is a useful ligand. It is used in many situations to 'mop up' metal ions. Examples include the following:
  - it is used in trace amounts in some foods to prevent metal ions catalysing the reaction that makes fat rancid
  - It is added to cosmetics to keep minerals and other trace elements from binding with other ingredients in a cosmetic formulation to prevent deterioration and skin deposition.
  - it is added to shampoos, bath foams and other cleansing products to help soften the water
  - it is used in medicine to prevent blood from clotting during operations, by chelating with calcium ions.

Examples of complexes with edta ligand: $[Cu(edta)]^{2-}$, $[Fe(edta)]^-$

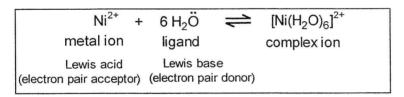| Type of ligand	Number of co-ordinate bonds which the ligand forms with the central metal ion	
monodentate ligand	1	1. A polydentate ligand is one which can form more than one co-ordinate bonds with the central metal ion. It has "many teeth".
polydentate ligand	> 1	2. The complex ions which are formed between polydentate ligands and cations are known as chelates or chelated compounds from a Greek work "chelos" meaning "a crab's claw", since the ligand forms a clawing pincer-like grip on the metal ion.
1. bidentate ligand	2	
2. tridentate ligand	3	
3. hexadentate ligand	6	

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

6.3 Transition Metal Ions and Complex Formation

- Complex formation

$$Ni^{2+} \ + \ 6\,H_2\ddot{O} \ \rightleftharpoons \ [Ni(H_2O)_6]^{2+}$$

metal ion   ligand   complex ion

Lewis acid   Lewis base
(electron pair acceptor)   (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
   / can be transition or non-transition.
2. the presence of a central metal ion capable of
   (a) attracting the lone pair of electrons from the ligand, and
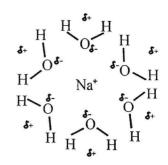   (b) accommodating the lone pair of electrons in its low-lying vacant orbitals to form a co-ordinate bond

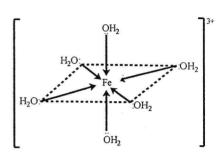- **Why do transition metal ions show a high tendency to form complexes?**

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 and Group 2 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.

- In aqueous solution, transition metal ions exist as aqua complexes. Each oxygen atom of a water molecule donates a lone pair into a low-lying vacant orbital of the transition metal ion and forms a coordinate bond. In general, aqua complexes are of the form $[M(H_2O)_6]^{n+}$, where n = 2 or 3.

Solution	Cation	Complex ions
$NaCl$(aq)	Na^+(aq)	-
$AlCl_3$(aq)	Al^{3+}(aq)	$[Al(H_2O)_6]^{3+}$(aq)
$Cr(NO_3)_3$(aq)	Cr^{3+}(aq)	$[Cr(H_2O)_6]^{3+}$(aq)
$FeCl_3$(aq)	Fe^{3+}(aq)	$[Fe(H_2O)_6]^{3+}$(aq)

Group 1 and 2 ⇒ ion-dipole interaction (hydration)

Transition metal ⇒ coordinate bonds (formation of complex)

6.5 Acidity of Aqua Complexes

- **Why is an aqueous solution of FeCl_3 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 H_2O molecules bonded to it, **weakening the O–H bonds** and enabling these H_2O molecules bonded to it to become proton donors. The free water molecules in the solution act as bases and the following equilibrium is established:

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

The Fe^{3+} 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**. ⤷ breaking OH bond in H_2O

- Note: The aqueous solutions of most transition metal compounds such as $CrCl_3$(aq), $FeCl_3$(aq), $CuSO_4$(aq) and $Co(NO_3)_2$(aq) are acidic.

- An aqueous solution containing either **Cr^{3+} or Fe^{3+}** ions is **acidic** enough to react with sodium carbonate to produce carbon dioxide gas together with the formation of a hydroxide precipitate.

-19-

- **What happens when Na_2CO_3 is added to an aqueous solution containing Fe^{3+} ions?**

The following three equilibria are relevant to the Fe^{3+} ion in aqueous solution:

$$[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Fe(OH)(H_2O)_5]^{2+}(aq) + H_3O^+(aq) \quad \ldots\ldots\ldots(1)$$

$$[Fe(OH)(H_2O)_5]^{2+}(aq) + H_2O(l) \rightleftharpoons [Fe(OH)_2(H_2O)_4]^+(aq) + H_3O^+(aq) \quad \ldots\ldots(2)$$

$$[Fe(OH)_2(H_2O)_4]^+(aq) + H_2O(l) \rightleftharpoons [Fe(OH)_3(H_2O)_3](s) + H_3O^+(aq) \quad \ldots\ldots\ldots(3)$$

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

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

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 $[Fe(OH)_3(H_2O)_3]$ (usually written simply as **$Fe(OH)_3$**) is obtained *together* with the evolution of CO_2. Precipitate is not $FeCO_3$ since solution is acidic, CO_3^{2-} will react.

Overall:
This reaction also occurs for $[Al(H_2O_6)]^{3+}$ and $[Cr(H_2O_6)]^{3+}$.

Ion	$H^+(aq)$	$Ca^{2+}(aq)$	$Al^{3+}(aq)$	$Cr^{3+}(aq)$
CO_2?	Yes	No	Yes	Yes
Ppt?	No	White ppt	White ppt	Greyish-green ppt
Identity of ppt	—	$CaCO_3$	$Al(OH)_3$	$Cr(OH)_3$

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	$[Ag(NH_3)_2]^+$ $[Ag(CN)_2]^-$ $[CuCl_2]^-$	$[H_3N:\longrightarrow Ag \longleftarrow :NH_3]^+$ $[Cl:\longrightarrow Cu\longleftarrow :Cl]^-$
4	tetrahedral	$Ni(CO)_4$ $[Zn(NH_3)_4]^{2+}$ $[CoCl_4]^{2-}$ $[Cu(CN)_4]^{3-}$	
4	square planar	$[Ni(CN)_4]^{2-}$ $[Cu(NH_3)_4]^{2+}$ $[CuCl_4]^{2-}$ (see below)	
6	octahedral	$[Fe(CN)_6]^{3-}$ $[Fe(CN)_6]^{4-}$ $[Ni(NH_3)_6]^{2+}$	

Note:
$[Cu(NH_3)_4(H_2O)_2]^{2+}$ vs $[Cu(NH_3)_4]^{2+}$: both are commonly used and accepted.

1 mol of free Cl^- ion

7.2 Structural isomerism

✱ free chloride ion reacts with $AgNO_3$, not the Cl^- in the complex

When green crystals of chromium(III) chloride, $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ is dissolved in water, the chloride ions in the complex are slowly replaced by water to give blue-green $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ and finally violet $[Cr(H_2O)_6]Cl_3$. The complexes can be distinguished by precipitation of the free chloride ion using aqueous silver nitrate. *3 mol of free 3 Cl^- ion.*

2 mol of free Cl^- ion

The complex ions $[Cr(H_2O)_4Cl_2]^+$, $[Cr(H_2O)_5Cl]^{2+}$, $[Cr(H_2O)_6]^{3+}$ are different cations even though the ionic compounds they are part of have the same chemical formula i.e. $CrCl_3 \cdot 6H_2O$.

✱ on adding aq $AgNO_3$, Cl^- datively bonded to central metal ion will not be precipitated out as $AgCl$.

Q1 – N02/17

The anti-cancer drug, *cisplatin* has the formula $PtCl_2(NH_3)_2$. In the human body, one of the chloride ions of *cisplatin* is replaced by one water molecule.

ligand exchange reaction : oxidation number generally remain the same.

$$\overset{+2}{PtCl_2(NH_3)_2} + H_2O \longrightarrow \overset{+2}{[PtCl(NH_3)_2(H_2O)]^+} + Cl^-$$

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.

What is the formula of this compound?

$[Pt(NH_3)_3Cl_3]^+ Cl^-$

A $Pt(NH_3)_3Cl_4$	**B** $Pt(NH_3)_4Cl_4$ *charge of Pt is*
C $Pt(NH_3)_6Cl_2$	**D** $Pt(NH_3)_6Cl_4$ $4+$

$[Pt(NH_3)_6]^{4+} 2Cl^-$ $[Pt(NH_3)_4]^{2+} 2Cl^-$ $[Pt(NH_3)_6]^{4+} 4Cl^-$

charge of Pt is 2+

Q3

Chromium(III) chloride combines with ammonia to form compound **X** in which the co-ordination number of chromium is 6. When solution **X** is treated with an excess of aqueous silver nitrate, only two thirds of the total chloride present is precipitated as $AgCl$. $\frac{2}{3}$ of Cl^- are free Cl^-, not bonded to Cr^{3+}

What is the formula of compound **X**? to Cr^{3+}

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

---

8. COLOUR OF COMPLEXES

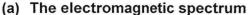Transition metal compounds are frequently coloured, both in the solid state and in solution.

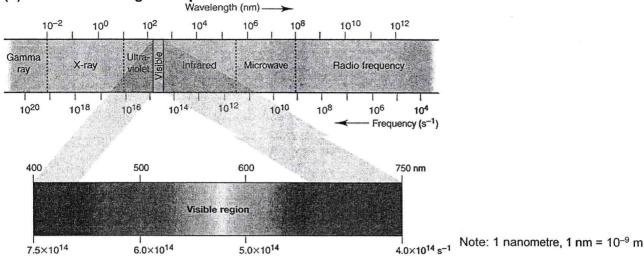- Typical colours for common ions (i.e. with H_2O as the ligand) are summarised below.

Aqua complex ion	Electronic configuration of the cation	Colour
$[Sc(H_2O)_6]^{3+}$	[Ar] $3d^0$	colourless
$[Ti(H_2O)_6]^{3+}$	[Ar] $3d^1$	violet
$[V(H_2O)_6]^{3+}$	[Ar] $3d^2$	green
$[V(H_2O)_6]^{2+}$	[Ar] $3d^3$	violet
$[Cr(H_2O)_6]^{3+}$	[Ar] $3d^3$	violet / green
$[Cr(H_2O)_6]^{2+}$	[Ar] $3d^4$	blue
$[Mn(H_2O)_6]^{3+}$	[Ar] $3d^4$	violet
$[Mn(H_2O)_6]^{2+}$	[Ar] $3d^5$	faint pink
$[Fe(H_2O)_6]^{3+}$	[Ar] $3d^5$	pale violet / yellow
$[Fe(H_2O)_6]^{2+}$	[Ar] $3d^6$	pale green
$[Co(H_2O)_6]^{2+}$	[Ar] $3d^7$	pink
$[Ni(H_2O)_6]^{3+}$	[Ar] $3d^8$	green
$[Cu(H_2O)_6]^{2+}$	[Ar] $3d^9$	blue
$[Zn(H_2O)_6]^{2+}$	[Ar] $3d^{10}$	colourless

Note:

1. **Vacant or fully filled d sub-shell is associated with a lack of colour.**

2. $[Cr(H_2O)_6]^{3+}$ is violet in cold aqueous solution. Green colour of solutions observed due to the partial replacement of water ligands by other ligands, e.g. Cl^- or SO_4^{2-}.

3. $[Fe(H_2O)_6]^{3+}$ is pale violet. Yellowish brown colour of solutions observed due to the partial loss of H^+ by a water ligand to form $[Fe(OH)(H_2O)_5]^{2+}$, which is yellowish-brown.

8.1 Occurrence of colour

(a) The electromagnetic spectrum

Note: 1 nanometre, 1 nm = 10^{-9} m

- 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 so that the transmitted or reflected light is richer in the remaining wavelengths of the visible spectrum.
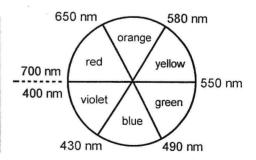
- **What determines the observed colour of a coloured object?**

  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.
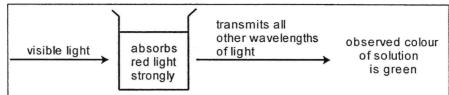
(c) Complementary colours

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

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.**
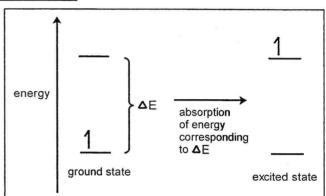
- **Example: A green object**

  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.

visible light →	absorbs red light strongly	transmits all other wavelengths of light →	observed colour of solution is green

- 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.**

energy $\}\Delta E$ | absorption of energy corresponding to ΔE →

ground state   excited state

8.3 Sodium chloride solution

Why is an aqueous solution of sodium chloride colourless?

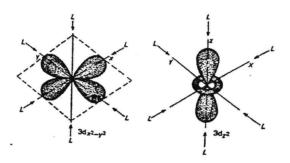- Consider the ground state and the excited state of the Na$^+$ ion.

  Na$^+$ (ground state) $1s^2 2s^2 2p^6$ ⟶ Na$^+$ (excited state) $1s^2 2s^2 2p^5 3s^1$ ⟶ *energy gap is relatively large.*

- The excitation of an electron from the lower energy 2p orbital to the higher energy 3s orbital requires wavelength of light well beyond the range of visible spectrum. Radiation from the visible spectrum does not provide sufficient energy to promote electrons in Na$^+$ ions to even the lowest of their possible excited electronic states.
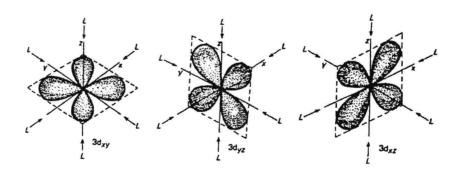
colourless solution → allows all light to pass through.

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.

- $3d_{x^2-y^2}$ and $3d_{z^2}$: 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.   ↑ repulsion

- $3d_{xy}$, $3d_{yz}$, $3d_{xz}$: 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.   ↓ repulsion .

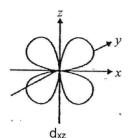- Thus **the five 3d orbitals are affected differently by the approach of the ligands**. The orbitals are split into two energy levels with an energy gap between them, and the degeneracy of the five 3d orbitals is destroyed in complexes.

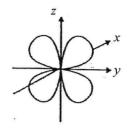
Note:
In **tetrahedral** complexes, the situation is reversed. The four ligands in these complexes approach the central metal ion **in between** the axes. Electrons in the $3d_{xy}$, $3d_{yx}$ and $3d_{xz}$ now experience the **greatest** repulsion from ligand lone pairs, and so have a **higher** energy than electrons in the $3d_{x^2-y^2}$ or $3d_{z^2}$ orbitals (see *Section 8.6*).

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

d_{xz}
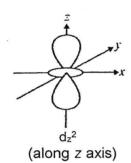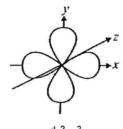(in between x and z axes)

d_{xy}
(in between x and y axes)

d_{yz}
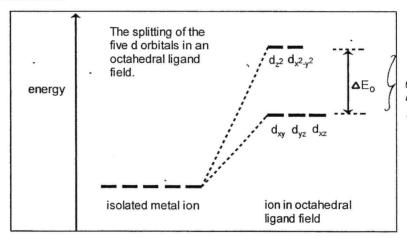(in between y and z axes)

d_{z^2}
(along z axis)

$d_{x^2-y^2}$
(along x and y axes)

(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.

energy

The splitting of the five d orbitals in an octahedral ligand field.

d_{z^2} $d_{x^2-y^2}$

ΔE_o

d_{xy} d_{yz} d_{xz}

isolated metal ion

ion in octahedral ligand field

corresponds to energy of radiation in visible region of spectrum.

- 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 NiCl_2 coloured?**

> In aqueous solution, Ni^{2+} exists as an octahedral complex $[Ni(H_2O)_6]^{2+}$.
> The presence of the H_2O ligands causes the splitting of the five originally degenerate 3d orbitals in the Ni^{2+} ion into two sets of slightly different energy levels.
> Since the 3d subshell is partially filled (Ni^{2+}, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8$), the electrons 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.
> Such d-d transitions are responsible for the colour observed in NiCl_2(aq). The colour observed is the complement of the colour absorbed.

L S P E C	
	• presence of **ligands** causes the
	• **splitting** of the five 3d orbitals into two sets of slightly different energy levels.
	• Since these 3d subshell is **partially filled**,
	• **electrons** 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)
	• The **colour observed** 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).**

   - Compounds of the same element in different oxidation states show different colours.
   - $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ 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.

$[Cr(H_2O)_6]^{2+}$(aq)	$[Cr(H_2O)_6]^{3+}$(aq)	$[Fe(H_2O)_6]^{2+}$(aq)	$[Fe(H_2O)_6]^{3+}$(aq)
[Ar] $3d^4$	[Ar] $3d^3$	[Ar] $3d^6$	[Ar] $3d^5$
blue	green	pale green	yellow

2. **The nature of the ligands bonded to the central metal ion/atom.**
   - Different ligands have different capacities of splitting the d orbitals of a particular transition metal cation and hence leading to different colours observed.

$[Ni(H_2O)_6]^{2+}$(aq)	green	$[Cu(H_2O)_6]^{2+}$(aq)	blue
$[Ni(NH_3)_6]^{2+}$(aq)	blue	$[Cu(NH_3)_4(H_2O)_2]^{2+}$(aq)	deep blue

   Why do different transition metal complexes (e.g. $[Ni(H_2O)_6]^{2+}$ and $[Ni(NH_3)_6]^{2+}$) containing the same metal ion in the same oxidation state show different colours?
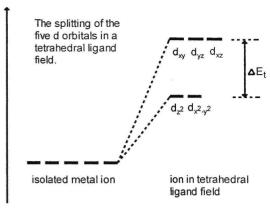
   > Different transition metal complexes containing the same metal ion show different colours because of the presence of **different ligands**.
   >
   > Different ligands split the d orbitals of the metal ion into two sets of slightly different energy levels to **different extents**. Hence different transition 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 $3d_{xy}$, the $3d_{yz}$ and the $3d_{xz}$ orbitals now experience the greatest electrostatic repulsion from the ligand lone pairs, so have a higher energy than electrons in the $3d_{x^2-y^2}$ or the $3d_{z^2}$ orbitals.

energy

The splitting of the five d orbitals in a tetrahedral ligand field.

d_{xy} d_{yz} d_{xz}

ΔE_t

d_{z^2} $d_{x^2-y^2}$

isolated metal ion   ion in tetrahedral ligand field

---

9. LIGAND EXCHANGE

9.1 Stability constant

- An aqueous solution of nickel(II) sulfate contains $[Ni(H_2O)_6]^{2+}$ ions. When **excess** aqueous ammonia is added to this solution, there is a noticeable change of colour because some of the $[Ni(H_2O)_6]^{2+}$ ions are converted into $[Ni(NH_3)_6]^{2+}$ ions.

- A **ligand exchange reaction** occurs and the following equilibrium is established:

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

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

remove square bracket for complex !

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

- K_{stab} is known as the **stability constant** for the $[Ni(NH_3)_6]^{2+}$ ion. It is a measure of how stable the $[Ni(NH_3)_6]^{2+}$ ion is as compared to the $[Ni(H_2O)_6]^{2+}$ 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:

> o The equilibrium position for the above reaction lies very much to the right.
>
> o The $[Ni(NH_3)_6]^{2+}$ ion is **relatively more stable** than the $[Ni(H_2O)_6]^{2+}$ ion.
>
> o NH_3 is a **stronger ligand** than H_2O.
>
> o NH_3 forms a **stronger dative covalent bond** with the Ni^{2+} ion.
>
> o There will be **replacement of the H_2O ligands by the NH_3 ligands** when excess NH_3 is added to $NiSO_4(aq)$ (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	$[CuCl_4]^{2-}$	$[Cu(NH_3)_4(H_2O)_2]^{2+}$	$[Cu(edta)]^{2-}$
log K_{stab}	5.6	13.1	18.8
colour	yellow	deep blue	light blue

📖 Worked Example 2

N93/2/1a

i) Describe and explain what happens when dilute aqueous ammonia is gradually added to an aqueous solution containing Cu^{2+}(aq).

$$[Cu(H_2O)_6]^{2+}(aq) \xrightarrow{\ NH_3(aq)\ } Cu(OH)_2(s) \xrightarrow[\ NH_3(aq)\ ]{excess} [Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$$

blue solution   light blue precipitate   deep blue solution

Aqueous NH_3 is a weak base containing OH^- ions.

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

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 to the blue solution, 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 $Cu(OH)_2$.

> $[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons [Cu(OH)_2(H_2O)_4](s) + 2H_2O(l)$ ....(1)
> blue solution   pale blue precipitate
>
> 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.

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

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. In this case, NH_3 is a stronger ligand than H_2O and so displaces H_2O from $[Cu(H_2O)_6]^{2+}$ to form $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

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 deep blue solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

① stronger ligand

② formation of more stable aqua complex.

equilibrium position of (1) shifts left.

write it required to describe and explain in equilibrium shift.

Note:

1. In this case, there exist two **competing equilibria**, (1) and (2). Both NH_3 and OH^- compete to combine with $Cu^{2+}(aq)$. With a large excess of NH_3 (i.e. higher $[NH_3]$), the formation of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ 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 NH_3.

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

✳ → write this if only 1 balanced equation required.

N93/2/1a
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>deep 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 NH_3 and H_2O 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.

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

The above reaction is **entropy favoured** as more aqueous particles are formed when the $edta^{4-}$ ligands substitute the NH_3 and H_2O ligands. ($\Delta n_{aq\ particles} = 5 - 2 = +3$)

Note: The formation of the $[Cu(edta)]^{2-}$ is more favourable. (log K_{stab} = 18.8)

📖 **Worked Example 3**

J91/4/1bii Describe and explain what is seen when concentrated hydrochloric acid is added to a solution of Cu^{2+} 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. Upon the addition of concentrated HCl, <u>the blue solution turns green</u> as a ligand exchange reaction occurs. 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:

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

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 HCl to the green solution increases the Cl^- concentration, causing the equilibrium position of the above reaction to shift further right in accordance to LeChatelier's principle. <u>The green solution turns yellow</u> as more yellow $[CuCl_4]^{2-}$ ions are formed. Dilution of the solution by adding water reverses the colour changes.

equilibrium position shifts left.

(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
↓ add NaCl(aq)		
$AgCl(s)$	Cl^-	White precipitate
↓ add NH_3 (aq)		
$[Ag(NH_3)_2]^+(aq)$	NH_3	Colourless solution
↓ add KBr(aq)		
$AgBr(s)$	Br^-	Cream precipitate
↓ add $Na_2S_2O_3$(aq)		
$[Ag(S_2O_3)_2]^{3-}(aq)$	$S_2O_3^{2-}$	Colourless solution
↓ add KI(aq)		
$AgI(s)$	I^-	Yellow precipitate
↓ add KCN(aq)		
$[Ag(CN)_2]^-(aq)$	CN^-	Colourless solution
↓ add Na_2S(aq)		
$Ag_2S(s)$	S^{2-}	Black precipitate
↓ add Na_2edta(aq)		
$[Ag(edta)]^-(aq)$	$edta^{2-}$	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^+: $H_2O < Cl^- < NH_3 < Br^- < S_2O_3^{2-} < I^- < CN^- < S^{2-} < edta^{2-}$

↓ stronger ligand can displace weaker ligands.
↓ increasing ligand strength.

*Recap: Periodicity (II) Tutorial Q14(c)

📖 Exercise 6: (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_{stab}
Fe^{3+}	SCN^-	1	9×10^2
Fe^{3+}	CN^-	6	1×10^{31}
Co^{3+}	CN^-	6	1×10^{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.

(ii) 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 of Fe^{3+}(aq) and Co^{3+}(aq) ions was added to a solution containing CN^- ions. [5]

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

$$K_{stab} = \frac{[Fe(CN)_6^{3-}]}{[Fe(H_2O)_6^{3+}][CN^-]^6}$$

Units: $mol^{-6} dm^{18}$

(ii) 1: $[Fe(CN)_6]^{3-}$ formed as CN^- is a stronger ligand than SCN^- due to the larger K_{stab} value for the complex.

2: $[Co(CN)_6]^{3-}$ due to the larger K_{stab} value for the Co(III) complex.

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:
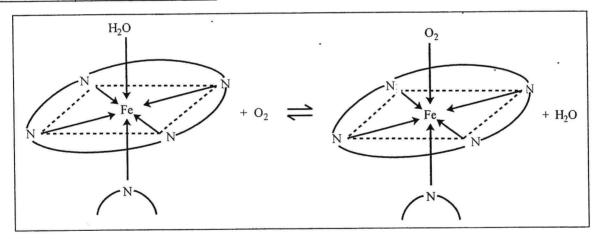
- The iron(II) exhibits hexa co-ordination.

- 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.

haem

- 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.

Schematic representation of haem:

9.4 Effect of Ligand Exchange on $E^{\ominus}$ values

- Replacement of H_2O 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)

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

- Replacing the H_2O ligand by the CN^- ligand causes the $E^{\ominus}$ value for the Fe(III)/Fe(II) system to become less positive i.e. Fe(III) becomes less oxidising.

- Hence there is stabilisation of the +3 oxidation state of iron relative to the +2 state of iron by the CN^- ligand.

- It is energetically easier for the positively charged $[Fe(H_2O)_6]^{3+}$ ion to accept an electron since oppositely charged species attract each other naturally.

- It is energetically more difficult for the negatively charged $[Fe(CN)_6]^{3-}$ ion to accept an electron 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: $\frac{1}{2}I_2(aq) + e^- \rightleftharpoons I^-(aq)$ $E^\ominus = +0.54$ V
>
> $[Fe(H_2O)_6]^{3+}(aq) + I^-(aq) \longrightarrow [Fe(H_2O)_6]^{2+}(aq) + \frac{1}{2}I_2(aq)$ $E^\ominus_{cell} = +0.23$ V > 0 V
> Since $E^\ominus_{cell} > 0$ V, the reaction is thermodynamically feasible under standard conditions.
> **Observation:** Brown solution of I_2(aq) formed.
>
> $[Fe(CN)_6]^{3-}(aq) + I^-(aq) \longrightarrow [Fe(CN)_6]^{4-}(aq) + \frac{1}{2}I_2(aq)$ $E^\ominus_{cell} = -0.18$ V < 0 V
> Since $E^\ominus_{cell} < 0$ V, the reaction is thermodynamically not feasible under standard conditions.
> **Observation:** Brown solution of I_2(aq) is not produced.

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

> $[Co(H_2O)_6]^{3+}(aq) + e^- \rightleftharpoons [Co(H_2O)_6]^{2+}(aq)$ $E^\ominus = +1.82$ V
> $[Co(NH_3)_6]^{3+}(aq) + e^- \rightleftharpoons [Co(NH_3)_6]^{2+}(aq)$ $E^\ominus = +0.10$ V
> $[Co(CN)_6]^{3-}(aq) + e^- \rightleftharpoons [Co(CN)_6]^{4-}(aq)$ $E^\ominus = -0.80$ V
> $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $E^\ominus = +1.23$ V
> $O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$ $E^\ominus = +0.40$ V

- The $E^\ominus$ values show that there is stabilisation of Co(III) with respect to Co(II) by the NH_3 and the CN^- ligands.

- $[Co(H_2O)_6]^{3+}$ ions are so strongly oxidising that they react with water to produce oxygen.

- $[Co(NH_3)_6]^{2+}$(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: NH_3(aq), NaOH(aq)
  - See the QA Handout for details
  - Explanation is usually couched in terms of ionic product exceeding K_{sp}

$$Cu^{2+}(aq) + 2OH^-(aq) \xrightarrow{\quad NH_3(aq) \quad} Cu(OH)_2(s)$$
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.

$$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \xrightarrow{\text{excess } NH_3(aq)} [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 2H_2O(l)$$
blue solution   deep blue solution

$$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \xrightarrow{\text{conc. } HCl} [CuCl_4]^{2-} + 6H_2O(l)$$
blue solution   yellow solution

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

$$[Fe(H_2O)_6]^{3+}(aq) + 3C_2O_4^{2-}(aq) \xrightarrow{Na_2C_2O_4(aq)} [Fe(C_2O_4)_3]^{3-}(aq) + 6H_2O(l)$$
yellow solution   colourless solution

$$[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \xrightarrow{\text{conc. } HCl} [CoCl_4]^{2-}(aq) + 6H_2O(l)$$
pink solution   blue solution

(c) Redox reactions

- Justification of whether a redox reaction can occur is usually based on $E^\ominus$ values

$$2Fe^{2+}(aq) + Cl_2(aq) \longrightarrow 2Fe^{3+}(aq) + 2Cl^-(aq)$$
pale green solution   yellow solution

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

$$2Cu^{2+}(aq) + 4I^-(aq) \longrightarrow 2CuI(s) + I_2(aq)$$
                               cream ppt.   brown solution

$$Cu^{2+}(aq) + Zn(s) \longrightarrow Cu(s) + Zn^{2+}(aq)$$
                                pink solid

(d) Other reactions

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

hydrolysis of aqua complex ions reaction with sodium carbonate to give CO_2

$$2CrO_4^{2-}(aq) + 2H^+(aq) \longrightarrow Cr_2O_7^{2-}(aq) + H_2O(l)$$
yellow solution   orange solution

$$Cr_2O_7^{2-}(aq) + 2OH^-(aq) \longrightarrow 2CrO_4^{2-}(aq) + H_2O(l)$$
orange solution   yellow solution

APPENDIX

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

1. The symbol for the central atom is written first, followed by anionic ligands and neutral ligands in that order.
   Example: $[Fe(OH)(H_2O)_5]^{2+}$

2. Within each ligand class, the order should be alphabetical in terms of the symbol for the donor atom of the ligand.
   Example: $[Cu(NH_3)_4(H_2O)_2]^{2+}$
   N is the donor atom in NH_3.
   O is the donor atom in H_2O.

3. Polyatomic ligands, but not monatomic ligands, are enclosed in curved brackets, and the formula of the whole complex is enclosed in square brackets.
   Example: $[CrCl_2(NH_3)_4]^+$

(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**).

A

Monodentate ligands		Polydentate ligands	
H_2O	aqua	en or $H_2NCH_2CH_2NH_2$	ethane-1,2-diamine
NH_3	ammine	$C_2O_4^{2-}$	ethanedioato
NO	nitrosyl	edta	ethylenediaminetetraaceto
CO	carbonyl		
Cl^-	chloro		
CN^-	cyano		
OH^-	hydroxo		
NO_2^-	nitro		
SCN^-	thiocyanato		

B

Prefixes used for monodentate ligands:

2 = di,
3 = tri,
4 = tetra,
5 = penta,
6 = hexa, etc.

Prefixes used for polydentate ligands:

2 = bis,
3 = tris,
4 = tetrakis

C

Names used for some metals in anionic complexes

Element	Name in complex
Ti	titanate
V	vanadate
Cr	chromate
Mn	manganate
Fe	ferrate
Co	cobaltate
Ni	niccolate (ASE: nickelate)
Cu	cuprate
Zn	zincate
Ag	argentate
Au	aurate
Al	aluminate
Sn	stannate
Pb	plumbate