

THE TRANSITION ELEMENTS

Introduction

- ❖ Transition elements are those that occur in either the *d* – or *f* – blocks in the Periodic Table.
- ❖ In this topic, we shall only consider the chemistry of d-block elements that stretch from scandium to zinc (i.e. the first d-block series of elements).
- ❖ Thus, some important definitions are:
 - A **transition element** is one with a partially filled 3d subshell/3d sub energy level/3d orbitals in any of its stable oxidation states as well as the uncombined/atomic state.
 - A **d-block element** is one with the outermost electrons filled in the d-subshell/d-sub energy level/d-orbitals.
- ❖ The general electronic configuration of the elements that stretch from Sc to Zn is in the form $[Ar]3d^x4s^2$ or $[Ar]4s^23d^x$; where $x=1-10$ and [Ar] is the argon core; $1s^22s^22p^63s^23p^6$.
- ❖ The elements in the first d-block series of elements and their electronic configurations are shown in the table below:

Element	Symbol	Atomic number	Electronic configuration
Scandium	Sc	21	$1s^22s^22p^63s^23p^64s^23d^1$
Titanium	Ti	22	$1s^22s^22p^63s^23p^64s^23d^2$
Vanadium	V	23	$1s^22s^22p^63s^23p^64s^23d^3$
Chromium	Cr	24	$1s^22s^22p^63s^23p^64s^13d^5$
Manganese	Mn	25	$1s^22s^22p^63s^23p^64s^23d^5$
Iron	Fe	26	$1s^22s^22p^63s^23p^64s^23d^6$
Cobalt	Co	27	$1s^22s^22p^63s^23p^64s^23d^7$
Nickel	Ni	28	$1s^22s^22p^63s^23p^64s^23d^8$
Copper	Cu	29	$1s^22s^22p^63s^23p^64s^13d^{10}$
Zinc	Zn	30	$1s^22s^22p^63s^23p^64s^23d^{10}$

Note:

The anomalous behaviour of Cr and Cu is due to the extra stability of the half-filled and fully filled 3d sub energy levels respectively than neither fully filled nor half-filled 3d sub energy levels.

Ions formed by transition elements

- ❖ Transition elements form ions by losing electrons first from the 4s sub energy level rather than the 3d sub energy level.

Reason:

The 3d sub energy level electrons closer to the nucleus repel the 4s sub energy level electrons even further away from the nucleus. The electrons in the 4s sub energy level are less strongly attracted by the nucleus than the electrons in the 3d sub energy level. Thus, the electrons in the 4s subshell are lost before the electrons in the 3d subshell during ion formation.

For example;

<p>Cu ...3d¹⁰4s¹ forms</p> <p>Cu⁺ ...3d¹⁰</p> <p>Cu²⁺ ...3d⁹</p>	<p>Sc ...3d¹4s² forms</p> <p>Sc⁺ ...3d¹4s¹ (rare)</p> <p>Sc²⁺ ...3d¹ (rare)</p> <p>Sc³⁺ ...3p⁶</p>	<p>Cr ...3d⁵4s¹ forms</p> <p>Cr⁺ ...3d⁵ (rare)</p> <p>Cr²⁺ ...3d⁴</p> <p>Cr³⁺ ...3d³</p> <p>Cr⁴⁺ ...3d²</p> <p>Cr⁵⁺ ...3d¹</p> <p>Cr⁶⁺ ...3p⁶</p>
<p>Zn ...3d¹⁰4s² forms</p> <p>Zn²⁺ ...3d¹⁰4s¹ (rare)</p> <p>Zn²⁺ ...3d¹⁰</p>		

Note:

- The definition of the term transition elements excludes:
 - Atomic copper, Cu and copper(I) ion, **Cu⁺**(in compounds); since their 3d sub energy levels are fully filled.
 - Scandium(III) ion, **Sc³⁺**(in compounds); since the 3d sub energy level is empty/vacant.
 - Atomic zinc, Zn and Zinc(II) ion, **Zn²⁺**(in compounds); because both have fully filled 3d sub energy level.
- The elements Sc and Zn are however, included amongst the first series of transition elements:
 - Because their compounds chemically resemble those of the transition metal compounds.
 - To complete the series of ten elements which corresponds to the filling of the 3d sub shell.

Atomic radius the elements in the first transition series

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number	21	22	23	24	25	26	27	28	29	30
Atomic radius (nm)	0.144	0.132	0.122	0.117	0.117	0.116	0.116	0.115	0.117	0.125
1 st I.E (kJ mol ⁻¹)	632	661	648	653	716	762	757	736	745	908

Activity 1

- (a) Plot a graph of atomic radius against the atomic number of the elements.
- (b) Explain the shape of your graph.
- (c) Comment about the first ionization energies of the elements.

- ❖ The outstanding features of the transition elements (d-block elements) which differentiate them from the elements in the s-block and p-block elements are:
The d-block elements:
- ✓ form compounds/ions in variable oxidation states. For example; copper forms compounds/ions in +1 and +2 oxidation states while, calcium forms ions/compounds in only +2 oxidation state.
 - ✓ form complexes/complex ions.
 - ✓ form coloured compounds/ions. For example; iron(II) ions/compounds are generally green and iron(III) ions/compounds are generally brown/yellow/reddish brown. The s-block and p-block elements form compounds which are white and in aqueous solution, their soluble salts are colourless.
 - ✓ and their compounds are catalysts. For example; MnO_2 is used as a catalyst in the decomposition of hydrogen peroxide; finely divided iron is a catalyst in the Haber process (synthesis of ammonia) and so on.
 - ✓ form interstitial 'compounds' with non-metals with small atomic radii. The non-metals include; hydrogen, boron, carbon and nitrogen.
 - ✓ and many of their compounds are paramagnetic.

Activity 2:

Give reasons for each of the following observations.

- (a) Zinc is a d-block element but not a transition element.
- (b) Copper is a transition element.

THE GENERAL CHARACTERISTICS OF TRANSITION ELEMENTS

❖ Transition elements and their compounds have a number of characteristics as outlined below:

1. All are typical metals. Thus, they exhibit the usual physical properties common to all metals. For example; make sound when hit, conduct electricity and heat and so on.
2. Their boiling and melting points are generally much higher than those of the s-block elements (in the same period).

For example:

Variation of melting point across the first transition series

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number	21	22	23	24	25	26	27	28	29	30
Melting point (°C)	1400	1680	1917	1890	1247	1535	1490	1452	1083	420
Boiling point (°C)	2730	3260	3450	2642	2100	3000	2900	2730	2600	906

Activity 3:

- (a) Plot a graph of melting point against the atomic number of the elements.
- (b) Explain the shape of your graph.
- (c) Explain each of the following observations.
 - (i) The melting points of calcium and iron are 850°C and 1535°C respectively.
 - (ii) The melting points of the transition metals are generally high.
 - (iii) Both manganese and zinc melt at an expectedly low temperatures.

(iv) Melting points of the d-block elements decrease with increase in the number of electrons in the 3d orbitals.

3. They form ions/compounds in variable oxidation states.

Definition:

Oxidation state is the net charge that would remain on an atom in a compound when all the other atoms bonded to it were removed.

Or:

It is a net charge on an atom in a compound assuming the compound is ionic.

The elements form ions/compounds in variable oxidation states since there is a very small energy difference between the 4s and 3d sub energy levels. Therefore, electrons are lost from the 3d sub energy level as easily as they are lost from the 4s sub energy level. Transition elements therefore, utilize both the 4s and 3d sub shell electrons for bonding during chemical reactions and this results into variable oxidation states.

For example;

Mn ...3d ⁵ 4s ² forms <i>Mn</i> ²⁺ ...3d ⁵ <i>Mn</i> ³⁺ ...3d ⁴ <i>Mn</i> ⁴⁺ ...3d ³ <i>Mn</i> ⁵⁺ ...3d ² <i>Mn</i> ⁶⁺ ...3d ¹ <i>Mn</i> ⁷⁺ ...3p ⁶	Ca 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² forms <i>Ca</i> ²⁺ ...3p ⁶ (very stable EC)
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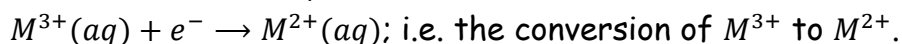
The oxidation states of transition elements exhibit in ions/compounds are:

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Oxidation states					+7					
				+6	+6	+6				
			+5	+5	+5	+5				
		+4	+4	+4	+4	+4	+4	+4		
	+3	+3	+3	+3	+3	+3	+3	+3	+3	
		+2	+2	+2	+2	+2	+2	+2	+2	+2
				+1					+1	

Note:

- Some oxidation states are uncommon and unstable.
- +2 and +3 are found in most elements.

The relative stability of the two oxidation states is governed by the value for electrode potential for the half-reaction;



The relative stability of +2 and +3 oxidation states in Mn and Fe can be interpreted using their ECs as follows:

$Fe^{2+}; 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$	$Mn^{2+}; 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$
$Fe^{3+}; 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$	$Mn^{3+}; 1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$

In both Mn^{2+} and Fe^{3+} ions, the 3d sub energy levels are half filled and this makes the ions stable whereas in both Mn^{3+} and Fe^{2+} ions, the 3d sub energy levels have both 4 and 6 electrons. These make the 3d sub energy levels neither half-filled nor fully filled and thus, the ions are unstable.

- The elements show highest oxidation states in compounds with oxygen, fluorine and some extent with chlorine. This is because oxygen and fluorine are the most electronegative elements. Thus, both oxide and fluoride ions are less polarized by the highly charged cations.
- In lower oxidation states, compounds are mainly ionic and oxides are mainly basic; whereas in higher oxidation states, compounds are mainly covalent and oxides are acidic. In intermediate oxidation states; bonding in compounds is partly ionic and partly covalent, and the oxides are amphoteric.
- Acidity in the oxides of the transition metals increase with increase in the oxidation states. For example;

Oxide	Oxidation state of metal	Nature of oxide
MnO	+2	Basic
Mn ₂ O ₃	+3	Basic
MnO ₂	+4	Amphoteric
Mn ₂ O ₇	+7	Acidic

- Vanadium, chromium, manganese and iron **never** form simple ions in their highest oxidation states. This is due to the very high charge density associated with the cations.
- The zero (0) oxidation state in compounds is encountered in carbonyls. For example; Ni(CO)_4 , Fe(CO)_5 , Co(CO)_8 and so on.

Activity 4:

Calculate the oxidation state of the transition metal atom in the following ions and compounds.

- (i) $[\text{CuCl}_4]^{2-}$ (iv) $[\text{Cu(NH}_3)_4]^{2+}$ (v) $[\text{Fe(CN)}_6]^{3-}$ (vi) $[\text{Fe(CN)}_6]^{4-}$
 (ii) $[\text{Cr(H}_2\text{O)}_4(\text{OH})_2]^+$ (vii) MnO_4^- (viii) $\text{K}_2\text{Cr}_2\text{O}_7$ (ix) $[\text{Co(NH}_3)_5\text{Cl}]\text{Cl}$
 (iii) CrO_4^{2-} (x) Ni(CO)_4

4. The elements form coloured ions/compounds.

Colours of some aqueous transition metal ions are shown in the table below:

Ion	$\text{Sc}^{3+}(\text{aq})$	$\text{Ti}^{3+}(\text{aq})$	$\text{V}^{3+}(\text{aq})$	$\text{Cr}^{3+}(\text{aq})$	$\text{Ni}^{2+}(\text{aq})$	$\text{Mn}^{2+}(\text{aq})$
Colour	Colourless	Purple/ violet	Green	Green/ Violet	Green	Pale pink
No. of electrons in 3d orbitals	$3d^0$	$3d^1$	$3d^2$	$3d^3$	$3d^8$	$3d^5$

Ion	$\text{Fe}^{2+}(\text{aq})$	$\text{Fe}^{3+}(\text{aq})$	$\text{Co}^{2+}(\text{aq})$	$\text{Cu}^+(\text{aq})$	$\text{Cu}^{2+}(\text{aq})$	$\text{Zn}^{2+}(\text{aq})$
Colour	Green	Yellow/ Brown Reddish -brown	Pink	Colourless	Blue	Colourless
No. of electrons in 3d orbitals	$3d^6$	$3d^5$	$3d^7$	$3d^{10}$	$3d^9$	$3d^{10}$

Coloured ion/compound formation in transition metals is associated with incompletely filled 3d sub energy level, the nature of the ligand and the charge on the cation.

The main cause of colour in transition metal ions/compounds is due to d–d electron transitions when white light falls on the ion/compound. The observed colour is due to the colour of the light transmitted not absorbed. For example; hydrated copper(II) ion is blue because it absorbs red light (i.e. white light minus red light gives blue).

Sc^{3+} ions have no electrons in the 3d sub energy level; hence no d-d electron transitions are possible when white light falls on the ion/compound containing the ions. This makes the ion/compounds colourless in aqueous solution and its solid compounds white.

Both Cu^+ and Zn^{2+} ions have fully filled 3d sub energy level; hence no d-d electron transitions are possible when white light falls on the ions/compound containing the ions. This makes the ions/compounds in aqueous solution colourless and their compounds in solid state are white.

Different ligands affect electrons in the 3d sub energy level differently. Thus, the colours will vary if the same metal cation is bonded to different ligands. For example;

$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$; pale blue	$[\text{Cu}(\text{NH}_3)_4]^{2+}$; deep blue
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Cationic charge and radius also affect the colour of the ions/compounds differently. For example;

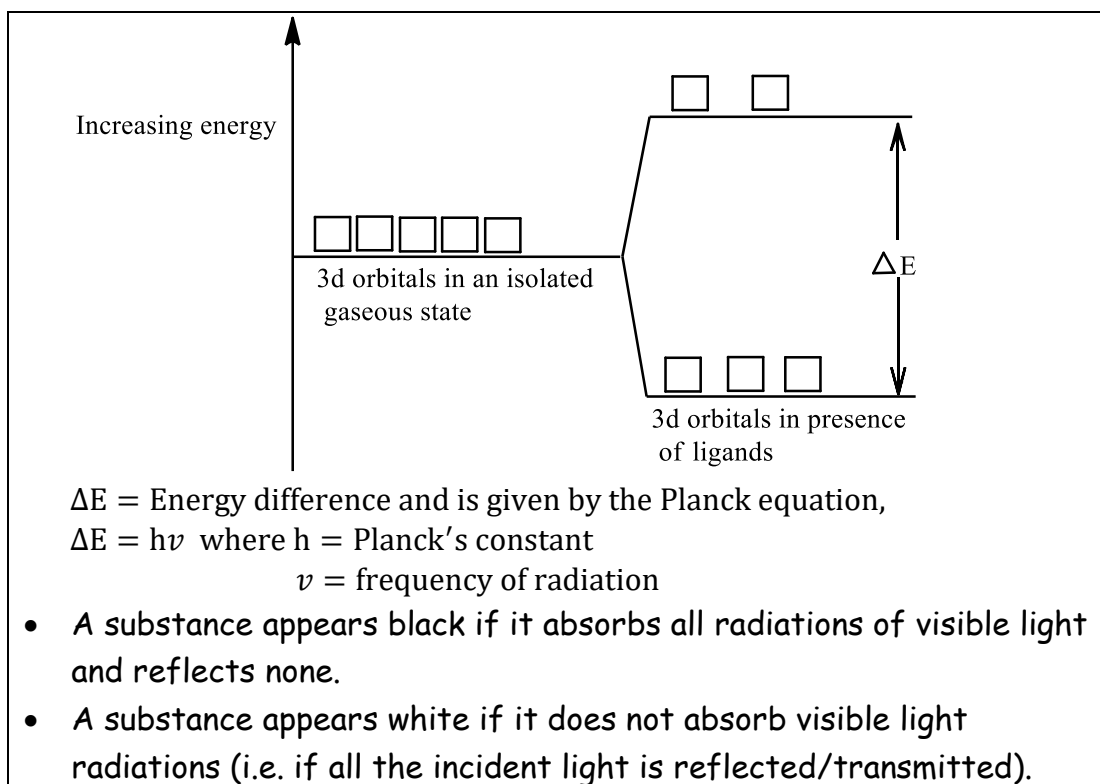
Fe^{2+} ; green	Fe^{3+} ; brown/reddish-brown/yellow
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Supplement:

Theory (origin) of colour of transition metal ions/compounds

When a transition metal ion is in an isolated gaseous state (i.e. in absence of external disturbance), all its five 3d orbitals are degenerate (i.e. have exactly the same energy).

However, under external influence (e.g. in presence of ligands), the 3d orbitals split into two sets of orbitals having different energies, the higher energy set with two orbitals having the same energy while the lower energy set with three equal energy orbitals. This can be shown as in the diagram below:



Activity 5:

Explain each of the following observations:

- Aqueous solutions of scandium(III) and zinc salts are colourless.
- Copper(II) chloride is green whereas copper(I) chloride is white.

- Most transition elements and their compounds are catalysts/show catalytic activity.

Examples of some transition metals and their compounds that are used as catalysts are:

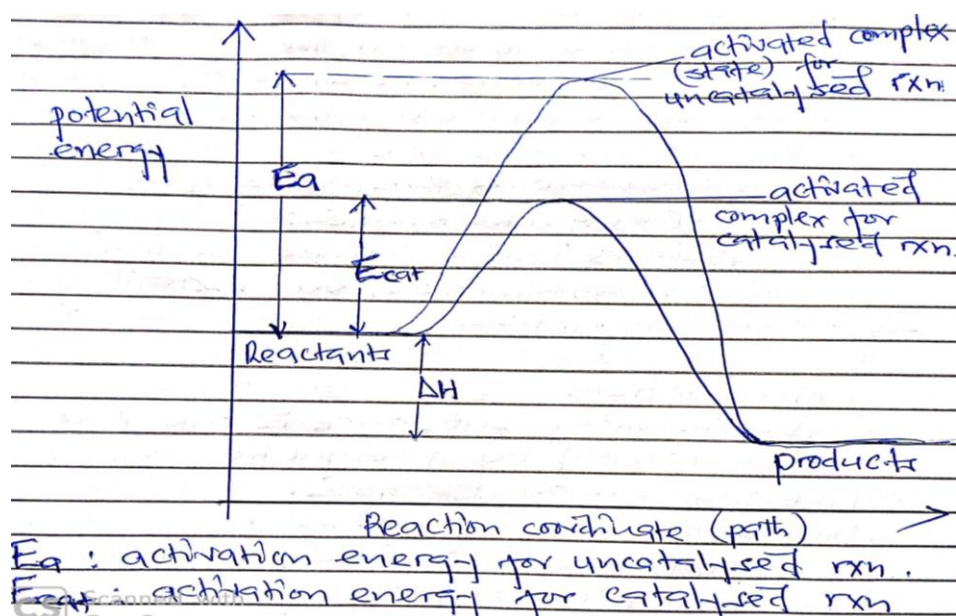
Vanadium(V) oxide in contact process	Finely divided iron in Haber process
Nickel in the catalytic hydrogenation of alkenes and alkynes	Copper in oxidation of ethanol to ethanal
Manganese(IV) oxide in decomposition of hydrogen peroxide	

Their catalytic activity is either homogeneous (both the reactants and catalysts are in the same phase) or heterogeneous (reactants and the catalysts are in different phases).

Transition metals and their compounds are able to alter the rate of a chemical reaction because:

- They form ions with variable oxidation states. This enables them to take part in a sequence of reaction stages and emerge unchanged at the end. As a result, the elements/their ions provide alternative reaction paths/routes of a much lower activation energy compared to the uncatalyzed reaction.
- The metals or their ions **have partially filled 3d orbitals**. This allows the reactant particles to get adsorbed on their surfaces and thus, form temporary/weak bonds with them. This weakens the bonds in the reactant particles and also increases the concentration of the reactant particles (brings reactant particles closer to each other) on the surface of the catalyst. As a result, the frequency of collision between the reacting particles increases, an activated complex forms more easily and hence, faster rate of reaction.

Energy diagram for a catalyzed and uncatalyzed reaction takes the following form:



Activity 6:

- (a) Using the same axes, draw a labelled diagram for energy-reaction coordinate for a catalysed and un-catalysed reaction.
- (b) State:
- (i) the difference in your diagrams in (a).
 - (ii) how a catalyst increases the rate of a reaction.

6. Transition metals and their compounds are paramagnetic.

When transition metal cations or compounds are placed in a magnetic field, they exhibit different behaviors which include:

(i) **Paramagnetism**

A paramagnetic substance is one that is weakly attracted by a magnetic field. Some transition metal ion/compounds are paramagnetic. This is due to the **presence of unpaired electrons in the 3d orbitals** which spin to generate a magnetic moment (field) that can be attracted by an external magnetic field. The greater the number of unpaired electrons in the 3d orbitals; the more paramagnetic the ion/compound is.

(ii) **Diamagnetism:**

Diamagnetic substances are those that are repelled by a magnetic field. They are repelled due to lack of unpaired electrons in their 3d orbitals. Scandium(III) and zinc ions, and their compounds are diamagnetic. This is because both Sc^{3+} and Zn^{2+} ions do not have unpaired electrons in their 3d orbitals and this makes their net magnetic moment zero.

(iii) **Ferromagnetism:**

Substances are said to be ferromagnetic if they are strongly attracted to a magnetic field. This arises due to the high number of unpaired electrons in their 3d orbitals. Examples of some transition metals that are ferromagnetic include: **iron, cobalt and nickel**. Such metals can be magnetized.

7. They form interstitial 'compounds'.

Transition metals can allow atoms of some non-metal to occupy the interstices (spaces between their atoms) in their crystal lattices and thus, form interstitial 'compounds'. The number of atoms that can be

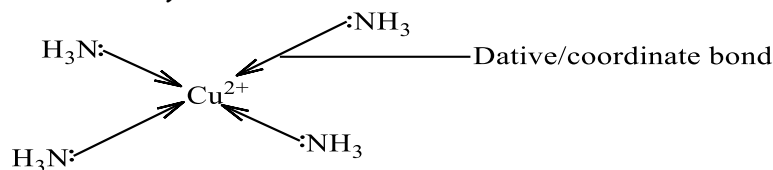
accommodated by a given metal is not fixed and thus, interstitial 'compounds' are non-stoichiometric.

Interstitial 'compounds' have many useful properties. For example, they are very hard, have high melting points and are good electrical conductors.

8. Transition elements form complex ions/complexes

A **complex** is an ion or a neutral compound consisting a central metal atom or cation linked/bonded a number of neutral molecules with lone pair of electrons or negatively charged ions through dative (or coordinate) bonds.

A **complex ion** is either a negatively charged ion or positively charged ion that contains a central metal cation linked to atoms or group of atoms with a negative charge or lone pair of electrons through dative (or coordinate) bonds.



Transition metals have much greater tendency to form complexes because they:

- (a) possess vacant 3d orbitals of suitable/appropriate energy which can accept and accommodate lone pairs of electrons from the surrounding ligands.
- (b) form cations with small ionic radii and high charge; and hence, high charge density. This enables the cations to strongly attract the lone pairs of electrons from the ligands and as a result form strong dative bonds with the ligands.

Coordination number is the total number of ligands which are directly bonded to the central metal atom or cation.

Or:

It is the total number of dative bonds formed between the ligands and the central metal atom or ion.

The common coordination numbers are; 2, 4 and 6 and they depend on the size of the:

(a) central metal atom/cation.

(b) ligands.

For example;

Complex ion/compound	Coordination number	Oxidation state
$[\text{Cu}(\text{NH}_3)_4]^{2+}$	4	+2
$[\text{CuCl}_4]^{2-}$	4	+2
$[\text{Fe}(\text{CN})_6]^{4-}$	6	+2
$[\text{Cr}(\text{H}_2\text{O})_4(\text{OH})_2]^+$	6	+3
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	6	+3
$[\text{Co}(\text{NH}_3)_6]^{3+}$	6	+3
$[\text{Ni}(\text{NH}_3)_6]^{2+}$	6	+2
$[\text{CrCl}(\text{H}_2\text{O})_5]^+$	6	+2
$[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$	6	+3
$\text{K}_4[\text{Fe}(\text{CN})_6]$	6	+2
$[\text{Cr}(\text{H}_2\text{O})_6]\text{Br}_3$	6	+3
$[\text{Ni}(\text{H}_2\text{O})_4](\text{OH})_2$	4	+2
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}$	6	+2

A **ligand** refers to a molecule with lone pair of electrons or a negatively charged ion that bonds to the central metal atom/cation via a dative (or coordinate) bond.

Structurally a complex is represented as $[\text{ML}_n]^y$:

M is the central metal atom/cation; y is the charge on the complex; n is the coordination number and **L** represents the ligands directly bonded to **M**.

Note:

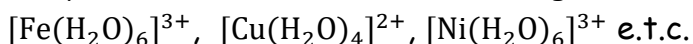
(a) The coordination number of **M** is the same regardless of the type of ligand. For example:

$[\text{Cu}(\text{NH}_3)_4]^{2+}$	$[\text{CuCl}_4]^{2-}$	$[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	$[\text{Cr}(\text{OH})_6]^{3-}$	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

(b) Common coordination numbers for metal atoms/ions are:

Ion/ atom	Fe^{2+} Fe^{3+}	Fe	Cr^{3+}	Cu^{2+}	Mn^{2+}	Ni^{2+}	Ni	Co^{2+}	Zn^{2+}	Ag^+ Cu^+
C.N	6	5	6	4/6	6	4/6	4	4/6	4	2

(c) In aqueous solution, transition metal ions exist as hydrated complexes with water molecules as ligands. For example;

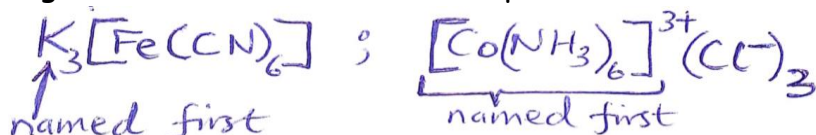


NOMENCLATURE OF COMPLEXES

- ❖ The names of complexes identify the following features about the complexes:
 - (i) Whether the complex is ionic, an ion or neutral.
 - (ii) Oxidation number/state of the central metal atom/cation.
 - (iii) Number of ligands directly bonded to the central metal atom/cation.

❖ The IUPAC rules followed are:

- (i) The names of the complexes consist of two parts written as one word.
- (ii) If the complex is ionic, the cation is always named first before the anion; regardless of whether it is a complex or not.



- (iii) Names of the ligands precede the name of the central metal atom/ion.
Prefixes; di, tri, tetra, penta, hexa etc. are used to denote the number of ligands in the complex.
- (iv) When two or more ligands are directly bonded to the central metal atom/cation, their names are written in alphabetical order disregarding the Greek prefixes denoting their number.
- (v) The oxidation state of the central metal atom/cation is indicated in Roman numerals immediately after its name.
- (vi) If the complex is negatively charged, the name of the central metal cation ends with 'ate'.
- (vii) The names of anionic ligands end with 'o'. For example:

Cl^- ; chloro	CN^- ; cyano	OH^- ; hydroxo	$C_2O_4^{2-}$; oxalato
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Neutral ligands usually possess their normal names except:

H_2O ; aqua	NH_3 ; ammine	CO ; carbonyl
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❖ Examples of complexes and their names:

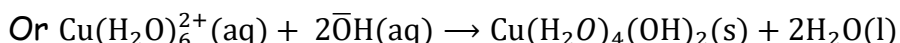
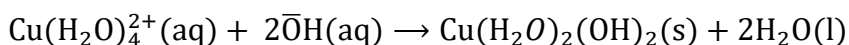
Complex	Name
$[\text{Cu}(\text{NH}_3)_4]^{2+}$	Tetraamminecopper(II) ion
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	Hexaaquacopper(II) ion
$[\text{Cr}(\text{H}_2\text{O})_4(\text{OH})_2]^+$	Tetraaquadihydroxochromium(III) ion
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	Hexaaquairon(III) ion
$[\text{Co}(\text{NH}_3)_6]^{3+}$	Hexaamminecobalt(III) ion
$[\text{Ni}(\text{NH}_3)_6]^{2+}$	Hexaamminenickel(II) ion
$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	Hexaaquacobalt(II) ion
$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	Hexaaquanickel(II) ion
$[\text{CrCl}(\text{H}_2\text{O})_5]^+$	Pentaaquachlorochromium(II) ion
$[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$	Pentaaquahydroxochromium(III) ion
$[\text{Co}(\text{NH}_3)_5\text{SO}_4]^+$	Pentaamminesulphatocobalt(III) ion
$[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$	Tetraamminediaquachromium(II) ion
$[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$	Pentaamminebromocobalt(III) ion
$[\text{CuCl}_4]^{2-}$	Tetrachlorocuprate(II) ion
$\text{Ni}(\text{CO})_4$	Tetracarbonylnickel(0)
$[\text{Fe}(\text{CN})_6]^{4-}$	Hexacyanoferrate(II) ion
$[\text{Ni}(\text{CN})_4]^{2-}$	Tetracyanonickelate(II) ion
$[\text{Zn}(\text{OH})_4]^{2-}$	Tetrahydroxozincate(II) ion
$[\text{Co}(\text{NO}_2)_6]^{2-}$	Hexanitrocobaltate(IV) ion
$[\text{Fe}(\text{CN})_6]^{4-}$	Hexacyanoferrate(II) ion
$[\text{Ni}(\text{CN})_4]^{2-}$	Tetracyanonickelate(II) ion
$[\text{CoCl}_4]^{2-}$	Tetrachlorocobaltate(II) ion
$[\text{Zn}(\text{OH})_4]^{2-}$	Tetrahydroxozincate(II) ion
$[\text{Co}(\text{NO}_2)_6]^{2-}$	Hexanitrocobaltate(IV) ion
$[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$	Pentacyanonitrosylferrate(III) ion
$[\text{CrNH}_3(\text{OH})_5]^{3-}$	Aminepentahydroxochromate(II) ion
$[\text{CrCl}(\text{NH}_3)_5]\text{Cl}_2$	pentaamminechlorochromium(III) chloride
$[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{SO}_4$	Tetraamminediaquachromium(II) sulphate
$\text{Na}_2[\text{Zn}(\text{OH})_4]$	Sodium tetrahydroxozincate(II)
$\text{K}_4[\text{Fe}(\text{CN})_6]$	Potassium hexacyanoferrate(II)

Activity 7:

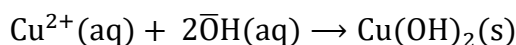
- (a) Define the term **complex ion**.
- (b) Explain why transition metals form many complexes.
- (c) $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{CuCl}_4]^{2-}$ are complex ions formed by iron and copper respectively.
 - (i) State the oxidation of iron and copper in the complex ions,
 - (ii) State the coordination number of iron and copper in the complex ions.
 - (iii) Name each of the complex ions.

DISPLACEMENT REACTIONS IN COMPLEXES

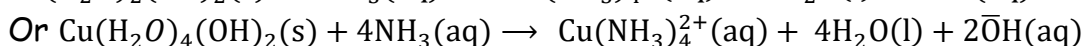
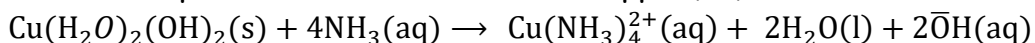
- ❖ These reactions involve displacement of a ligand by another. The reactions usually bring about change in colour or solubility or both and can be used to identify the metal cations.
- ❖ The reactions depend on:
 - (a) Nature of the ligand
 - (b) Concentration of the ligand
- ❖ Examples of some displacement reactions are:
 - (i) Copper(II) ions in aqueous solution are hydrated and exist as $\text{Cu}(\text{H}_2\text{O})_6^{2+}(\text{aq})$ or $\text{Cu}(\text{H}_2\text{O})_4^{2+}(\text{aq})$; which make the solution appear pale blue.
When little aqueous ammonia solution is added, a pale blue precipitate forms.



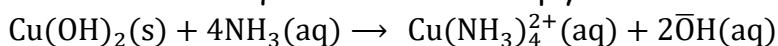
The above two equations can simply be written as follows:



When excess ammonia solution is added, the ammonia molecules displaces the water molecules and hydroxide ions as ligands completely to form a soluble complex ion called tetraamminecopper(II) ions.



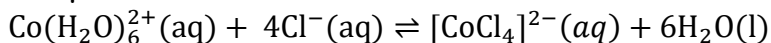
The above two equations can be simply written as follows:



On dilution, the deep blue solution turns pale blue again.

(ii) Cobalt(II) ions in aqueous solution are pink due to $\text{Co}(\text{H}_2\text{O})_6^{2+}(\text{aq})$ ions.

On addition of concentrated hydrochloric acid or any other soluble chloride, the pink solution turns blue due to the formation of $[\text{CoCl}_4]^{2-}$ ions.

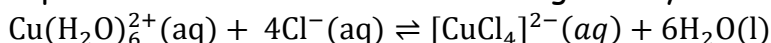


On dilution, the blue solution turns pink again.

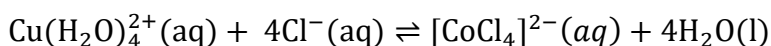
(iii) Aqueous solutions of copper(II) ions are pale blue due to $\text{Cu}(\text{H}_2\text{O})_4^{2+}(\text{aq})$ or $\text{Cu}(\text{H}_2\text{O})_6^{2+}(\text{aq})$ ions.

If sufficient concentrated hydrochloric acid or a concentrated solution of any soluble chloride is added to the pale blue solution, it turns green and then yellow.

The yellow solution is due to the $[\text{CuCl}_4]^{2-}$ ions formed by complete replacement of water molecules as ligands by chloride ions.



Or



On dilution, the yellow solution turns green and then, finally pale blue.

Activity 8:

- Compound **R** contains cobalt 24.8%, chlorine 29.8% and water 45.4%.
 - (i) Calculate the empirical formula of **R**.
 - (ii) Determine the molecular formula of **R**. (RFM of **R** = 237.9)
 - To a solution of **R** in water was added concentrated hydrochloric acid dropwise until in excess.
 - (i) State what was observed.
 - (ii) Write equation for the reaction that took place.
 - The resultant solution in (b) was diluted.
 - (i) State what was observed.
 - (ii) Write equation for the reaction that took place.
 - State what would be observed when aqueous ammonia is added dropwise to an aqueous solution of **R**.
- When to an aqueous solution of copper(II) sulphate was added concentrated hydrochloric acid dropwise until in excess, the pale blue solution turns yellow. On dilution, the solution turns to pale blue again. Explain this observation.

3. Compound **T** contains 25.6% copper, 12.8% sulphur, 25.6% oxygen and the rest being water.
- (a) (i) Calculate the empirical formula of **T**.
 (ii) Determine the molecular formula of **T**. ($M_r = 260$)
- (b) To a solution of **T** in water was added concentrated hydrochloric acid dropwise until in excess.
- (i) State what was observed.
 (ii) Write equation for the reaction that took place.
- (c) The resultant solution in (b) was diluted.
- (i) State what was observed.
 (ii) Write equation for the reaction that took place.
- (d) State what would be observed when aqueous sodium hydroxide is added dropwise to an aqueous solution of **T** and the mixture heated strongly.
- (e) To an aqueous solution of **T** was added dilute nitric acid followed by barium nitrate solution.
- (i) State what was observed.
 (ii) Write equation for the reaction that took place.

Supplement!!!

Structure and shape of complex ions

The shape of a complex ion depends on its coordination number.

Complexes with a coordination number of two are linear. Those with the coordination number of four are usually tetrahedral. However, some complex ions with coordination number of four are square planar.

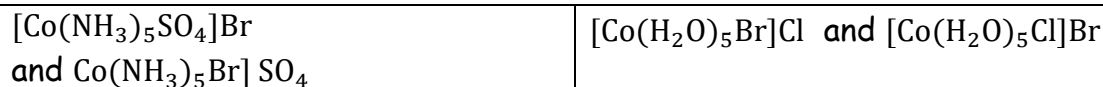
Complex ions with a coordination number of six often have octahedral structures.

ISOMERISM IN TRANSITION METAL COMPLEXES

❖ Some isomerism of interest in complexes are:

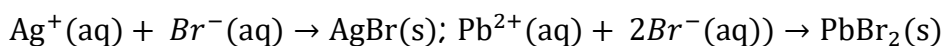
(a) Ionisation isomerism

This occurs when due to interchange of ions inside and outside the coordination sphere. Example are:

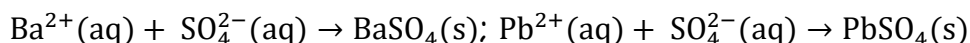


The isomers have chemical properties that differ. For example;

In $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$; the bromide ions are free and thus, an aqueous solution of the isomer gives a positive test with acidified silver nitrate solution/lead(II) nitrate (ethanoate) solution.



While in $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$; the sulphate ions are free and thus, an aqueous solution of the isomer gives a positive test with acidified solution of barium nitrate /lead(II) nitrate (ethanoate).



(b) Hydrate isomerism

Arises due to the difference in the number of water molecules which are coordinated to the central metal ion.

For example; hydrated chromium(III) chloride, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ has four isomers below:

Isomer	No. of moles of free chloride ions per molecule of isomer	Colour of the isomer	No. of conducting ions per molecule of isomer
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{Cl}^-)_3$ Or $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$	3	Violet/grey-blue	4
$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}(\text{Cl}^-)_2 \cdot \text{H}_2\text{O}$ Or $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$	2	Light green	3
$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+(\text{Cl}^-) \cdot 2\text{H}_2\text{O}$ Or $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$	1	Dark green	2
$[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$	0		0

The isomers can be distinguished by:

- Conductivity measurements
- Depression of freezing point
- Addition of excess (of standard) silver nitrate solution

Activity 9:

1.
 - (a) State why chromium is considered a transition element.
 - (b) Write the formulae of all the possible isomers of chromium(III) chloride-6-water, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$.
 - (c) To an aqueous solution of chromium(III) chloride was added ammonia solution dropwise until in excess. State what was observed and write equation(s) for the reaction(s) that would take place.
2. The molecular formula of a complex of cobalt is $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})]\text{Cl}_3$.
 - (a)
 - (i) Write the name of the complex.
 - (ii) State the coordination number of cobalt in the complex.
 - (b) Excess ammonia solution was added to the complex. State what was observed and write equation for the reaction that took place.
 - (c) To 10.0 cm^3 of a 0.5 M solution of the complex was added excess silver nitrate solution.
 - (i) State what observed.
 - (ii) Write the equation for the reaction that took place.
 - (d) The mixture from (c) above was filtered and the residue dried. Calculate the mass of the dried residue.