6. TRANSITION METALS

Learning outcomes

After the lesson, learners should be able to:

- Explain the characteristics of transition metals.
- Explain oxidation states of transition metals.
- Describe complex ions and metal complexes.
- Show shapes of complex ions.
- Describe d-orbitals in complex ions (simple explanation by crystal field theory) for the octahedral complex.
- Explain the reasons for the colours of transition-metal compounds.
- Explain the catalytic properties of transition metals.

Introduction

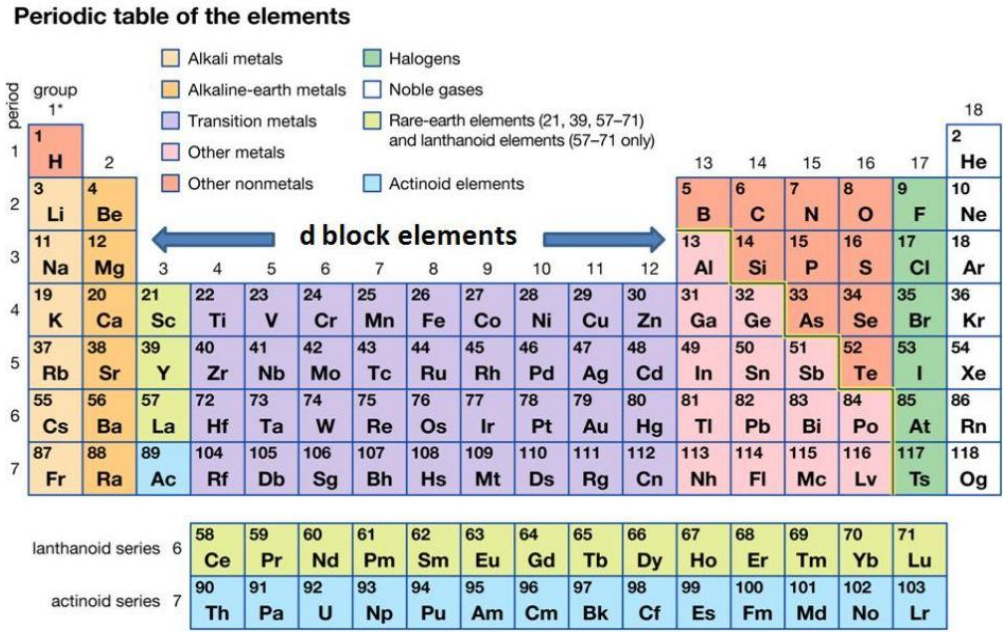
d-block elements: the elements of groups 3-12 in the periodic table, in which the electrons are progressively filled in the d orbitals of the penultimate shell (second last orbit).
According to IUPAC, a transition element (or transition metal) is defined as:

An element that has a **partially filled d subshell** in its ground state or in any of its common oxidation states.

This means:

- Elements like Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu are transition metals because they have partially filled d orbitals either as atoms or as ions.
- Zn, Cd, and Hg are **not transition** metals because they have completely filled d orbitals (d^{10}) both as atoms and in their common +2 oxidation state. Yet they are d- block elements.

Why the word "transition" metals?
They fall between the s-block and p-block elements and show a gradual transition in properties from highly reactive metals on the left to less reactive metals on the right.



Electronic Configuration (EC)

The general electronic configuration of d-block elements is $(n-1)d^{1-10}\ ns^{1-2}$. The last electron in transition elements enters the (n-1)d orbital, which is in the penultimate shell.

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Exceptions (due to stability of half-filled and fully filled subshells):

- **Cr**: [Ar] $3d^5\ 4s^1$ (instead of $3d^4\ 4s^2$)
- **Cu**: [Ar] $3d^{10}\ 4s^1$ (instead of $3d^9\ 4s^2$)

Key concept for ion formation:

When transition metals form ions, they lose the n s electrons first, then (n–1)d electrons.

Example:

Fe: [Ar] $3d^6\ 4s^2$

Fe^{2+}: [Ar] $3d^6$ (loses 4s electrons first)

Fe^{3+}: [Ar] $3d^5$ (loses one more from 3d)

Characteristics of transition metals

Magnetic properties

- Due to the unpaired electrons in the (n-1)d orbitals, transition metals are **paramagnetic** substances.
- These substances are attracted to the magnetic field.
- The paramagnetic character increases as the number of unpaired electrons increase.
- Paramagnetic substances show an increase in weight in a magnetic field, whereas diamagnetic substances a decrease.
- Total magnetic moment (μ) of $M^+ = \sqrt{n(n+2)}$ BM (Bohr Magneton)
  n = no. of unpaired electrons.
- The transition elements that contain only paired electrons are diamagnetic substances. These substances are repelled by the magnetic field.

Metallic character

- The transition elements form strong metallic bonds involving both ns and (n–1)d electrons.
- So, all the transition elements exhibit metallic characters, like hard, lustrous, malleable, ductile, high melting and boiling points, and good conductors of heat and electricity.
- As the number of unpaired d electrons increases, the strength of the metallic bond, hence, the metallic character also increases.

Ionization energy

- The ionization energies of the first row elements gradually increase due to increasing nuclear charge.
- The third ionization energy of Mn is much higher than the others, as the electronic configuration for Mn is $[Ar]3d^5\ 4s^2$, but after losing the 2s electrons, it becomes $[Ar]3d^5$. All five d orbitals are half-filled in this case. Half-filled orbitals have extra stability.

Ionic radii

- In the first-row transition elements, the ionic radii decrease slightly with increasing atomic number.
- The ionic radii also depend on the oxidation state of metals.
  As the oxidation states increase, the ionic radii decrease.
  $Fe > Fe^{2+} > Fe^{3+}$; $Mn > Mn^{2+} > Mn^{7+}$

Alloy formation

- Metals mix with other metals, and alloys are formed.

- As the d-block elements have similar atomic sizes, they can easily take up positions of one another in a crystal lattice. This causes alloy formation.
- E.g., Cr, V, Mn, etc., are present in alloy steels.

Variable oxidation states

- Most of the transition elements exhibit a variable oxidation state because:
  - The energy difference between ns and (n–1)d orbitals is small.
  - Both ns and (n–1)d electrons can participate in bonding.

Formation of complexes

- Transition metals form **complex ions** by accepting lone pairs from ligands due to:
  - Small size of metal ions
  - High ionic charge
  - Presence of vacant d orbitals

Catalytic property

- The first-row transition elements exhibit catalytic properties due to
  - Variable oxidation states (can accept and donate electrons)
  - Vacant d orbitals (can form intermediates)
  - Surface adsorption (in heterogeneous catalysis

Oxidation states of transition metals

- The EC of transition metals shows that these exhibit variable oxidation states, as both **ns** and **(n-1)d** electrons come into play. This is due to the small energy difference of the electrons in the ns and (n-1) d orbitals; both ns and (n-1) d electrons could be lost during the formation of compounds.
- The participation of ns electrons in bonding leads to a +2 oxidation state, which is a lower oxidation state. It is the most common oxidation state of the elements of the first transition series
- The participation of (n-1) d electrons in bonding leads to higher oxidation states like +3, +4, +5, +6, etc.
- The oxidation state increases with atomic number. This increase is related to groups.

Ionic bonds are formed in lower oxidation state transition elements, whereas covalent bonds are formed in higher oxidation states.

Oxidation States of First-Row Transition Metals

(Sc)	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	(Zn)
								+1	1 possible ion
1 possible ion	+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					

The oxidation states in bold represent the most common/ stable oxidation states.

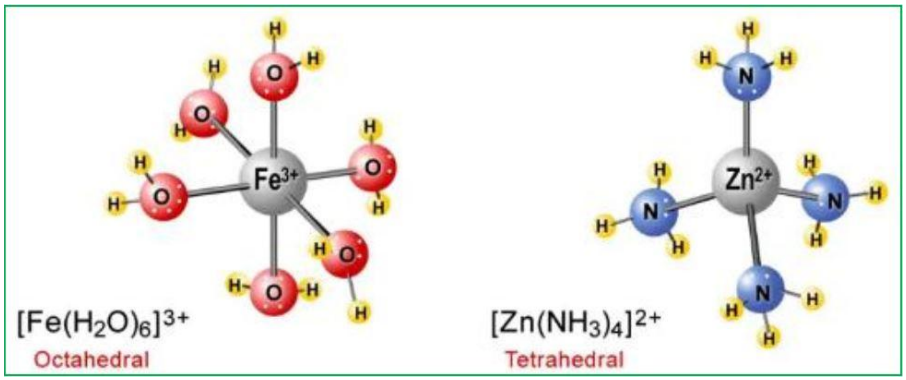
- Not all (n-1) d electrons participate in bonding; only the unpaired (n-1) d electrons take part.

Complex ions and metal complexes

- A **complex ion** is a species consisting of a central metal ion bonded to a fixed number of molecules or ions (called **ligands**) by coordinate (dative) bonds.
- **Ligand**: An ion or molecule with at least one lone pair of electrons (e.g., H_2O, NH_3, Cl^-, CN^-).
- **Ligands are bases and also nucleophiles.**
- **Coordination number (CN)**: The number of coordinate bonds formed between the central metal and the ligands.

- Transition metals form complex ions due to their small size and presence of vacant d –orbitals.
- E.g., $K_3[Fe(CN)_6]$ contains simple K^+ ion and $[Fe(CN)_6]^{3-}$ as complex ion.
- They are electrically charged with a metal ion in the center, surrounded and linked by some neutral molecules or negative ions.
- All the first-row transition elements form complexes.
- Some examples of complex ions

Complex formula	Central ion	Ligands	Coordination number
$[Fe(H_2O)_6]^{3+}$	Fe^{3+}	H_2O	6
$[Cu(NH_3)_4]^{2+}$	Cu^{2+}	NH_3	4
$[Ni(CN)_4]^{2-}$	Ni^{2+}	CN^-	4
$[Co(NH_3)_5Cl]^{2+}$	Co^{3+}	NH_3, Cl^-	6



IUPAC naming of coordination complexes

1. Write the name of the cation followed by an anion with a space in between (just like simple salts).
2. Write the name of the ligand first, and kept in alphabetical order, followed by the metal.
3. Neutral coordination compound is given in one word.
4. Oxidation state of metal in roman numerals in parentheses.
5. If the complex is an anion, the metal name ends in **-ate** (e.g., ferrate, cuprate).
6. For anionic ligands, use: chloro (Cl^-), cyano (CN^-), aqua (H_2O), ammine (NH_3).

e.g.

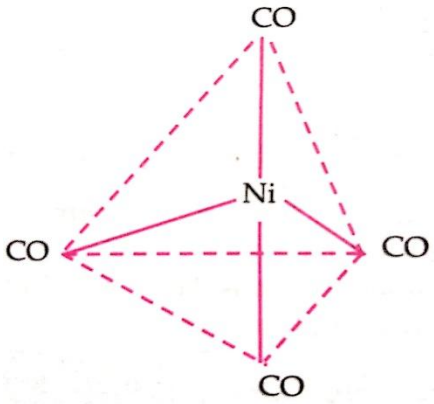
$K_3[Fe(CN)_6]$	Common: Potassium ferrocyanide `
	IUPAC: Potassium hexacyanoferrate (III)
$[Cu(NH_3)_4]SO_4$	Common: Tetraammine cupric sulphate
	IUPAC: Tetraammine copper (II) sulphate
$Fe(CO)_5$	IUPAC: Pentacarbonyliron

Shapes of complex ions

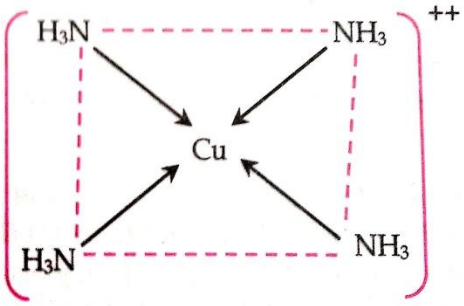
In a complex compound, the metal ion is surrounded by ligands forming a coordination sphere. The shape of a complex ion depends upon the coordination number.

Complex ions having a coordination number of 4 have either a tetrahedral or a square structure. Similarly, complex ions having a coordination number of 6 have an octahedral structure e.g.

$Ni(CO)_4$ Coordination number = 4 Tetrahedral shape



$[Cu(NH_3)_4]^{2+}$ Coordination number = 4 Square planar shape



- Tetrahedral: ligands at four corners of a tetrahedron.
- Square planar: ligands at four corners of a square, metal in center.
- Octahedral: ligands at six corners (up, down, front, back, left, right).

Why different shapes?
Depends on:

- Size and charge of metal ion
- Type of ligand (strong vs weak field)
- d-electron configuration (explained by Crystal Field Theory)

d-orbitals in complex ions for an octahedral complex (explanation by crystal field theory)

In an isolated metal atom/ion, all five d orbitals are degenerate, meaning they have the same energy.

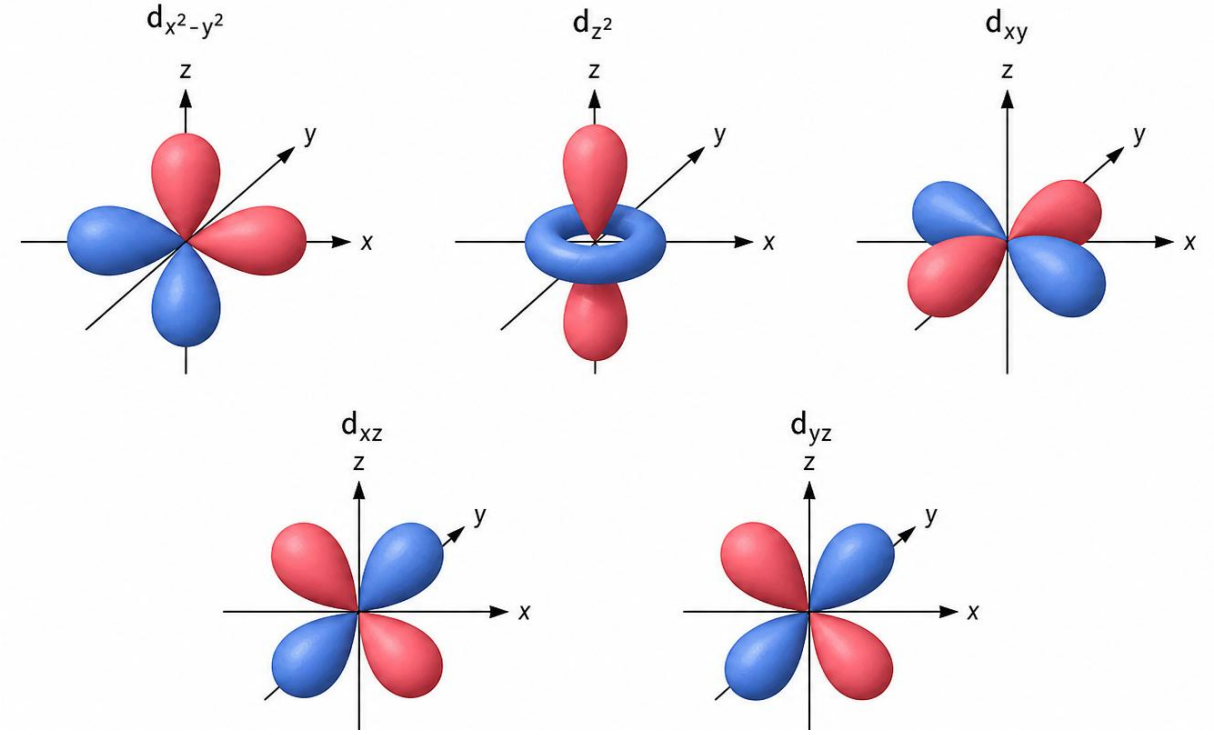


Fig: The five d- orbitals

Energy change of d-orbitals during formation of complex is explained by Crystal Field Theory (CFT) proposed by Bethe and Van Vleck.

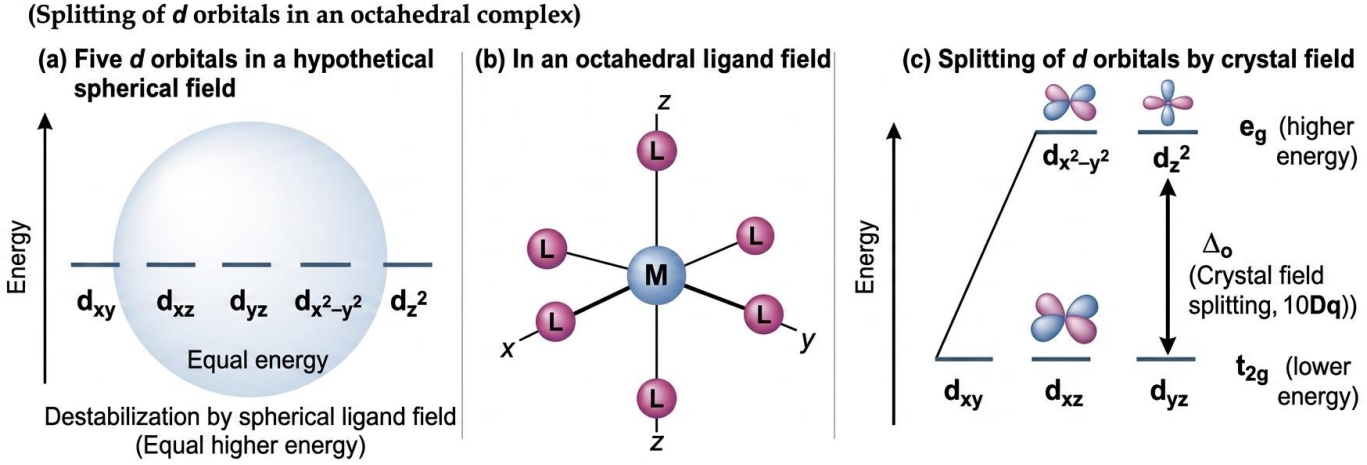
During the formation of a complex ion, ligands approach the central metal atom/ion. The lone pair of electrons in the ligands exerts a repulsive force on the d electrons of the metal, which changes the energy of the d orbitals.

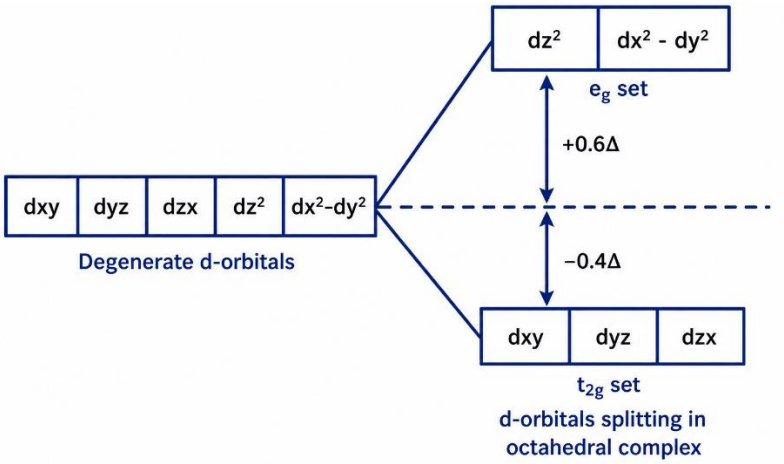
In an **octahedral complex**, the metal ion is the center of an octahedron, and six ligands approach along the x, y, and z axes. Two of the d orbitals dx^2-y^2 and dz^2, being directed toward the axes, experience strong repulsion. Hence, their energy increases. These d orbitals are called **eg set.**

dxy, dyz, and dzx orbitals are directed between axes. They experience less repulsion, meaning their relative energy is lower. These d orbitals are the **t_2g set.**

Thus, the octahedral field of the ligands removes the degeneracy of the d orbitals and splits them into two groups of different energy levels.

The energy difference between eg and t_2g sets is called Δ_o (crystal field splitting energy).





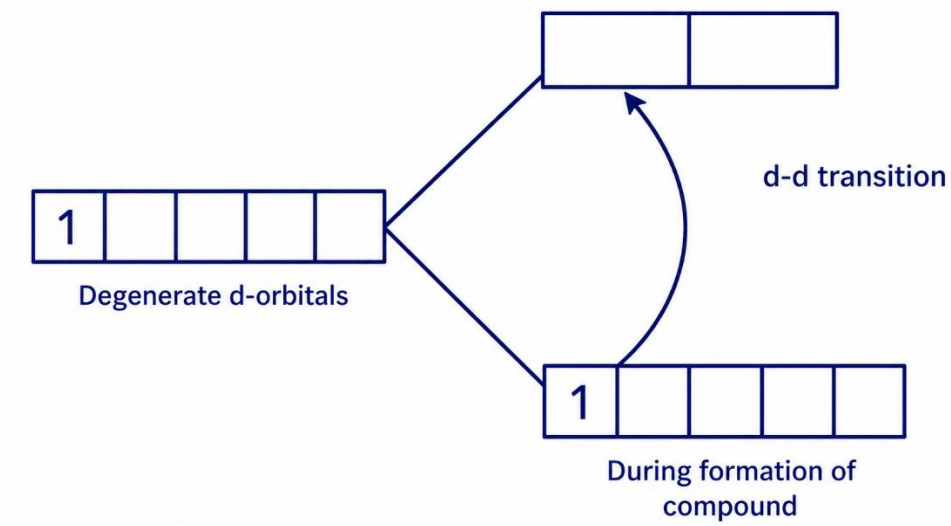
Colour of transition metal compounds

Have you ever wondered why Copper(II) sulfate is a brilliant blue or Potassium permanganate is a vibrant purple? It all comes back to the Crystal Field Theory.

- Most transition metal ions form-coloured compounds.
- When white light passes through a transition metal complex, some wavelengths are absorbed to excite an electron from t_2g to eg orbital(d-d transition.
- The remaining light is transmitted or reflected, and we see the **complementary colour**.
- For example, copper(II) ions absorb light from the red end of the spectrum, so the complementary colour seen is a pale blue (called cyan). Here is a list of complementary pairs of colours:

red	cyan
yellow	blue
green	magenta

- As discussed in CFT, the degenerate d orbitals of transition metals split into



If there is no d electron (d^0) or the d sub-shell is full (d^{10}), no d-d transition, hence the compounds are colourless.
e.g.,: Sc^{3+} (d^0), Zn^{2+} (d^{10}) – colourless.

Catalytic properties of transition metals

- The transition elements exhibit catalytic properties mainly due to
  -presence of vacant d orbitals
  –variable valencies &

-ability to form complexes.

having more than one stable oxidation state, and vacant d orbitals that are energetically accessible and can form dative bonds with ligands

The catalytic properties of these elements are explained by:

a. **Intermediate compounds Formation (Homogenous catalyst)**: Catalyst forms an unstable intermediate with the reactant, which decomposes to give the product and regenerates the catalyst. This provides an alternative path with lower activation energy.
b. **Adsorption theory (Heterogeneous catalyst)**: Transition metals adsorb reactants on their surface. This weakens the bonds in the reactant molecules, helping initiate the reaction and speed it up. e.g., Ni, Pd, Pt, etc., used in hydrogenation reaction.

Industrial Examples

Process	Catalyst	Reaction
Haber's process	Finely divided Fe	$N_2 + 3H_2 \rightleftharpoons 2NH_3$
Contact process	V_2O_5	$2SO_2 + O_2 \rightleftharpoons 2SO_3$
Hydrogenation of oils	Ni	Unsaturated oil → saturated fat
Decomposition of $KClO_3$	MnO_2	$2KClO_3 \rightarrow 2KCl + 3O_2$

Chapter Summary

- Transition metals have partially filled d orbitals in atoms or ions.
- General configuration: $(n-1)d^{1-10}\ ns^{1-2}$.
- Key properties: paramagnetism, variable oxidation states, complex formation, coloured compounds, catalytic activity.
- Crystal Field Theory explains the **splitting of d-orbitals** and related properties.
- In octahedral complexes, d orbitals split into t_{2o} (lower) and e_o (higher).
- Colour arises from d-d transitions.
- Catalytic ability comes from variable valency, vacant d orbitals, and adsorption.

*****This is not a complete note. It is to guide you. It is recommended to study the prescribed textbooks along with this material. *****