Unit 6 · Transition Metals

STUDY NOTES

WHAT NEB'S GRADE 12 EXAM ASKS

- **CDC's grid (2078):** Inorganic Chemistry (Units 6–7 together): 12 of 75 marks; 2 MCQs and 2 short questions, no long one
- **The paper:** 11 MCQs × 1 · 8 short × 5 · 3 long × 8; 3 hours; 1 mark per expected point
- **CDC's model paper:** MCQ: the general configuration of transition metals; short: the octahedral splitting of d orbitals by ligands (why it happens, why $[Cu(H_2O)_6]^{2+}$ is blue, Fe^{2+} or Fe^{3+} more stable, why such metals are good catalysts)
- **MCQ (1 mark)**
  - highest oxidation state (+8 overall, +7 in the 3d series, Mn the most states)
  - which ion is colorless (Cu^+, Zn^{2+}, Sc^{3+}); no d electrons; unpaired electrons in $[Fe(H_2O)_6]^{2+}$
  - coordination number of an octahedron; a strong-field ligand; Δ_o's name; the Haber catalyst
- **Short (5 marks, in parts)**
  - reasons: Zn non-typical; variable oxidation states; good catalysts; paramagnetic; colored
  - define ligand, coordination sphere, complex ion, coordination number, degenerate orbitals, crystal field splitting (energy)
  - two complex ions; an IUPAC name; oxidation state of the metal in a complex
  - Fe^{2+} vs Cr^{3+} unpaired electrons; high or low spin with H_2O and CN^-; spin-only μ; square planar or tetrahedral Ni(II)
- **Long-style (asked as 5-mark parts)**: CFT and its postulates; splitting in an octahedral field; characteristics; catalysis; color and its factors; **draw** complexes of C.N. 4 and 6

Key terms

Transition metals: d-block, groups 3–12; last electron enters (n − 1)d; properties between the s and p blocks.

Transition element (IUPAC): atom or a common cation with an **incomplete** d subshell; Zn, Cd, Hg (d^{10}) **non-typical**.

Complex (coordination complex): central metal + molecules or ions bonded by **coordinate bonds**; charged → **complex ion**.

Ligand: gives a lone pair to the metal (Lewis base; metal Lewis acid); **donor atom**: O in H_2O, N in NH_3, C in CN^-.

Coordination number: number of **donor atoms** bonded to the metal.

Coordination sphere: metal + ligands bonded to it, in [ ]; ions outside are **counter ions** (SO_4^{2-} in $[Cu(NH_3)_4]SO_4$).

Chelate: ring formed by a ligand with 2+ donor atoms (claw); more stable than monodentate complexes.

Degenerate orbitals: of equal energy (five d orbitals of a free ion).

Crystal field splitting: d orbitals split into t_{2g} (lower) and e_g (higher) by ligands; gap Δ_o, the crystal field splitting energy.

CFSE: −0.4 Δ_o per t_{2g} electron, +0.6 Δ_o per e_g electron.

Pairing energy P: extra repulsion of two electrons in one orbital.

Paramagnetic: pulled into a field (unpaired electrons); **diamagnetic**: all paired; **ferromagnetic**: Fe, Co, Ni.

Formulas

configuration $(n-1)d^{1-10}\,ns^{1-2}$	Cr, Cu one s electron; Pd $4d^{10}$ $5s^0$ the exception **Use:** general
$\text{CFSE} = -0.4\Delta_o \times n_{t_{2g}} + 0.6\Delta_o \times n_{e_g}$	+ P for each extra pair (low spin) **Use:** stability
$\mu = \sqrt{n(n+2)}$ BM	n unpaired electrons **Use:** spin-only moment

- μ: 1 → 1.73, 4 → 4.90, 5 → 5.92 BM
- Cr^{3+} (d^3): $3 \times (-0.4\ \Delta_o) = -1.2\ \Delta_o$, all three unpaired

Characteristics (6.2)

1. center of the table, groups 3–12
2. $(n-1)d^{1-10}\,ns^{1-2}$
3. variable oxidation states
4. colored compounds (d–d transitions)
5. good conductors (Cu, Ag best)
6. high density, mp, bp: s **and** d electrons in metallic bonding (W 3,422 °C)
7. catalysts

8. paramagnetic (unpaired d electrons)
9. complexes: small, highly charged ions, empty low-energy d orbitals
10. alloys: atoms of nearly the same size (steel, brass Cu + Zn, bronze Cu + Sn)
11. hard, malleable, ductile, lustrous

Variable oxidation states (6.3)

- (n − 1)d and ns **close in energy**: both lost, each step costs little more
- d^0, d^5, d^{10} especially stable: Sc^{3+}, Mn^{2+}, **Fe^{3+} (d^5) more stable than Fe^{2+} (d^6)**, Zn^{2+}; Ti^{4+} (d^0) more stable than Ti^{3+}
- ions lose **4s first**: Fe^{2+} = [Ar] $3d^6$
- highest state = 4s + 3d electrons up to Mn: Sc +3, Ti +4, V +5, Cr +6, **Mn +7**; then falls (d held tighter)
- Na only +1: next electron from a full inner shell
- Cr: +2 Cr^{2+} sky blue; +3 $[Cr(H_2O)_6]^{3+}$ violet (green with Cl^-), Cr_2O_3 green; +6 CrO_4^{2-} yellow, $Cr_2O_7^{2-}$ orange

	Z	States	Configuration
Sc	21	+3 (+2 rare)	[Ar] $3d^1\ 4s^2$
Ti	22	+2 to +4	[Ar] $3d^2\ 4s^2$
V	23	+2 to +5	[Ar] $3d^3\ 4s^2$
Cr	24	+1 to +6	[Ar] $3d^5\ 4s^1$
Mn	25	+2 to +7	[Ar] $3d^5\ 4s^2$
Fe	26	+2 to +6	[Ar] $3d^6\ 4s^2$
Co	27	+2, +3, +4	[Ar] $3d^7\ 4s^2$
Ni	28	+2, +3, +4	[Ar] $3d^8\ 4s^2$
Cu	29	+1, +2	[Ar] $3d^{10}\ 4s^1$
Zn	30	+2	[Ar] $3d^{10}\ 4s^2$

Complexes and ligands (6.4)

- **monodentate**: X^-, CN^-, OH^-, H_2O, NH_3, CO, NO
- **bidentate**: en ($H_2N–CH_2–CH_2–NH_2$), oxalate $C_2O_4^{2-}$; CO_3^{2-}, SO_4^{2-} sometimes
- **tridentate**: diethylenetriamine (3 N)
- **polydentate**: EDTA, hexadentate (2 N + 4 O)

Complexes are

- cations: $[Ag(NH_3)_2]^+$
- anions: $[Ag(CN)_2]^-$
- neutral: $Ni(CO)_4$, $Fe(CO)_5$

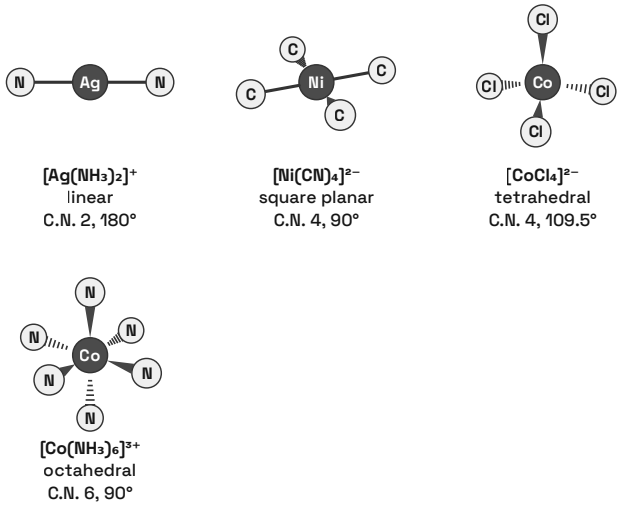
Naming: ligands A–Z with di-, tri-, tetra-, hexa-, then metal (oxidation state); **ammine** NH_3, **aqua** H_2O, **chlorido** Cl^-, **cyanido** CN^-; anion: **-ate** (ferrate, cuprate, argentate)

Formula	Name
$[Cu(NH_3)_4]SO_4$	tetraamminecopper(II) sulphate
$[Cr(H_2O)_4Cl_2]Cl$	tetraaquadichloridochromium(III) chloride
$K_3[Fe(CN)_6]$	potassium hexacyanidoferrate(III)
$K_4[Fe(CN)_6]$	potassium hexacyanidoferrate(II)
$[Cr(H_2O)_6]^{3+}$	hexaaquachromium(III) ion

- $[Co(NH_3)_5Cl]Cl_2$: Co +3, C.N. 6, $AgNO_3$ precipitates 2 Cl^-

Shapes (6.5)

C.N.	Shape	Examples
2	linear	$[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$
4	square planar	$[Ni(CN)_4]^{2-}$, $[PtCl_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$
4	tetrahedral	$[CoCl_4]^{2-}$, $[CuCl_4]^{2-}$, $Ni(CO)_4$, $[Zn(NH_3)_4]^{2+}$
6	octahedral	$[Cu(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{3-}$



Linear, square planar, tetrahedral and octahedral complexes (C.N. 2, 4, 4, 6).

Shape depends on

1. coordination number
2. size of the metal ion
3. kind and size of ligands
4. configuration and oxidation state (d^8 + strong field: square; d^{10}: tetrahedral)
5. steric repulsion between ligands

- same formula, two shapes: $[Ni(CN)_4]^{2-}$ square planar, diamagnetic; $[NiCl_4]^{2-}$ tetrahedral, 2 unpaired (2.83 BM)

Crystal field theory (6.6)

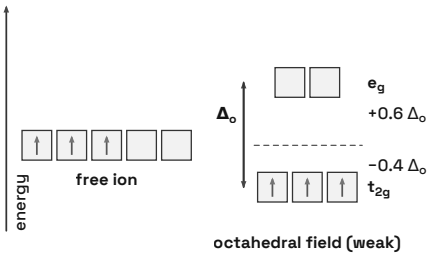
Bethe 1929; Van Vleck, magnetism, early 1930s.

Postulates

1. ligands make an electric field round the metal ion
2. metal–ligand bonding purely **electrostatic**
3. metal is a positive ion, charge = oxidation state
4. no ligands: five d orbitals **degenerate**
5. ligands: split into t_{2g} (d_{xy}, d_{yz}, d_{zx}) and e_g ($d_{x^2-y^2}$, d_{z^2})
6. size of split depends on the ligands and their arrangement
7. the split gives the **CFSE**: stability, color, magnetism
8. weak-field ligands → **high spin**
9. strong-field ligands → **low spin**

Octahedral splitting

- six ligands along ±x, ±y, ±z
- $d_{x^2-y^2}$, d_{z^2} point **at** the ligands → repelled, raised (e_g, $+0.6\ \Delta_o$)
- d_{xy}, d_{yz}, d_{zx} point **between** → lowered (t_{2g}, $-0.4\ \Delta_o$)
- average energy unchanged: $2 \times 0.6 = 3 \times 0.4$



Octahedral splitting of Cr^{3+} (d^3): one electron in each t_{2g} orbital.

High and low spin (choice only for d^4–d^7)

- $\Delta_o < P$ (weak field): spread over all five first → **high spin**, many unpaired
- $\Delta_o > P$ (strong field): fill t_{2g} first → **low spin**, few unpaired
- $[Fe(H_2O)_6]^{2+}$ high spin, 4 unpaired, paramagnetic; $[Fe(CN)_6]^{4-}$ low spin, 0, **diamagnetic**
- Fe^{2+} CFSE: high spin $-0.4\ \Delta_o$; low spin $-2.4\ \Delta_o + 2P$
- Fe^{3+} (d^5): with H_2O 5 unpaired; with CN^- 1
- $[Co(NH_3)_6]^{3+}$ low spin, d^6, 0 unpaired; NH_3 **mid-series** (Fe^{2+}, Co^{2+} ammines high spin)
- Δ_o larger for 3+ than 2+ ions, larger still for 4d, 5d

Spectrochemical series (weak → strong)

$$I^- < Br^- < Cl^- < F^- < OH^- < H_2O$$

$$< NH_3 < en < NO_2^- < CN^- < CO$$

Color (6.7)

1. **d–d transition**: absorbs light of energy Δ_o; shows the **complementary** color; metal, oxidation state, ligands and shape change Δ_o
2. **d^0 and d^{10} colorless**: nothing to jump, or nowhere to jump (Sc^{3+}, Ti^{4+}, Zn^{2+}, Cu^+ white; Cu^{2+} d^9 colored)
3. **charge transfer**: ligand → metal, intense: MnO_4^- (Mn +7, d^0) purple, CrO_4^{2-} yellow, $Cr_2O_7^{2-}$ orange

- $[Cu(H_2O)_6]^{2+}$: $3d^9$ split; absorbs red-orange (peak near 800 nm) → **blue**
- NH_3 stronger field: Δ up, absorbs orange-yellow → royal blue $[Cu(NH_3)_4]^{2+}$
- anhydrous $CuSO_4$ **white** (weaker sulphate field, absorbs in the infrared); water turns it blue (a test for water)

Catalysis (6.8)

1. **variable oxidation states**: easier path, lower activation energy via intermediates; Fe^{3+}/Fe^{2+}: $2\,Fe^{3+} + 2\,I^- \longrightarrow 2\,Fe^{2+} + I_2$, then $2\,Fe^{2+} + S_2O_8^{2-} \longrightarrow 2\,Fe^{3+} + 2\,SO_4^{2-}$
2. **surface adsorption** (partly filled d orbitals): reactants held close, bonds weakened; finely divided works better

Catalyst	Use
Fe (K_2O, Al_2O_3 promoters)	Haber process, NH_3
Ni (or Pd)	vanaspati ghee (hydrogenation)
MnO_2	$KClO_3 \rightarrow O_2$; H_2O_2 decomposition
$TiCl_4 + Al(C_2H_5)_3$ (Ziegler–Natta)	polyethene
Cu	alcohols → aldehydes, ketones
V_2O_5 (or Pt)	contact process, $SO_2 \rightarrow SO_3$

COMMON MISTAKES

✗ NH_3 always a strong-field ligand
✓ mid-series: low spin with Co^{3+}, high spin with Fe^{2+}, Co^{2+}.

✗ $Fe^{2+} = [Ar]\ 3d^4\ 4s^2$
✓ 4s lost first: $[Ar]\ 3d^6$.

✗ tetraamine, aquo, chloro
✓ tetraammine, aqua, chlorido (IUPAC).

✗ $K_3[Fe(CN)_6]$ is hexacyanidoferrate(II)
✓ (III); $K_4[Fe(CN)_6]$ is (II).

✗ Sc +2, Co +3 only
✓ Sc +3 (+2 rare); Co +2, +3, +4.

✗ Haber catalyst Fe–Mo
✓ iron with K_2O, Al_2O_3 promoters.

✗ $[TiO_6]^{4-}$ intensely colored
✓ Ti(IV) oxides white; MnO_4^-, CrO_4^{2-}, $Cr_2O_7^{2-}$ are the charge-transfer colors.

✗ four ligands means tetrahedral
✓ $[Ni(CN)_4]^{2-}$ is square planar.