FREE NOTES · NCERT + JEE/NEET LEVEL

The d- and f-Block Elements

Transition metals: configuration and general trends (size, ionisation enthalpy, oxidation states, E°, magnetic moment, colour, catalysis, complexes, alloys), $K_2Cr_2O_7$ and $KMnO_4$, lanthanoids, lanthanoid contraction and actinoids.

01 Position & electronic configuration
02 Physical properties & atomic size
03 Ionisation enthalpy & oxidation states
04 E° values & stability
05 Magnetism, colour, catalysis, complexes, alloys
06 Potassium dichromate & permanganate
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01 Position & electronic configuration

d-block = groups 3–12, the last electron enters the (n-1)d orbital. Four series: 3d (Sc–Zn), 4d (Y–Cd), 5d (La, Hf–Hg), 6d (Ac, Rf–Cn). General configuration: $(n-1)d^{1-10}\ ns^{1-2}$.

A **transition element** has an incompletely filled d subshell in the atom or in any common ion. So **Zn, Cd, Hg are not transition elements** (d^{10} in atom and ion). Cu is (Cu^{2+} is d^9).

EXCEPTIONS TO LEARN

Cr: $3d^5\ 4s^1$ (not $3d^4 4s^2$) and Cu: $3d^{10}\ 4s^1$ (not $3d^9 4s^2$), because half-filled and fully filled d subshells are extra stable (exchange energy).

02 Physical properties & atomic size

- Hard, high melting and boiling points (strong metallic bonding using many unpaired d electrons). M.p. peaks near the middle (d^5); Mn and Tc are irregular; Zn, Cd, Hg are soft and low melting (Hg is liquid).
- High enthalpy of atomisation. Heavier series (4d, 5d) have higher values.
- **Size:** decreases slowly across a series (poor shielding by d electrons), then nearly constant. 4d and 5d of the same group have almost the **same radius** (Zr 160 pm ≈ Hf 159 pm) because of **lanthanoid contraction**.
- Density increases across a series (Sc to Cu).

03 Ionisation enthalpy & oxidation states

IE increases slowly across the series. Irregular because of the 3d/4s energy closeness: e.g. high IE_2 of Cr and Cu (d^5, d^{10} broken), high IE_3 of Mn (Mn^{2+} is d^5) and Zn.

Variable oxidation states because 3d and 4s electrons have similar energies. Maximum number of states in the middle: **Mn shows +2 to +7**.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+3	+2…+4	+2…+5	+2…+6	+2…+7	+2…+6	+2…+4	+2…+4	+1, +2	+2

PATTERNS

- Highest states show up in oxides and fluorides (Mn_2O_7, CrO_3, VF_5): O can form multiple bonds.
- Low states in complexes with CO ($Ni(CO)_4$, oxidation state 0).
- Higher oxides are acidic (Mn_2O_7), lower are basic (MnO).

04 E° values & stability

- **Cu** has positive $E°(M^{2+}/M) = +0.34$ V, so it doesn't release H_2 from acids. Its high atomisation energy and low hydration energy explain this.
- **Mn^{2+} (d^5), Zn^{2+} (d^{10}), Ni^{2+}** (high hydration energy) give more negative E° than expected ⇒ these ions are very stable.
- $E°(Mn^{3+}/Mn^{2+})$ is very high (+1.57): Mn^{3+} is a strong oxidant because Mn^{2+} d^5 is stable. $E°(Fe^{3+}/Fe^{2+})$ is low because Fe^{3+} (d^5) is stable.
- **Cr^{2+} is reducing** (goes to Cr^{3+}, t_2g^3) while **Mn^{3+} is oxidising** (goes to Mn^{2+}, d^5), even though both are d^4.
- Cu^+ disproportionates in water: $2Cu^+ \rightarrow Cu^{2+} + Cu$ (Cu^{2+} has much higher hydration energy).

05 Magnetism, colour, catalysis, complexes, alloys

$$\mu = \sqrt{(n(n+2))}\ \text{BM}$$

n = number of unpaired electrons. Unpaired electrons ⇒ **paramagnetic**; all paired ⇒ diamagnetic. n = 1, 2, 3, 4, 5 ⇒ μ = 1.73, 2.83, 3.87, 4.90, 5.92 BM.

- **Colour:** d–d transition. Light of one colour is absorbed, the complementary colour is seen. d^0 (Sc^{3+}, Ti^{4+}) and d^{10} (Zn^{2+}, Cu^+) ions are colourless. Cu^{2+} blue, Ni^{2+} green, Mn^{2+} pale pink, Fe^{3+} yellow.
- **Catalysts:** variable oxidation states and a surface for adsorption. V_2O_5 (Contact process), Fe (Haber), Ni (hydrogenation), $TiCl_4 + Al(CH_3)_3$ (Ziegler-Natta).
- **Complexes:** small size, high charge, vacant d orbitals.
- **Interstitial compounds:** small atoms (H, C, N) trapped in the metal lattice (TiC, Fe_3H). Hard, high melting, chemically inert.
- **Alloys:** similar atomic sizes (brass Cu-Zn, bronze Cu-Sn, stainless steel).

06 Potassium dichromate & permanganate

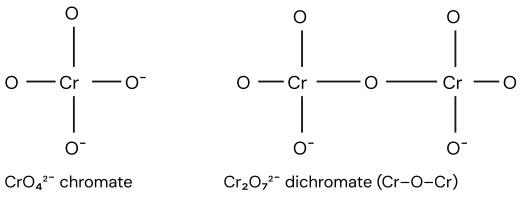
$K_2Cr_2O_7$ preparation (from chromite ore $FeCr_2O_4$):

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$
$$2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$$
$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$$

Chromate (yellow) ⇌ dichromate (orange) depends on pH: acid → dichromate, base → chromate.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \ (E^\circ = 1.33\ V)$$

Oxidises $I^- \rightarrow I_2$, $Fe^{2+} \rightarrow Fe^{3+}$, $H_2S \rightarrow S$, $Sn^{2+} \rightarrow Sn^{4+}$



Structures of chromate and dichromate ions

$KMnO_4$

From pyrolusite MnO_2: fuse with KOH + O_2 → K_2MnO_4 (green) → disproportionation/oxidation → $KMnO_4$ (purple). Diamagnetic; colour from charge transfer.

Acidic: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ $(5\ e^-)$

Neutral/weakly basic: $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$ $(3\ e^-)$

Acidic $KMnO_4$ oxidises Fe^{2+}, oxalate, $I^- \rightarrow I_2$, H_2S, SO_2. HCl is not used to acidify it (Cl^- gets oxidised); dilute H_2SO_4 is used.

07 Lanthanoids & lanthanoid contraction

14 elements after La (Ce to Lu), 4f filling. Configuration [Xe] $4f^{1-14}$ $5d^{0-1}$ $6s^2$. Common oxidation state **+3**. Ce^{4+} (f^0) is a good oxidant; Eu^{2+}, Yb^{2+} (f^7, f^{14}) are reductants.

LANTHANOID CONTRACTION

Steady decrease in size from La to Lu because 4f electrons shield poorly. Results: (1) 4d and 5d elements of a group have almost the same size (Zr/Hf, Nb/Ta) and are hard to separate; (2) basicity of $Ln(OH)_3$ falls from $La(OH)_3$ to $Lu(OH)_3$; (3) lanthanoids are hard to separate from each other.

Uses: **misch metal** (Ln 95% + Fe 5%, lighter flints), catalysts in petroleum cracking, phosphors in TV screens.

08 Actinoids

- 14 elements after Ac (Th to Lr), 5f filling. All are **radioactive**; elements after U are man-made.
- **More oxidation states** than lanthanoids (+3 to +7; U, Np, Pu) because 5f, 6d, 7s have similar energies.
- **Actinoid contraction** is larger than lanthanoid contraction (5f shields even more poorly).
- Reactive metals, finely divided form is pyrophoric.

09 JEE Extra + Tricks

JEE LEVEL

- Colour of ions from d–d transitions: d^0 (Sc^{3+}, Ti^{4+}) and d^{10} (Zn^{2+}, Cu^{+}) are colourless.
- Lanthanoid contraction ⇒ Zr and Hf almost same size (hard to separate); basicity of $Ln(OH)_3$ decreases La → Lu.
- $KMnO_4$ and $K_2Cr_2O_7$: chromate (yellow) ⇌ dichromate (orange) with pH; MnO_4^- purple. Preparation: pyrolusite (MnO_2) fusion with KOH → K_2MnO_4 (green) → $KMnO_4$.
- Highest oxidation state: Mn +7 ($KMnO_4$), Os +8 (OsO_4). Most common Ln state +3; Ce^{4+} (oxidant), Eu^{2+} (reductant).
- Interstitial compounds, catalytic properties (Fe in Haber, V_2O_5 in contact process, Ni in hydrogenation) and alloy formation.

10 Solved questions

Q1. Calculate μ of Fe^{2+} (Z = 26).

Fe^{2+}: $3d^6$ ⇒ 4 unpaired ⇒ μ = √(4×6) = √24 = **4.90 BM**.

Q2. Why is Sc^{3+} colourless while Ti^{3+} is coloured?

Sc^{3+} is $3d^0$: no d electron for d–d transition. Ti^{3+} is $3d^1$: a d–d transition absorbs visible light (purple colour).

Q3. Why do Zr and Hf have almost the same radius?

Lanthanoid contraction: the 14 4f elements before Hf shrink its size, cancelling the increase expected from an extra shell.

Q4. How many moles of $KMnO_4$ oxidise 1 mol Fe^{2+} in acid?

MnO_4^- takes $5e^-$, each Fe^{2+} gives $1e^-$ ⇒ **1/5 mol**.

11 Mistakes & practice

- Calling Zn a transition element.
- Writing Cr as $3d^44s^2$ or Cu as $3d^94s^2$.
- Saying $KMnO_4$ is coloured due to d–d transition (Mn^{7+} is d^0: it is charge transfer).
- Acidifying $KMnO_4$ with HCl.

1. Which 3d metal shows the most oxidation states?
2. Why is Cu^+ unstable in water?
3. Colour change when acid is added to yellow chromate?
4. μ of Cu^{2+}?
5. Name one consequence of lanthanoid contraction.

ANSWERS

1) Mn · 2) It disproportionates; Cu^{2+} has much higher hydration energy · 3) Yellow → orange (dichromate) · 4) 1.73 BM · 5) Zr and Hf have nearly equal size

12 Quick revision: 5 minutes before the exam

BASICS

- $(n-1)d^{1-10}\ ns^{1-2}$.
- Cr $3d^5 4s^1$, Cu $3d^{10} 4s^1$.
- Zn, Cd, Hg: not transition.

PROPERTIES

- $\mu = \sqrt{n(n+2)}$ BM.
- Colour: d–d; d^0, d^{10} colourless.
- Mn: +2 to +7.

REAGENTS

- $Cr_2O_7^{2-} \rightarrow Cr^{3+}$ ($6e^-$).
- $MnO_4^- \rightarrow Mn^{2+}$ acid ($5e^-$), MnO_2 neutral ($3e^-$).
- Chromate yellow ⇌ dichromate orange.

F-BLOCK

- Lanthanoids: +3, contraction.
- Zr ≈ Hf in size.
- Actinoids: radioactive, many states.

Have a doubt? Ask the AI Doubt Solver at padhaiadda.netlify.app, or take the mock test on this chapter.