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Class 12 (12th) Chemistry — NCERT 2026-27

Chapter 4: The d- and f-Block Elements

Electronic Configurations · Oxidation States · Magnetic Moment · $K_2Cr_2O_7$ & $KMnO_4$ · Lanthanoid & Actinoid Contraction

Key Data & Quick Facts for this Chapter

Quantity / Item	Symbol / Form	Value / Note
d-block groups	Groups 3–12	3d, 4d, 5d, 6d series
General outer config (d-block)	$(n-1)d^{1-10}\,ns^{1-2}$	Pd is exception: $4d^{10}5s^{0}$
General config (lanthanoids)	$[\text{Xe}]\,4f^{1-14}\,5d^{0-1}\,6s^{2}$	most stable Ln^{3+}: $4f^{n}$
General config (actinoids)	$[\text{Rn}]\,5f^{1-14}\,6d^{0-1}\,7s^{2}$	5f less buried than 4f
Bohr magneton (BM)	μ_B	9.274×10^{-24} J T^{-1}
μ for 1 unpaired electron	$\mu=\sqrt{n(n+2)}$	1.73 BM
E° $Cr_2O_7^{2-}/Cr^{3+}$ (acidic)	—	$+1.33$ V
E° MnO_4^-/Mn^{2+} (acidic)	—	$+1.52$ V
E° Ce^{4+}/Ce^{3+}	—	$+1.74$ V (strong oxidant)
E° Cu^{2+}/Cu (unique +ve)	—	$+0.34$ V (only +ve in 3d)
E° Ln^{3+}/Ln (typical)	—	-2.2 to -2.4 V (Eu: -2.0)

1 Position & Electronic Configurations

General outer configuration (d-block)

$\boldsymbol{(n-1)d^{1-10}\,ns^{1-2}}$

where n = principal quantum number of outermost shell (4, 5, 6, 7 for 3d, 4d, 5d, 6d series). Inner $(n-1)d$ subshell is being filled. **Pd is an exception** with $4d^{10}5s^{0}$ ($n=5$).

Special stability exceptions in 3d

Cr $(Z=24):\ 3d^{5}\,4s^{1}$ (not $3d^{4}4s^{2}$)
Cu $(Z=29):\ 3d^{10}\,4s^{1}$ (not $3d^{9}4s^{2}$)
Half-filled (d^5) and fully filled (d^{10}) sets gain **extra exchange-energy stability**. One $4s$ electron promotes to $3d$ because the energy gap is small.

Configurations of d-block cations

d-block ions lose ns electrons **before** $(n-1)d$.
e.g. Fe ($3d^{6}4s^{2}$) $\rightarrow$ Fe^{2+} ($3d^{6}$); Fe^{3+} ($3d^{5}$).
e.g. Cu ($3d^{10}4s^{1}$) $\rightarrow$ Cu^{+} ($3d^{10}$); Cu^{2+} ($3d^{9}$).
Most M^{2+} ions of 3d have configuration $3d^{n}$ with **no** $4s$ **electrons**. Crucial for predicting magnetic moment and colour.

Zn, Cd, Hg, Cn — not "true" transition metals

These Group 12 elements have $(n-1)d^{10}ns^2$ in the ground state *and* in their common $+2$ ions. Since their d subshell is completely filled in both states, they fail the IUPAC definition of a transition metal but are still studied with the d-block.

Why d-block elements are distinctive

Partly filled d-orbitals *protrude* to the periphery of the atom, making them sensitive to the surroundings. This gives transition metals: **variable oxidation states, coloured ions, paramagnetism, complex formation, catalytic activity, and alloy formation**.

2 General Trends in Physical Properties

Trend in atomic / ionic radii

Within a series ($\rightarrow$): radii **decrease** (irregularly).
Down a group: $3d \rightarrow 4d$: **increase**; $4d \rightarrow 5d$: **nearly equal**.
e.g. Zr $= 160$ pm, Hf $= 159$ pm.
$4d$ and $5d$ radii match because of **lanthanoid contraction** — the gradual decrease in size on filling $4f$ before $5d$.

Melting point trend

Maximum at $\sim d^5$ configuration (mid-series).
$3d$: max at Cr/V; $4d$: max at Mo; $5d$: max at W.
High m.p. due to involvement of $(n-1)d$ + ns **electrons** in strong interatomic metallic bonding.
Mn and Tc are anomalously low because of stable $d^5\ ns^2$ configuration.

Enthalpy of atomisation

$\Delta_a H^\circ$ peaks at the middle of each series.
Order across series: $\mathbf{5}d > \mathbf{4}d > \mathbf{3}d$ (in general).
Greater number of unpaired d-electrons $\Rightarrow$ stronger metal–metal bonds $\Rightarrow$ higher $\Delta_a H^\circ$. Heavy transition metals form more frequent metal–metal bonds in their compounds.

Density trend (1st series, Ti $\rightarrow$ Cu)

Density **increases** from Ti (4.1) to Cu (8.9 g cm^{-3}).
NCERT Table 4.2: Sc 3.43, Ti 4.1, V 6.07, Cr 7.19, Mn 7.21, Fe 7.8, Co 8.7, Ni 8.9, Cu 8.9, Zn 7.1 g cm^{-3}.
Atomic radius decreases while atomic mass increases $\Rightarrow$ atoms pack more mass into less volume.
$4d$ and $5d$ densities are higher still due to lanthanoid contraction.

Lattice structures of $3d$ transition metals

Structure	Metals (NCERT Table)
hcp (bcc)	Sc, Ti, Y, Zr, La, Hf
bcc only	V, Cr, Nb, Mo, Ta, W
hcp	Tc, Ru, Re, Os
bcc (hcp,ccp) for Mn; bcc (hcp) for Fe	Mn, Fe
ccp (hcp)	Co, Rh, Ir
ccp	Ni, Pd, Pt, Cu, Ag, Au
X (atypical)	Mn, Zn, Cd, Hg

Mn, Zn, Cd, Hg show **atypical** (non-standard) lattice structures and have anomalously low melting

points within their series.

Lanthanoid contraction

The cumulative regular decrease in atomic/ionic radii from La ($Z = 57$) to Lu ($Z = 71$). Caused by **poor shielding of one 4f electron by another** as nuclear charge rises across the series. Its main consequence: 4d and 5d transition metals have nearly identical radii (hence very similar chemistry — e.g. Zr/Hf, Nb/Ta).

3 Ionisation Enthalpies

Trend in ionisation enthalpy

$\Delta_i H_1, \Delta_i H_2, \Delta_i H_3$ **increase** along a series (irregularly).
Increase is **much smaller** than in non-transition s, p blocks.
Across a 3d series, added electrons enter $(n-1)d$ which **shields** ns electrons from the rising nuclear charge $\Rightarrow$ effective charge increases only slowly.

Exchange-energy stabilisation

$E_{\text{exch}} \propto \binom{N}{2}$ where N = number of parallel-spin electrons.
Half-filled (d^5) and fully filled (d^{10}) sets maximise parallel spins. Removing an electron **costs the lost exchange energy**, raising the ionisation enthalpy.

Break at Mn^+ & Fe^{2+}

$\Delta_i H_2(\text{Mn}) < \Delta_i H_2(\text{Cr})$ (Cr^+: d^5 stable).
$\Delta_i H_3(\text{Fe}) < \Delta_i H_3(\text{Mn})$ (Mn^{2+}: d^5 stable).
Whenever ionisation produces the half-filled d^5 ion, the loss of exchange energy is **minimum** $\Rightarrow$ that ionisation step is unusually easy.

Why second IE matters for M^{2+} stability

To form $M^{2+}_{(aq)}$, both $\Delta_a H$ and $\Delta_i H_1 + \Delta_i H_2$ must be supplied (offset by hydration). The **second ionisation enthalpy is the dominant** term: it is unusually high for Cr ($d^5 \to d^4$) and Cu ($d^{10} \to d^9$), making Cr^{2+} and Cu^{2+} chemistry distinctive.

Ionisation enthalpy data — key 3d values (kJ mol^{-1})

Metal	$\Delta_i H_1$	$\Delta_i H_2$	$\Delta_i H_3$	Note
Sc	631	1235	2393	smallest 1st IE
Cr	653	**1592**	2990	high $\Delta_i H_2$ (loss of d^5)
Mn	717	1509	**3260**	high $\Delta_i H_3$ (loss of d^5)
Fe	762	1561	2962	low $\Delta_i H_3$ ($d^6 \to d^5$)
Cu	745	**1958**	3556	high $\Delta_i H_2$ (loss of d^{10})
Zn	906	1734	3837	highest $\Delta_i H_1$

Breaks at Mn^+ ($d^5 4s^1$) and Fe^{2+} (d^6): producing the half-filled d^5 ion involves **no loss of exchange energy**, so the next ionisation is unusually easy.

4 Oxidation States

Oxidation states of 3d metals (NCERT)

Sc: $+3$ Ti: $+2, +3, +4$ V: $+2, +3, +4, +5$
Cr: $+2, +3, +4, +5, +6$ Mn: $+2, +3, +4, +5, +6, +7$
Fe: $+2, +3, +4, +5, +6$ Co: $+2, +3, +4$
Ni: $+2, +3, +4$ Cu: $+1, +2$ Zn: $+2$
Bold = most stable. Greatest variety at the centre (Mn) where $s + d$ electrons are most numerous and d-orbitals not yet too contracted.

Rule for highest oxidation states

Highest O.S. is reached only with $\mathbf{O^{2-}}$ or $\mathbf{F^-}$.
e.g. $Mn_2^{VII}O_7$, V^VF_5, $Cr^{VI}F_6$, MnO_4^-.
O and F are **small and very electronegative** $\Rightarrow$ can form strong π-bonds (oxide) or high lattice/bond energies (fluoride) that compensate the high ionisation cost.

Highest fluoride vs highest oxide of Mn

Highest fluoride: MnF_4 ($+4$).
Highest oxide: Mn_2O_7 ($+7$).
Oxygen out-performs fluorine here because O can form **multiple bonds** (Mn=O), while F can only form single Mn–F bonds. Note: MnO_3F is the only known Mn(VII) halide-oxide — not a true Mn(VII) halide.

Acidic / basic character of 3d oxides

Trend: O.S. rises $\Rightarrow$ oxide becomes more **acidic**.
- Basic: TiO, VO, CrO, MnO, FeO, CoO, NiO, CuO, ZnO.
- Amphoteric: Cr_2O_3, V_2O_4, V_2O_5.
- Acidic: V_2O_5 (also amphoteric), CrO_3, Mn_2O_7.

Reactions: $Mn_2O_7 + H_2O \rightarrow 2\,HMnO_4$
$CrO_3 + H_2O \rightarrow H_2CrO_4$; $2\,CrO_3 + H_2O \rightarrow H_2Cr_2O_7$
As ionic character of the oxide decreases (going to higher O.S.), the metal–oxygen bond becomes more covalent and the oxide behaves as an acid anhydride.

Oxocations of early 3d metals

Common high-O.S. oxocations stabilise the metal:
- Ti^{IV} as TiO^{2+} (titanyl)
- V^{IV} as VO^{2+} (vanadyl, blue)
- V^V as VO_2^+ (yellow, in acid) and as VO_4^{3-} (in alkali)
- Fe^{VI} as $[FeO_4]^{2-}$ (ferrate, in alkali; decomposes to Fe_2O_3 + O_2)

Beyond Mn (Group 7), the only oxide of Fe above Fe_2O_3 is the ferrate(VI) ion, formed in alkaline media; no neutral oxide higher than Fe_2O_3 exists.

Variability of O.S. in d-block

d-block: states differ by **unity** ($V^{II}, V^{III}, V^{IV}, V^V$).
p-block: states differ by **two** (Sn^{2+}/Sn^{4+}).
Because d-electrons can be removed *one at a time* without disrupting an inert pair, giving the long ladder of O.S.

Stability of low / zero oxidation states

Low (0, $+1$) states are stabilised by **π-acceptor ligands** (CO, CN^-, NO) that accept electron density from filled metal d-orbitals via back-donation. Examples: $Ni(CO)_4$ and $Fe(CO)_5$ with O.S. of metal $= 0$.

Halides of 3d metals — highest known states

TiX_4 (X = F→I), VF_5, CrF_6, CrF_5
Mn: max halide is **MnF_4** ($+4$); Fe: max trihalide is **FeX_3**; Co: **CoF_3** only.
Low-O.S. instability: VX_2 (X = Cl, Br, I) and CuX (X = Cl, Br, I) tend to disproportionate.
V^{+5} as VF_5; VOX_3 (oxohalide) by hydrolysis:
$$2\,VX_5 + H_2O \rightarrow 2\,VOX_3 + 4\,HX$$
Fluorine wins the highest halides because of its small size + high lattice energy (CoF_3) and high bond enthalpy in covalent fluorides (VF_5, CrF_6).

Disproportionation

A species in an intermediate O.S. becomes **both oxidised and reduced** when one O.S. is less stable than a higher and a lower one.
$3\,Mn^{VI}O_4^{2-} + 4\,H^+ \rightarrow 2\,Mn^{VII}O_4^- + Mn^{IV}O_2 + 2H_2O$
$2\,Cu^+ \rightarrow Cu^{2+} + Cu^0$ (in aqueous solution).

5 Standard Electrode Potentials & Reactivity

$E^\circ(M^{2+}/M)$ values (3d series, V)

Ti -1.63, V -1.18, Cr -0.90, Mn -1.18, Fe -0.44,
Co -0.28, Ni -0.25, **Cu** $+0.34$, Zn -0.76.
General trend: E° becomes **less negative** from Ti → Cu, tracking the rise in $\Delta_i H_1 + \Delta_i H_2$. Mn, Ni, Zn deviate due to d^5, hydration, d^{10} stability.

Why Cu has positive E°

$E^\circ(Cu^{2+}/Cu) = +0.34$ V.
High $\Delta_a H$ + high $\Delta_i H_1 + \Delta_i H_2$ is **not offset** by hydration enthalpy of Cu^{2+}. Cu therefore does **not** liberate H_2 from dilute non-oxidising acids; only oxidising acids (HNO_3, hot conc. H_2SO_4) react with Cu.

Reactivity rule (3d series)

Metals with $E^\circ(M^{2+}/M) < 0$ **liberate H_2** from 1 M H^+.
$$2\,Cr^{2+}(aq) + 2\,H^+(aq) \rightarrow 2\,Cr^{3+}(aq) + H_2(g)$$
Ti, V, Cr^{2+} are strong reducing agents. Cu and the noble metals do not displace H_2 from dilute acids.

$E^\circ(M^{3+}/M^{2+})$ — key values

Cr^{3+}/Cr^{2+}: -0.41 V (Cr^{2+} **reducing**, $d^4 \rightarrow d^3$ stable t_{2g}^3).
Mn^{3+}/Mn^{2+}: $+1.57$ V (Mn^{3+} **oxidising**; Mn^{2+} is d^5).
Fe^{3+}/Fe^{2+}: $+0.77$ V (Fe^{3+} d^5 favoured).
Co^{3+}/Co^{2+}: $+1.97$ V (Co^{3+} very strong oxidant in water).
Compare via stability of d^5, d^{10}, or t_{2g}^3 configurations on both sides of the half-cell.

Cr^{2+} vs Mn^{3+} — same d^4, opposite behaviour

Both have d^4 but:
- Cr^{2+} **reduces** ($d^4 \rightarrow d^3$ gives the stable half-filled t_{2g}^3).
- Mn^{3+} **oxidises** ($d^4 \rightarrow d^5$ of Mn^{2+} gives the extra-stable half-filled d^5).

Decide reducing/oxidising by looking at the configuration of the product, not the starting ion.

6 Magnetic Properties — Spin-Only Formula

Spin-only magnetic moment

$\mu_s = \sqrt{n\,(n+2)}$ BM
where n = number of unpaired electrons; BM = Bohr magneton.
For first-row d-block ions, orbital contribution is **quenched**, so μ_{calc} depends only on n. Observed $\mu \approx \mu_{calc}$ within ± 0.3 BM.

Step-by-step usage

1. Find the d^n configuration of the ion.
2. Distribute electrons by Hund's rule $\rightarrow$ count unpaired n.
3. Compute $\mu = \sqrt{n(n+2)}$ BM.

e.g. $Mn^{2+}(3d^5)$: $n = 5$, $\mu = \sqrt{35} \approx 5.92$ BM.
Diamagnetic ions ($n = 0$, e.g. Sc^{3+}, Zn^{2+}): $\mu = 0$. A non-zero μ proves paramagnetism.

Magnetic moments of common $3d^n$ ions

Ion	Config	n	μ_{calc} (BM)
Sc^{3+}, Ti^{4+}, Zn^{2+}	d^0, d^0, d^{10}	0	0
Ti^{3+} / Cu^{2+}	d^1 / d^9	1	1.73
Ti^{2+} / Ni^{2+}	d^2 / d^8	2	2.84
V^{2+} / Co^{2+}	d^3 / d^7	3	3.87
Cr^{2+} / Fe^{2+}	d^4 / d^6	4	4.90
Mn^{2+} / Fe^{3+}	d^5	5	5.92

JEE/NEET Extension: When orbital contribution matters

The spin-only formula assumes L quenching, which holds for $3d$ aqua-complexes. For **4d, 5d and lanthanoid** ions (deep-lying f orbitals), use $\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}$. Lanthanoid ions often have μ much higher than spin-only because L is not quenched.

7 Coloured Ions, Catalysis, Interstitial & Alloys

Origin of colour: d–d excitation

$h\nu = \Delta_o$ (or Δ_t)
where Δ_o = crystal-field splitting in an octahedral complex.
Electron jumps from a lower-energy d-orbital to a higher one, **absorbing visible light**. Observed colour is the *complementary* colour of the absorbed wavelength. d^0 (Sc^{3+}, Ti^{4+}) and d^{10} (Zn^{2+}, Cu^{+}) are **colourless**.

Colours of aqueous $3d^n$ ions

Ion	Config	Ion	Colour (aq)
Ti^{3+} ($3d^1$) purple	Mn^{2+} ($3d^5$) pink	Co^{2+} ($3d^7$) pink	Cu^{2+} ($3d^9$) blue
V^{2+} ($3d^3$) violet	Fe^{3+} ($3d^5$) yellow	Ni^{2+} ($3d^8$) green	Sc^{3+}/Zn^{2+} none
Cr^{3+} ($3d^3$) violet	Fe^{2+} ($3d^6$) green	Cu^{+} ($3d^{10}$) none	Ti^{4+} (d^0) none

Catalytic activity

Transition metals catalyse reactions because they (a) offer a **surface for adsorption** (weakening reactant bonds), and (b) can **switch between oxidation states** to mediate electron transfer. Examples: V_2O_5 (Contact, $SO_2 \to SO_3$), Fe (Haber, N_2+H_2), Ni (hydrogenation), $TiCl_4/Al(C_2H_5)_3$ (Ziegler–Natta).

Catalysis example — Fe^{3+} catalyses $I^-/S_2O_8^{2-}$

Overall: $2I^- + S_2O_8^{2-} \to I_2 + 2SO_4^{2-}$
Step 1: $2\,Fe^{3+} + 2\,I^- \to 2\,Fe^{2+} + I_2$
Step 2: $2\,Fe^{2+} + S_2O_8^{2-} \to 2\,Fe^{3+} + 2\,SO_4^{2-}$
Fe shuttles between $+2$ and $+3$, providing a **low-energy pathway**; net Fe is unchanged $\Rightarrow$ catalysis.

Interstitial compounds

Small atoms (H, C, N, B) occupy interstitial voids in the metal lattice. Examples: TiC, Mn_4N, Fe_3H, $VH_{0.56}$, $TiH_{1.7}$. Properties: **non-stoichiometric**, very hard, high m.p., retain metallic conductivity, chemically inert.

Alloys

A solid solution of metals with metallic radii within ~15%. Transition metals form alloys readily $\Rightarrow$ **hard, high-m.p. steels** (with Cr, V, W, Mo, Mn). Brass = Cu–Zn; bronze = Cu–Sn.

8 Potassium Dichromate $K_2Cr_2O_7$

Preparation from chromite ore

Step 1 (alkaline roast in air):
$4\,FeCr_2O_4 + 8\,Na_2CO_3 + 7\,O_2 \to 8\,Na_2CrO_4 + 2\,Fe_2O_3 + 8\,CO_2$
Step 2 (acidify):
$2\,Na_2CrO_4 + 2\,H^+ \to Na_2Cr_2O_7 + 2\,Na^+ + H_2O$
Step 3 (KCl exchange):
$Na_2Cr_2O_7 + 2\,KCl \to K_2Cr_2O_7 + 2\,NaCl$
$K_2Cr_2O_7$ is less soluble than $Na_2Cr_2O_7$, so it **crystallises out** preferentially in step 3.

Chromate–dichromate interconversion

Acidic: $2\,CrO_4^{2-} + 2\,H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$
Basic: $Cr_2O_7^{2-} + 2\,OH^- \rightleftharpoons 2\,CrO_4^{2-} + H_2O$
Both species contain Cr in the same $+6$ state. **Increase pH $\Rightarrow$ yellow CrO_4^{2-}**; decrease pH $\Rightarrow$ orange $Cr_2O_7^{2-}$.

Oxidising half-reaction in acid

$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \to 2\,Cr^{3+} + 7\,H_2O$
$E^\circ = +1.33$ V.
Acidified $K_2Cr_2O_7$ is a **strong oxidant**; it accepts 6 electrons and needs 14 H^+ per dichromate ion.

Common ionic equations of $K_2Cr_2O_7$

$Cr_2O_7^{2-} + 14H^+ + 6\,I^- \to 2Cr^{3+} + 3I_2 + 7H_2O$
$Cr_2O_7^{2-} + 14H^+ + 6\,Fe^{2+} \to 2Cr^{3+} + 6Fe^{3+} + 7H_2O$
$Cr_2O_7^{2-} + 8H^+ + 3\,H_2S \to 2Cr^{3+} + 3S + 7H_2O$
$Cr_2O_7^{2-} + 14H^+ + 3\,Sn^{2+} \to 2Cr^{3+} + 3Sn^{4+} + 7H_2O$
Oxidises $I^- \to I_2$, $Fe^{2+} \to Fe^{3+}$, $S^{2-} \to S$, $Sn^{2+} \to Sn^{4+}$. Dichromate **tolerates dil. HCl** since E°

(+1.33 V) is below the Cl_2/Cl^- value.

Cu^{2+}/I^- reaction & Cu^+ disproportionation

$2\,Cu^{2+} + 4\,I^- \rightarrow Cu_2I_2(s) + I_2$
$2\,Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$
All Cu^{II} halides exist **except CuI_2**: Cu^{2+} instead oxidises I^- to I_2 and precipitates white Cu_2I_2. Cu^+ is unstable in water because the much more negative $\Delta_{hyd}H^\circ$ of Cu^{2+} more than offsets the second IE of Cu.

Structures of CrO_4^{2-} and $Cr_2O_7^{2-}$

- CrO_4^{2-}: **tetrahedral**, all four Cr–O bonds equivalent.
- $Cr_2O_7^{2-}$: two CrO_4 tetrahedra sharing **one corner O**. Terminal Cr–O = 1.63 Å, bridging = 1.79 Å; Cr–O–Cr angle = 126°.

9 Potassium Permanganate $KMnO_4$

Preparation from pyrolusite MnO_2

Step 1 (alkaline fusion with KOH + air or KNO_3):
$2\,MnO_2 + 4\,KOH + O_2 \rightarrow 2\,K_2MnO_4 + 2\,H_2O$
Step 2 (electrolytic oxidation of MnO_4^{2-}):
$MnO_4^{2-} \longrightarrow$ [anode] $MnO_4^- + e^-$
Disproportionation route (neutral / acidic):
$3\,MnO_4^{2-} + 4\,H^+ \rightarrow 2\,MnO_4^- + MnO_2 + 2\,H_2O$
Green manganate MnO_4^{2-} disproportionates in neutral/acidic medium to give the purple permanganate.

Thermal decomposition of $KMnO_4$

$2\,KMnO_4 \longrightarrow$ [513 K] $K_2MnO_4 + MnO_2 + O_2$
Used to generate a **small steady supply of O_2** in the lab. $KMnO_4$ crystals are dark purple, almost black, isostructural with $KClO_4$.

Oxidising half-reactions of MnO_4^-

Acidic: $MnO_4^- + 8H^+ + 5\,e^- \rightarrow Mn^{2+} + 4H_2O$ ($E^\circ = +1.52$ V)
Neutral / weakly alkaline: $MnO_4^- + 2H_2O + 3\,e^- \rightarrow MnO_2 + 4OH^-$ ($E^\circ = +1.69$ V)
Strongly alkaline: $MnO_4^- + e^- \rightarrow MnO_4^{2-}$ ($E^\circ = +0.56$ V)
Acidic medium is the most powerful: 5-electron change to Mn^{2+}. Alkaline medium delivers 3 e^-, giving MnO_2.

Common ionic equations of $KMnO_4$ (acidic)

$10\,I^- + 2\,MnO_4^- + 16\,H^+ \rightarrow 2\,Mn^{2+} + 8\,H_2O + 5\,I_2$
$5\,Fe^{2+} + MnO_4^- + 8\,H^+ \rightarrow Mn^{2+} + 4\,H_2O + 5\,Fe^{3+}$
$5\,C_2O_4^{2-} + 2\,MnO_4^- + 16\,H^+ \rightarrow 2\,Mn^{2+} + 8\,H_2O + 10\,CO_2$
$5\,SO_3^{2-} + 2\,MnO_4^- + 6\,H^+ \rightarrow 2\,Mn^{2+} + 3\,H_2O + 5\,SO_4^{2-}$
$5\,NO_2^- + 2\,MnO_4^- + 6\,H^+ \rightarrow 2\,Mn^{2+} + 3\,H_2O + 5\,NO_3^-$
$5\,H_2S + 2\,MnO_4^- + 6\,H^+ \rightarrow 2\,Mn^{2+} + 8\,H_2O + 5\,S$
Standard set for redox titrations. Oxalate titration is run **at 333 K** (slow at room temp.); HCl medium avoided (Cl^- oxidised). $NO_2^- \rightarrow NO_3^-$ and $SO_3^{2-}/H_2SO_3 \rightarrow SO_4^{2-}$ are both 2-electron oxidations of the S/N species.

$Mn^{2+} \rightarrow MnO_4^-$ by peroxodisulphate (lab synthesis)

$2\,Mn^{2+} + 5\,S_2O_8^{2-} + 8\,H_2O \rightarrow 2\,MnO_4^- + 10\,SO_4^{2-} + 16\,H^+$

Lab route to permanganate from a Mn(II) salt: peroxodisulphate ($S_2O_8^{2-}$) is a stronger oxidant than MnO_4^- ($E^\circ \approx +2.01$ V) and drives Mn(II) through +4, +6 right up to +7. Ag^+ traces are used as catalyst.

Permanganate in neutral / faintly alkaline

$2\,MnO_4^- + H_2O + I^- \rightarrow 2\,MnO_2 + 2\,OH^- + IO_3^-$

$8\,MnO_4^- + 3\,S_2O_3^{2-} + H_2O \rightarrow 8\,MnO_2 + 6\,SO_4^{2-} + 2\,OH^-$

$2\,MnO_4^- + 3\,Mn^{2+} + 2\,H_2O \rightarrow 5\,MnO_2 + 4\,H^+$ *(Guyard rxn)*

Brown MnO_2 is the reduced form. Used for thiosulphate, iodide-to-iodate, and $Mn^{2+} \rightarrow MnO_2$ oxidations. The Guyard reaction is catalysed by Zn^{2+} or zinc oxide.

Structures of MnO_4^- & MnO_4^{2-}

Both ions are **tetrahedral**. π-bonding via overlap of O $2p$ with Mn $3d$ orbitals.

- MnO_4^{2-} (green): **paramagnetic**, 1 unpaired electron.
- MnO_4^- (purple): **diamagnetic**, no unpaired electrons.

Never titrate $KMnO_4$ in HCl

HCl is oxidised to Cl_2 by MnO_4^-, so the titre is inflated. Use **dil. H_2SO_4** for permanganate titrations. (Dichromate titrations are fine in dil. HCl since E° is too low to oxidise Cl^-.)

10 Lanthanoids (f-Block, $4f$)

General lanthanoid configurations

Atom: [Xe] $4f^{1-14}\,5d^{0-1}\,6s^2$

Ln^{3+} (most stable): [Xe] $4f^n$ $(n = 0\text{–}14)$

Exceptions in $5d$ occupancy: La, Ce, Gd, Lu have $5d^1$.

Tripositive Ln^{3+} ions are the chemistry workhorse: stable, similar in size, mostly coloured (except $4f^0$ La^{3+} and $4f^{14}$ Lu^{3+}).

Lanthanoid contraction — size data

$r(La^{3+}) = 106$ pm $\quad r(Lu^{3+}) = 85$ pm

$r(Zr) = 160$ pm $\quad r(Hf) = 159$ pm

Cumulative effect of **poor $4f$–$4f$ shielding**. Consequence: $4d$ and $5d$ congeners (Zr/Hf, Nb/Ta, Mo/W) are **chemically very similar** and hard to separate.

Oxidation states of lanthanoids

Dominant: $+3$ for all Ln.

$+2$: Sm^{2+}, Eu^{2+}, Yb^{2+} (reducing).

$+4$: Ce^{4+} (in solution), Pr^{4+}, Nd^{4+}, Tb^{4+}, Dy^{4+} (only in oxides).

$E^\circ(Ce^{4+}/Ce^{3+}) = +1.74$ V

$+2/+4$ states are stabilised when they give f^0, f^7 or f^{14} configurations (extra empty/half/full f-shell stability).

Standard reduction potential (Ln^{3+}/Ln)

$Ln^{3+}(aq) + 3\,e^- \rightarrow Ln(s)$

$E^\circ \approx -2.2$ to -2.4 V $\quad$ (Eu: -2.0 V)

Strongly negative $\Rightarrow$ Ln metals are **very reactive**, behave like Ca. React with water to give $Ln(OH)_3$ + H_2, with halogens to give LnX_3, with acids to give H_2.

General reactions of lanthanoid metal Ln

Burn in O_2: $Ln + O_2 \rightarrow Ln_2O_3$
With H_2O: $Ln + H_2O \rightarrow Ln(OH)_3 + H_2$
With halogen X_2: $Ln + X_2 \rightarrow LnX_3$
With acid: $Ln + H^+ \rightarrow Ln^{3+} + H_2$
With N_2 (heat): $Ln \rightarrow LnN$; with S: LnS
$Ln(OH)_3$ are **definite basic** hydroxides (like alkaline-earth hydroxides), not just hydrated oxides.

Magnetism in lanthanoids

All Ln^{3+} except La^{3+} (f^0), Yb^{3+} partly, and Lu^{3+} (f^{14}) are **paramagnetic**. Unlike d-block, orbital angular momentum is **not quenched**, so the spin-only formula *underestimates* the moment. Use $\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}$ for lanthanoids.

Key lanthanoid configurations (NCERT Table 4.9)

La ($Z = 57$): [Xe] $5d^1\,6s^2 \rightarrow La^{3+}\ 4f^0$
Ce ($Z = 58$): [Xe] $4f^1\,5d^1\,6s^2 \rightarrow Ce^{3+}\ 4f^1$, $Ce^{4+}\ 4f^0$
Eu ($Z = 63$): [Xe] $4f^7\,6s^2 \rightarrow Eu^{2+}\ 4f^7$, $Eu^{3+}\ 4f^6$
Gd ($Z = 64$): [Xe] $4f^7\,5d^1\,6s^2 \rightarrow Gd^{3+}\ 4f^7$
Tb ($Z = 65$): [Xe] $4f^9\,6s^2 \rightarrow Tb^{4+}\ 4f^7$ (half-filled)
Yb ($Z = 70$): [Xe] $4f^{14}\,6s^2 \rightarrow Yb^{2+}\ 4f^{14}$
Lu ($Z = 71$): [Xe] $4f^{14}\,5d^1\,6s^2 \rightarrow Lu^{3+}\ 4f^{14}$
$5d^1$ **exceptions:** La, Ce, Gd, Lu (empty/half/full f pushes one d electron).

Ionisation enthalpies of lanthanoids

$\Delta_i H_1$ (Ln) ≈ 600 kJ mol^{-1}
$\Delta_i H_2$ (Ln) ≈ 1200 kJ mol^{-1} (*compare Ca: 1145*)
$\Delta_i H_3$ (Ln): **anomalously low** for La, Gd, Lu (gives f^0, f^7, f^{14}).
Hence $+2$ chemistry of Eu (after losing 2 s-electrons leaves $4f^7$) and $+4$ chemistry of Ce/Tb (gives $4f^0$/$4f^7$). Empty, half-, fully-filled f rule.

Mischmetall & uses

Mischmetall = ~ 95% lanthanoid metal + ~ 5% Fe + traces of S, C, Ca, Al. Used in Mg-based alloys for **bullets, shells, lighter flints**; lanthanoid oxides catalyse petroleum cracking and serve as TV phosphors.

11 Actinoids (f-Block, 5f)

General actinoid configurations

Atom: [Rn] $5f^{1-14}\,6d^{0-1}\,7s^2$
e.g. Th: $6d^2\,7s^2$; U: $5f^3\,6d^1\,7s^2$; Am: $5f^7\,7s^2$.
5f, 6d and 7s are close in energy $\Rightarrow$ many electronic configurations are possible. All actinoids are **radioactive**.

Oxidation states of actinoids

Dominant: $+3$ throughout the series.
Early actinoids show much higher states:
Th: $+4$; Pa: $+4, +5$; U: $+3, +4, +5, +6$;
Np: $+3$ to $+7$; Pu: $+3$ to $+7$; Am: $+3$ to $+6$.
Wider range than lanthanoids because 5f electrons are **less buried** and can participate in bonding.
$+3$ becomes the only common state from Bk onwards.

Actinoid contraction

Gradual decrease in size of An and An^{3+} across Ac $\rightarrow$ Lr.
$r(Ac^{3+}) = 111$ pm $\rightarrow r(Cf^{3+}) \approx 98$ pm.
Larger element-to-element decrease than in lanthanoid contraction because $5f$ electrons shield each other even more poorly than $4f$ electrons do.

Why $5f$ behave differently from $4f$

$5f$ orbitals **penetrate less** into the core than $4f$, so $5f$ electrons are *available for bonding* to a far greater extent. This explains: (a) wider range of oxidation states, (b) greater actinoid contraction, (c) more covalent character in actinoid complexes.

Key actinoid configurations (NCERT Table 4.10)

Ac ($Z = 89$): [Rn] $6d^1\,7s^2$; Th: [Rn] $6d^2\,7s^2$ (**no** $5f$).
U ($Z = 92$): [Rn] $5f^3\,6d^1\,7s^2$; Am: [Rn] $5f^7\,7s^2$; Cm: [Rn] $5f^7\,6d^1\,7s^2$; Lr: [Rn] $5f^{14}\,6d^1\,7s^2$.
Th has no $5f$ electron in ground state; $5f^7$ appears at Am (half-filled stability). $6d^1$ also at Cm and Lr.

Lanthanoids vs Actinoids — comparison

Feature	Lanthanoids ($4f$)	Actinoids ($5f$)
General config	[Xe] $4f^{1-14}\,5d^{0-1}\,6s^2$	[Rn] $5f^{1-14}\,6d^{0-1}\,7s^2$
Common O.S.	Mostly $+3$ (rare $+2$, $+4$)	$+3$ *plus* $+4, +5, +6, +7$ (early)
Radii contraction	Regular, smaller per element	Larger per element
Bonding	Largely ionic; basic	More covalent; complex chemistry
Magnetism	μ from spin + orbital; not quenched	Similar but harder to predict
Radioactivity	Only Pm radioactive	**All** actinoids radioactive

Inner transition $\neq$ "next to" transition

Inner transition elements have *atomic numbers* 58–71 (lanthanoids) and 90–103 (actinoids). $Z = 29$ (Cu) is d-block; $Z = 104$ (Rf) is d-block; $Z = 102$ (No) is f-block. Always check whether f orbitals are being filled.

12 Applications of d- and f-Block Elements

Catalysts & industrial materials

Catalysts: V_2O_5 (Contact, $SO_2 \rightarrow SO_3$); Fe (Haber, N_2+H_2); Ni (hydrogenation of oils); $TiCl_4/Al(C_2H_5)_3$ (Ziegler–Natta, polyethene); $PdCl_2$ (Wacker, ethyne$\rightarrow$ethanal); Cu/Cu(I) (coupling, organic synthesis).

Industrial materials: Steels = Fe + C alloyed with Cr, Mn, V, W, Mo, Ni; TiO (pigments); MnO_2 (dry-cell cathode); Zn and Ni–Cd (batteries); AgBr (photographic emulsions); Mischmetall (bullets, lighter flints); Th, Pa, U (nuclear fuels).

Quick Reference — Class 12 Chemistry Chapter 4

The d- and f-Block Elements

Quantity / Concept	Formula / Key Fact
General outer config (d-block)	$(n-1)d^{1-10}\,ns^{1-2}$ (Pd: $4d^{10}5s^{0}$)
Anomalous $3d$ configs	Cr: $3d^{5}4s^{1}$; Cu: $3d^{10}4s^{1}$
Spin-only magnetic moment	$\mu = \sqrt{n(n+2)}$ BM
μ for Mn^{2+} ($3d^5$)	$\sqrt{35} \approx 5.92$ BM
Highest O.S. achieved with	O^{2-} or F^{-} (e.g. Mn_2O_7, CrF_6)
Cu^{2+}/Cu standard E°	$+0.34$ V (unique +ve in $3d$)
$Cr_2O_7^{2-}$ half-reaction (acid)	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ ($+1.33$ V)
MnO_4^- half-reaction (acid)	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ ($+1.52$ V)
MnO_4^- half-reaction (alkaline)	$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$ ($+1.69$ V)
Chromate $\leftrightarrow$ dichromate	$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$
Disproportionation of Cu^+	$2Cu^+ \rightarrow Cu^{2+} + Cu$
Disproportionation of MnO_4^{2-}	$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$
Lanthanoid general config	$[Xe]\,4f^{1-14}\,5d^{0-1}\,6s^2$; Ln^{3+}: $4f^n$
Actinoid general config	$[Rn]\,5f^{1-14}\,6d^{0-1}\,7s^2$
Lanthanoid contraction	$r(Ln^{3+})$ falls $106 \rightarrow 85$ pm; Zr $=$ Hf $= 159$–160 pm
$E^\circ(Ln^{3+}/Ln)$	~ -2.2 to -2.4 V (Eu: -2.0 V)
$E^\circ(Ce^{4+}/Ce^{3+})$	$+1.74$ V
Stable Ln^{2+} ions	Sm^{2+}, Eu^{2+}, Yb^{2+}
Stable Ln^{4+} ions	Ce^{4+} (solution); Pr, Nd, Tb, Dy (oxides only)
d^0 / d^{10} colourless ions	Sc^{3+}, Ti^{4+}, Zn^{2+}, Cu^+
Highest melting point in d-block	W ($\sim$ 3680 K), $5d$ series, $\sim d^5$ filling
Mischmetall composition	$\sim$95% Ln + $\sim$5% Fe + traces of S, C, Ca, Al
Cu^{2+} vs I^- (unique)	$2Cu^{2+} + 4I^- \rightarrow Cu_2I_2 + I_2$ (no CuI_2)
Cu^+ disproportionation	$2Cu^+ \rightarrow Cu^{2+} + Cu$ (in water)
$Mn^{2+} \rightarrow MnO_4^-$ (lab)	$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$
Mn_2O_7 hydrolysis	$Mn_2O_7 + H_2O \rightarrow 2HMnO_4$
Oxocations (Ti, V)	TiO^{2+}, VO^{2+} ($+4$); VO_2^+ ($+5$)
$5d^1$ Ln (no $4f$ electron initially)	La, Ce, Gd, Lu
$\Delta_i H_1$ (Ln) typical	~ 600 kJ mol^{-1}; $\Delta_i H_2 \sim 1200$
Highest Mn fluoride vs oxide	MnF_4 ($+4$) vs Mn_2O_7 ($+7$); MnO_3F is sole Mn(VII) halide-oxide

End of Formula Sheet — Class 12 Chemistry Chapter 4: The d- and f-Block Elements (NCERT 2026-27).