

Collegedunia NCERT Formula Sheet

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
<i>d</i> -block groups	Groups 3–12	3 <i>d</i> , 4 <i>d</i> , 5 <i>d</i> , 6 <i>d</i> series
General outer config (<i>d</i> -block)	$(n - 1)d^{1-10} ns^{1-2}$	Pd is exception: $4d^{10}5s^0$
General config (lanthanoids)	$[Xe] 4f^{1-14} 5d^{0-1} 6s^2$	most stable Ln^{3+} : $4f^n$
General config (actinoids)	$[Rn] 5f^{1-14} 6d^{0-1} 7s^2$	5 <i>f</i> less buried than 4 <i>f</i>
Bohr magneton (BM)	μ_B	$9.274 \times 10^{-24} \text{ J T}^{-1}$
μ for 1 unpaired electron	$\mu = \sqrt{n(n + 2)}$	1.73 BM
$E^\circ \text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ (acidic)	—	+1.33 V
$E^\circ \text{MnO}_4^-/\text{Mn}^{2+}$ (acidic)	—	+1.52 V
$E^\circ \text{Ce}^{4+}/\text{Ce}^{3+}$	—	+1.74 V (strong oxidant)
$E^\circ \text{Cu}^{2+}/\text{Cu}$ (unique +ve)	—	+0.34 V (only +ve in 3 <i>d</i>)
$E^\circ \text{Ln}^{3+}/\text{Ln}$ (typical)	—	–2.2 to –2.4 V (Eu: –2.0)

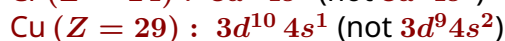
1 Position & Electronic Configurations

General outer configuration (*d*-block)



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

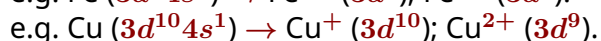
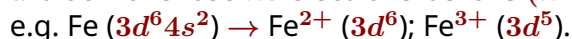
Special stability exceptions in 3*d*



Half-filled (d^5) and fully filled (d^{10}) sets gain **extra exchange-energy stability**. One 4*s* electron promotes to 3*d* because the energy gap is small.

Configurations of *d*-block cations

d-block ions lose ns electrons **before** $(n - 1)d$.



Most M^{2+} ions of 3*d* have configuration $3d^n$ with **no 4*s* 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: $5d > 4d > 3d$ (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 4*f* electron by another** as nuclear charge rises across the series. Its main consequence: 4*d* and 5*d* 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 3*d* 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+}

$\Delta_i H_2(Mn) < \Delta_i H_2(Cr)$ (Cr^{+} : d^5 stable).

$\Delta_i H_3(Fe) < \Delta_i H_3(Mn)$ (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 $M_{(\text{aq})}^{2+}$, 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 ($d^5 \rightarrow d^4$) and Cu ($d^{10} \rightarrow d^9$), making Cr^{2+} and Cu^{2+} chemistry distinctive.

Ionisation enthalpy data — key 3*d* 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 $\Delta_i H_3$ ($d^6 \rightarrow d^5$)
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 3*d* 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 O^{2-} or F^- .

e.g. $Mn^{VII}O_7$, 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 3*d* 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 3*d* 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.

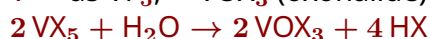
Halides of 3d metals — highest known states

TiX₄ (X = F→I), VF₅, CrF₆, CrF₅

Mn: max halide is **MnF₄** (+4); Fe: max trihalide is **FeX₃**; Co: **CoF₃** only.

Low-O.S. instability: VX₂ (X = Cl, Br, I) and CuX (X = Cl, Br, I) tend to disproportionate.

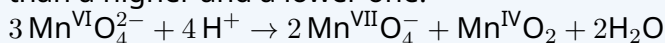
V⁺⁵ as VF₅; VOX₃ (oxohalide) by hydrolysis:



Fluorine wins the highest halides because of its small size + high lattice energy (CoF₃) and high bond enthalpy in covalent fluorides (VF₅, CrF₆).

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.

**5 Standard Electrode Potentials & Reactivity*****E*^o(M²⁺/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*^o becomes **less negative** from Ti → Cu, tracking the rise in Δ_iH₁ + Δ_iH₂. Mn, Ni, Zn deviate due to *d*⁵, hydration, *d*¹⁰ stability.

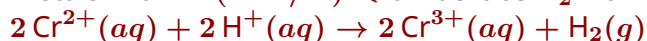
Why Cu has positive *E*^o

E^o(Cu²⁺/Cu) = **+0.34 V**.

High Δ_aH + high Δ_iH₁ + Δ_iH₂ is **not offset** by hydration enthalpy of Cu²⁺. Cu therefore does **not** liberate H₂ from dilute non-oxidising acids; only oxidising acids (HNO₃, hot conc. H₂SO₄) react with Cu.

Reactivity rule (3d series)

Metals with *E*^o(M²⁺/M) < 0 **liberate H₂** from 1 M H⁺.



Ti, V, Cr²⁺ are strong reducing agents. Cu and the noble metals do not displace H₂ from dilute acids.

***E*^o(M³⁺/M²⁺) — key values**

Cr³⁺/Cr²⁺: **-0.41 V** (Cr²⁺ **reducing**, *d*⁴ → *d*³ stable *t*_{2g}³).

Mn³⁺/Mn²⁺: **+1.57 V** (Mn³⁺ **oxidising**; Mn²⁺ is *d*⁵).

Fe³⁺/Fe²⁺: **+0.77 V** (Fe³⁺ *d*⁵ favoured).

Co³⁺/Co²⁺: **+1.97 V** (Co³⁺ 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.

Cr²⁺ vs Mn³⁺ — same *d*⁴, opposite behaviour

Both have *d*⁴ but:

- Cr²⁺ **reduces** (*d*⁴ → *d*³ gives the stable half-filled *t*_{2g}³).

- Mn³⁺ **oxidises** (*d*⁴ → *d*⁵ of Mn²⁺ 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

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

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 $\mu \approx \mu_{\text{calc}}$ 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. $\text{Mn}^{2+}(3d^5)$: $n = 5$, $\mu = \sqrt{35} \approx 5.92$ 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

$$h\nu = \Delta_o \text{ (or } \Delta_t)$$

where Δ_o = crystal-field splitting in an octahedral complex.

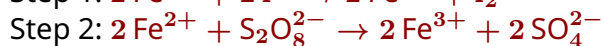
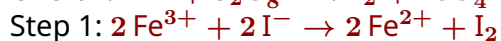
Electron jumps from a lower-energy d -orbital to a higher one, **absorbing visible light**. Observed colour is the *complementary* colour of the absorbed wavelength. d^0 (Sc^{3+} , Ti^{4+}) and d^{10} (Zn^{2+} , Cu^+) are **colourless**.

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	$\text{Sc}^{3+}/\text{Zn}^{2+}$ 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, $SO_2 \rightarrow SO_3$), Fe (Haber, $N_2 + H_2$), Ni (hydrogenation), $TiCl_4/Al(C_2H_5)_3$ (Ziegler-Natta).

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

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 $\sim 15\%$. 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**

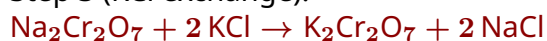
Step 1 (alkaline roast in air):



Step 2 (acidify):



Step 3 (KCl exchange):



$K_2Cr_2O_7$ is less soluble than $Na_2Cr_2O_7$, so it **crystallises out** preferentially in step 3.

Chromate-dichromate interconversion

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

$$E^\circ = +1.33 \text{ V}$$

Acidified $K_2Cr_2O_7$ is a **strong oxidant**; it accepts 6 electrons and needs 14 H^+ per dichromate ion.

Common ionic equations of $K_2Cr_2O_7$ 

Oxidises $I^- \rightarrow I_2$, $Fe^{2+} \rightarrow Fe^{3+}$, $S^{2-} \rightarrow S$, $Sn^{2+} \rightarrow Sn^{4+}$. Dichromate **tolerates dil. HCl** since E°

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

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



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 $\Delta_{\text{hyd}}H^\circ$ of Cu^{2+} more than offsets the second IE of Cu.

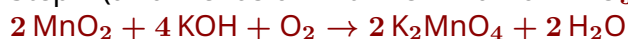
Structures of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$

- CrO_4^{2-} : **tetrahedral**, all four Cr–O bonds equivalent.
- $\text{Cr}_2\text{O}_7^{2-}$: 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):



Step 2 (electrolytic oxidation of MnO_4^{2-}):



Disproportionation route (neutral / acidic):



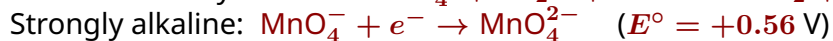
Green manganate MnO_4^{2-} disproportionates in neutral/acidic medium to give the purple permanganate.

Thermal decomposition of KMnO_4



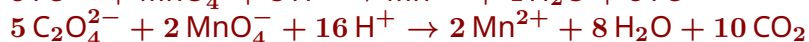
Used to generate a **small steady supply of O_2** in the lab. KMnO_4 crystals are dark purple, almost black, isostructural with KClO_4 .

Oxidising half-reactions of MnO_4^-



Acidic medium is the most powerful: 5-electron change to Mn^{2+} . Alkaline medium delivers 3 e^- , giving MnO_2 .

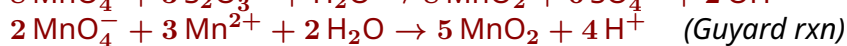
Common ionic equations of KMnO_4 (acidic)



Standard set for redox titrations. Oxalate titration is run **at 333 K** (slow at room temp.); HCl medium avoided (Cl^- oxidised). $\text{NO}_2^- \rightarrow \text{NO}_3^-$ and $\text{SO}_3^{2-}/\text{H}_2\text{SO}_3 \rightarrow \text{SO}_4^{2-}$ are both 2-electron oxidations of the S/N species.

Mn²⁺ → MnO₄⁻ by peroxodisulphate (lab synthesis)

Lab route to permanganate from a Mn(II) salt: peroxodisulphate (S₂O₈²⁻) is a stronger oxidant than MnO₄⁻ (*E*^o ≈ +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

Brown MnO₂ is the reduced form. Used for thiosulphate, iodide-to-iodate, and Mn²⁺ → MnO₂ oxidations. The Guyard reaction is catalysed by Zn²⁺ or zinc oxide.

Structures of MnO₄⁻ & MnO₄²⁻

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

- MnO₄²⁻ (green): **paramagnetic**, 1 unpaired electron.
- MnO₄⁻ (purple): **diamagnetic**, no unpaired electrons.

Never titrate KMnO₄ in HCl

HCl is oxidised to Cl₂ by MnO₄⁻, so the titre is inflated. Use **dil. H₂SO₄** for permanganate titrations. (Dichromate titrations are fine in dil. HCl since *E*^o is too low to oxidise Cl⁻.)

10 Lanthanoids (*f*-Block, 4*f*)**General lanthanoid configurations**

Atom: [Xe] 4*f*¹⁻¹⁴ 5*d*⁰⁻¹ 6*s*²

Ln³⁺ (most stable): [Xe] 4*f*^{*n*} (*n* = 0-14)

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

Tripositive Ln³⁺ ions are the chemistry workhorse: stable, similar in size, mostly coloured (except 4*f*⁰ La³⁺ and 4*f*¹⁴ Lu³⁺).

Lanthanoid contraction — size data

r(La³⁺) = 106 pm *r*(Lu³⁺) = 85 pm

r(Zr) = 160 pm *r*(Hf) = 159 pm

Cumulative effect of **poor 4*f*-4*f* shielding**. Consequence: 4*d* and 5*d* 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: Sm²⁺, Eu²⁺, Yb²⁺ (reducing).

+4: Ce⁴⁺ (in solution), Pr⁴⁺, Nd⁴⁺, Tb⁴⁺, Dy⁴⁺ (only in oxides).

E^o(Ce⁴⁺/Ce³⁺) = +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 (Ln³⁺/Ln)

Ln³⁺(aq) + 3 e⁻ → Ln(s)

E^o ≈ -2.2 to -2.4 V (Eu: -2.0 V)

Strongly negative ⇒ Ln metals are **very reactive**, behave like Ca. React with water to give Ln(OH)₃ + H₂, with halogens to give LnX₃, with acids to give H₂.

General reactions of lanthanoid metal LnBurn in O₂: $\text{Ln} + \text{O}_2 \rightarrow \text{Ln}_2\text{O}_3$ With H₂O: $\text{Ln} + \text{H}_2\text{O} \rightarrow \text{Ln}(\text{OH})_3 + \text{H}_2$ With halogen X₂: $\text{Ln} + \text{X}_2 \rightarrow \text{LnX}_3$ With acid: $\text{Ln} + \text{H}^+ \rightarrow \text{Ln}^{3+} + \text{H}_2$ With N₂ (heat): $\text{Ln} \rightarrow \text{LnN}$; with S: LnSLn(OH)₃ are **definite basic** hydroxides (like alkaline-earth hydroxides), not just hydrated oxides.**Magnetism in lanthanoids**

All Ln³⁺ except La³⁺ (*f*⁰), Yb³⁺ partly, and Lu³⁺ (*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): $[\text{Xe}] 5d^1 6s^2 \rightarrow \text{La}^{3+} 4f^0$ Ce (*Z* = 58): $[\text{Xe}] 4f^1 5d^1 6s^2 \rightarrow \text{Ce}^{3+} 4f^1, \text{Ce}^{4+} 4f^0$ Eu (*Z* = 63): $[\text{Xe}] 4f^7 6s^2 \rightarrow \text{Eu}^{2+} 4f^7, \text{Eu}^{3+} 4f^6$ Gd (*Z* = 64): $[\text{Xe}] 4f^7 5d^1 6s^2 \rightarrow \text{Gd}^{3+} 4f^7$ Tb (*Z* = 65): $[\text{Xe}] 4f^9 6s^2 \rightarrow \text{Tb}^{4+} 4f^7$ (half-filled)Yb (*Z* = 70): $[\text{Xe}] 4f^{14} 6s^2 \rightarrow \text{Yb}^{2+} 4f^{14}$ Lu (*Z* = 71): $[\text{Xe}] 4f^{14} 5d^1 6s^2 \rightarrow \text{Lu}^{3+} 4f^{14}$ **5*d*¹ exceptions:** La, Ce, Gd, Lu (empty/half/full *f* pushes one *d* electron).**Ionisation enthalpies of lanthanoids** $\Delta_i H_1$ (Ln) \approx 600 kJ mol⁻¹ $\Delta_i H_2$ (Ln) \approx 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 4*f*⁷) and +4 chemistry of Ce/Tb (gives 4*f*⁰/4*f*⁷). Empty, half-, fully-filled *f* rule.**Mischmetall & uses**

Mischmetall = \sim 95% lanthanoid metal + \sim 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, 5*f*)**General actinoid configurations**Atom: $[\text{Rn}] 5f^{1-14} 6d^{0-1} 7s^2$ e.g. Th: $6d^2 7s^2$; U: $5f^3 6d^1 7s^2$; Am: $5f^7 7s^2$.5*f*, 6*d* and 7*s* 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 5*f* 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.

$$r(\text{Ac}^{3+}) = 111 \text{ pm} \rightarrow r(\text{Cf}^{3+}) \approx 98 \text{ pm}.$$

Larger element-to-element decrease than in lanthanoid contraction because 5*f* electrons shield each other even more poorly than 4*f* electrons do.

Why 5*f* behave differently from 4*f*

5*f* orbitals **penetrate less** into the core than 4*f*, so 5*f* 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 ($Z = 89$): $[\text{Rn}] 6d^1 7s^2$; Th: $[\text{Rn}] 6d^2 7s^2$ (**no 5*f***).

U ($Z = 92$): $[\text{Rn}] 5f^3 6d^1 7s^2$; Am: $[\text{Rn}] 5f^7 7s^2$; Cm: $[\text{Rn}] 5f^7 6d^1 7s^2$; Lr: $[\text{Rn}] 5f^{14} 6d^1 7s^2$.

Th has no 5*f* electron in ground state; 5*f*⁷ appears at Am (half-filled stability). 6*d*¹ also at Cm and Lr.

Lanthanoids vs Actinoids — comparison

Feature	Lanthanoids (4 <i>f</i>)	Actinoids (5 <i>f</i>)
General config	$[\text{Xe}] 4f^{1-14} 5d^{0-1} 6s^2$	$[\text{Rn}] 5f^{1-14} 6d^{0-1} 7s^2$
Common O.S.	Mostly +3 (rare +2, +4)	+3 <i>plus</i> +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, $\text{SO}_2 \rightarrow \text{SO}_3$); Fe (Haber, $\text{N}_2 + \text{H}_2$); Ni (hydrogenation of oils); $\text{TiCl}_4/\text{Al}(\text{C}_2\text{H}_5)_3$ (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 (<i>d</i> -block)	$(n - 1)d^{1-10} ns^{1-2}$ (Pd: $4d^{10}5s^0$)
Anomalous 3 <i>d</i> configs	Cr: $3d^54s^1$; 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 3 <i>d</i>)
$Cr_2O_7^{2-}$ 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 <i>d</i> -block	W (~ 3680 K), 5 <i>d</i> 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)
5 <i>d</i> ¹ Ln (no 4 <i>f</i> 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