Collegedunia NCERT Notes

The Ultimate NCERT Revision Guide for Class 12 Chemistry

Chapter 4: The d- and f-Block Elements

NCERT 2026-27 / New NCERT, Class 12th Chemistry (Part 1)

What this chapter is about

The d-block consists of Groups 3–12, where $(n-1)d$ orbitals are progressively filled across four long periods (3d, 4d, 5d, 6d). The f-block sits outside the main table: lanthanoids (4f) and actinoids (5f). Because partially filled d and f orbitals are energetically close to the outer s orbital, transition elements show *variable oxidation states*, *coloured ions*, *paramagnetism*, *complex formation*, *catalytic activity*, and form *interstitial compounds* and *alloys*. The chapter then drills into two flagship oxoanions, $K_2Cr_2O_7$ and $KMnO_4$, and closes with the lanthanoids/actinoids and their applications.

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Quick Tip

Chapter 4 typically carries 6–8 marks on CBSE boards (one 3-mark trends question + one 5-mark preparation/oxidation reaction). For JEE/NEET, the most prolific testable items are: spin-only magnetic moment, lanthanoid contraction, oxidising power of E° couples, and the preparation/oxidation reactions of $KMnO_4$ and $K_2Cr_2O_7$. Master those first.

Also see for this chapter

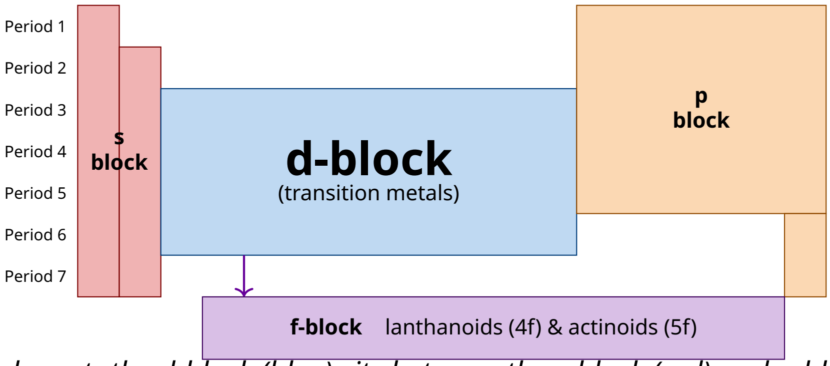
Step-by-step worked answers: NCERT Solutions for Class 12 Chemistry Chapter 4 The d- and f-Block Elements.
One-page revision: The d- and f-Block Elements Formula Sheet.
Tougher problems: NCERT Exemplar Solutions for The d- and f-Block Elements.

1 Position in the Periodic Table

The d-block occupies the large middle section of the periodic table, flanked by the s-block on the left and the p-block on the right. Four horizontal rows of transition metals are recognised:

- **3d series** (Sc to Zn), the only series CBSE expects you to know in detail.
- **4d series** (Y to Cd).
- **5d series** (La, Hf to Hg), skips the lanthanoids, which sit beneath.
- **6d series** (Ac, Rf to Cn), mostly synthetic and radioactive.

The two inner-transition (f-block) series are placed in a separate panel at the bottom: **4f lanthanoids** (Ce to Lu) and **5f actinoids** (Th to Lr).



Periodic-table layout: the d-block (blue) sits between the s-block (red) and p-block (orange); f-block (purple) is placed separately at the bottom.

1.1 IUPAC Definition of a Transition Element

Definition

A **transition element** is a metal that has an *incompletely filled d-subshell* either in the neutral atom or in any of its commonly occurring oxidation states.

Group 12 metals (Zn, Cd, Hg, Cn) have a full d^{10} configuration in both the ground state *and* in their stable +2 ion. Strictly, they are *not* transition elements, but since they sit at the right edge of the 3d, 4d, 5d and 6d series, their chemistry is taught alongside the transition metals.

Common Mistake

Don't say "zinc has no d electrons, that's why it isn't a transition metal". Zn^{2+} has ten d electrons. The point is that they are *all paired and the subshell is full*, leaving no vacancy to use in bonding or to produce d–d transitions.

2 Electronic Configurations of the d-Block Elements

The outer-orbital configuration of d-block elements is

General d-block configuration

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

with two well-known exceptions in the 3d series caused by the extra stability of half-filled and fully filled d-subshells:

$$\text{Cr}:\ [Ar]\,3d^5\,4s^1 \qquad \text{Cu}:\ [Ar]\,3d^{10}\,4s^1$$

The $(n-1)d$ and ns orbitals lie very close in energy, so small gains in exchange energy can flip an electron from the s to the d shell. Half-filled (d^5) and fully-filled (d^{10}) subshells maximise the number of parallel-spin electron pairs, which maximises exchange-energy stabilisation.

Memory Aid, Cr and Cu exceptions

"**Cr**azy **Cu**stomers want **half** or **full** d." Chromium and Copper both *borrow* one s electron to populate d^5 (half-filled) or d^{10} (fully-filled). All other 3d elements stick to the textbook $4s^2$.

Cr and Cu "borrow" one 4s electron into 3d to gain a half- or fully-filled subshell.

2.1 Configurations of the 3d Series at a Glance

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30
$3d$	1	2	3	5	5	6	7	8	10	10
$4s$	2	2	2	1	2	2	2	2	1	2

Quick Tip

When a transition metal forms an **ion**, the ns electrons leave *first*, not the $(n-1)d$ electrons. So Fe^{2+} is $[Ar]\,3d^6$ (not $3d^4\,4s^2$), and Fe^{3+} is $[Ar]\,3d^5$. This single rule fixes most "write the electronic configuration of …" questions.

2.2 Why the Exceptions Don't Repeat in 4d/5d

In heavier series the $4d$–$5s$ and $5d$–$6s$ gaps are larger, so more configurations stabilise by promoting electrons *into* d. That is why the 4d series has *several* "exceptions” (Nb, Mo, Ru, Rh, Pd, Ag) compared to two in the 3d row, and Pd uniquely shows $4d^{10}\,5s^{0}$.

3 General Properties of the Transition Elements (3d row)

3.1 Physical Properties: Metallic Strength, Hardness, Density

Nearly all 3d metals exhibit the classic metallic profile: *high tensile strength, ductility, malleability, lustre, high thermal and electrical conductivity*. The exceptions are Zn, Cd, Hg and Mn, which depart from a regular metallic close-packed structure (mercury is liquid at room temperature; manganese has a complex distorted cubic lattice).

Why are the M.P. and B.P. so high?

The melting point of a metal is set by the strength of its interatomic metallic bond. In transition metals, both the ns electrons *and* a variable number of $(n-1)d$ electrons participate in the bonding sea. More unpaired d-electrons $\Rightarrow$ stronger covalent overlap between adjacent atom cores $\Rightarrow$ higher m.p. and enthalpy of atomisation.

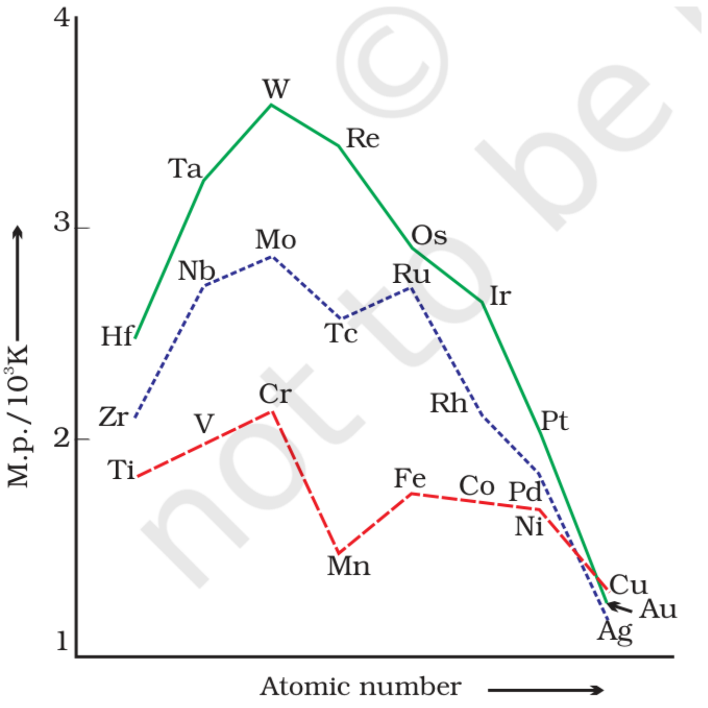


Fig. 4.1: Trends in melting points of transition elements

Source: NCERT Class 12 Chemistry Part I, Chapter 4. Fig. 4.1, Trends in melting points of the 3d, 4d and 5d transition metals.

Three patterns are visible in Fig. 4.1:

1. In any row, melting points *rise to a maximum near the middle* (W in 5d, Mo in 4d, around Cr/V in 3d) where the d^5 configuration delivers the maximum number of unpaired electrons.
2. Mn and Tc are anomalously low, their stable half-filled d^5 *atomic* configuration paradoxically *weakens* the metallic bonding because the bonding electrons are reluctant to delocalise out of the half-filled subshell.
3. The 5d series has the highest melting points overall (tungsten at 3683 K), the 3d series the lowest. More electrons available for bonding ⇒ stronger bonds.

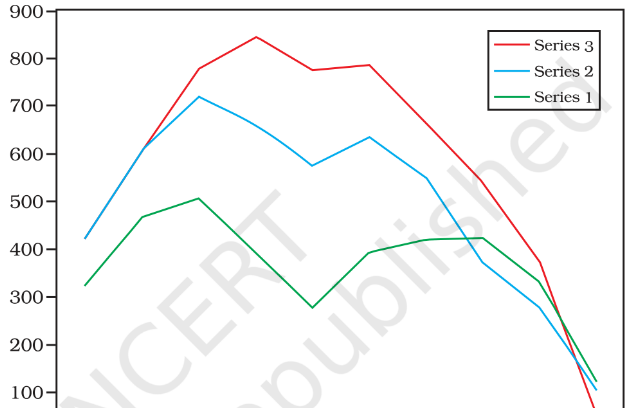


Fig. 4.2
Trends in enthalpies of atomisation of transition elements

Source: NCERT Class 12 Chemistry Part I, Chapter 4. Fig. 4.2, Trends in enthalpies of atomisation $\Delta_a H^\ominus$.

The same picture emerges for enthalpy of atomisation: a maximum near the middle of each series. Metals with *very high* $\Delta_a H^\ominus$ tend to be "noble", a lot of energy must be invested even to vaporise them into atoms, let alone to oxidise them. The 2nd and 3rd transition series also have larger atomisation enthalpies than the 1st, which is why heavy-metal–metal bonds (such as in $Re_2Cl_8{}^{2-}$) are far more common than 3d–3d metal–metal bonds.

Real-World Application

This is why tungsten is the filament metal of choice in old incandescent bulbs and in the cathodes of vacuum tubes: its melting point of 3683 K and very high enthalpy of atomisation mean it tolerates orange-hot operation without subliming away.

3.2 Atomic and Ionic Sizes

Within a series, atomic and ionic radii *decrease slowly* from left to right. As Z increases by one, an electron enters the inner $(n-1)d$ subshell, which only weakly shields the outer ns electrons from the rising nuclear charge.

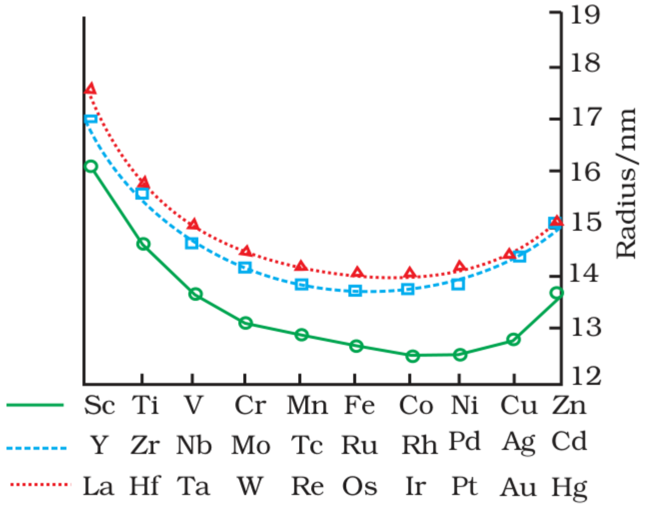


Fig. 4.3: *Trends in atomic radii of transition elements*

Source: NCERT Class 12 Chemistry Part I, Chapter 4. Fig. 4.3, Atomic radii of 3d, 4d and 5d series. Note how the 5d radii lie virtually on top of the 4d radii.

The really striking observation is the *vertical* trend: 3d → 4d radii increase as expected, but 4d → 5d radii *barely change* (e.g. Zr: 160 pm, Hf: 159 pm). This is the famous **lanthanoid contraction**.

Lanthanoid contraction

A regular decrease in atomic and ionic radii from La to Lu caused by the filling of the 4f subshell.

Reason: 4f electrons shield one another *very poorly*. Across the lanthanoid series, Z_{eff} on the 6s electrons increases steadily, pulling the whole atom inward.

Net result: by the time the 5d series begins (after the lanthanoids), 14 f-electron additions have "eaten" the expected vertical size increase.

Three consequences of lanthanoid contraction

1. Zr/Hf, Nb/Ta and Mo/W have nearly identical sizes and very similar chemistry, they are extremely hard to separate (Zr and Hf are famously cohabit in zircon ore).
2. The 2nd and 3rd transition series have similar densities, ionisation enthalpies, and reactivities (but the 1st series differs sharply).
3. The basicity of Ln^{3+} hydroxides decreases from $La(OH)_3$ (most basic) to $Lu(OH)_3$ (least basic), because cation polarising power rises as cation size falls.

Densities increase across the 3d series (Sc: 3.4 to Cu: 8.9 g/cm^3), driven by the combination of decreasing metallic radius and increasing atomic mass.

3.3 Ionisation Enthalpies

Ionisation enthalpy generally *increases* along a 3d series with increasing nuclear charge, but the rise is gentle compared with main-group elements, because added d-electrons partially shield the outer $4s$ electrons.

Three components of an ionisation enthalpy

$$\begin{aligned}\Delta_i H = &(\text{attraction to nucleus})\\ &-(\text{inter-electron repulsion})\\ &-(\text{exchange energy lost})\end{aligned}$$

Exchange energy is the dominant "stability bonus" for half-filled and fully filled configurations. Removing an electron from d^5 or d^{10} requires *additional* energy to break this stabilisation.

That is why:

- $\Delta_i H_1$ of Cr (4s^1, easy to remove) is slightly low, but $\Delta_i H_2$ is unusually *high* (removes from d^5).
- $\Delta_i H_1$ of Cu is high (removing from $d^{10}4s^1$ destroys the d^{10} shell only on second ionisation; first ionisation removes $4s^1$).
- $\Delta_i H_3(\text{Fe}) < \Delta_i H_3(\text{Mn})$ because the third ionisation of Fe converts $d^6 \to d^5$ (gaining half-filled stability), whereas Mn's third ionisation *breaks* the d^5 shell.

Numerical handle

The second ionisation enthalpies of Cr and Cu are unusually high *because* their +1 ions hold d^5 and d^{10} configurations respectively. This single fact explains both their high $\Delta_i H_2$ and the unique E° behaviour of copper.

3.4 Oxidation States, the Defining Feature

Transition elements show a remarkable variety of oxidation states. Three rules sum up the trends:

1. Oxidation states differ from one another by *1*, not 2 (e.g. V shows +2, +3, +4, +5). This is unlike p-block elements, where the inert-pair effect produces ± 2 jumps.
2. The *maximum* oxidation state in the early-to-mid 3d series equals the sum of $s + d$ valence electrons: Sc(+3), Ti(+4), V(+5), Cr(+6), Mn(+7).
3. After Mn, the maximum drops sharply: too many d electrons make it hard to share or lose them all. Fe reaches +6 only with difficulty; Cu barely manages

+2; Zn is exclusively +2.

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Maximum	+3	+4	+5	+6	+7	+6	+4	+4	+2	+2
Most stable	+3	+4	+4	+3	+2	+3	+2	+2	+2	+2

Memory Aid, highest OS of 3d series

“Sc Ti V Cr Mn Fe ...” $\rightarrow$ **“3 4 5 6 7 6 ...”**. The maximum rises by one each step from Sc to Mn (which is $d^5\,s^2$, all 7 outer electrons), then *decreases* from Fe onwards as d-electron pairs lock up.

Down-group trend in d-block oxidation states

Heavier d-block elements favour the *higher* oxidation state. Cr(VI) (in $Cr_2O_7{}^{2-}$) is a powerful oxidant, but Mo(VI) and W(VI) (in MoO_3, WO_3) are mild and almost non-oxidising. This is the *opposite* of the p-block inert-pair trend.

Low oxidation states (zero or negative) are stabilised by π-acceptor ligands such as CO. Hence in $Ni(CO)_4$ and $Fe(CO)_5$ the metal is in the zero oxidation state.

Why only oxides and fluorides reach the highest OS. Oxygen forms multiple bonds (Mn_2O_7 has $Mn{=}O$ bridges) and fluorine has very high bond enthalpy and small size; both stabilise big positive charges on the metal centre.

3.5 Standard Electrode Potentials $E^\circ(M^{2+}/M)$

The E° values across the 3d series follow the trend in $(\Delta_a H + \Delta_i H_1 + \Delta_i H_2 - \Delta_{\text{hyd}} H)$. As we move left to right, this sum becomes less negative because $\Delta_i H_1 + \Delta_i H_2$ rises faster than the hydration enthalpy.

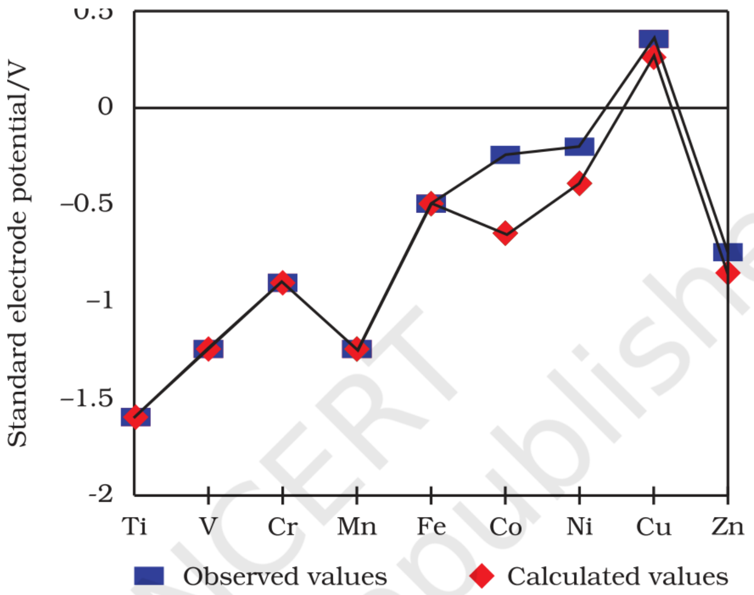


Fig. 4.4: Observed and calculated values for the standard electrode potentials ($M^{2+} \rightarrow M^{\circ}$) of the elements Ti to Zn

Source: NCERT Class 12 Chemistry Part I, Chapter 4. Fig. 4.4, Observed and calculated values for $E^{\circ}(\text{M}^{2+}/\text{M})$ across the 3d series.

Three outliers explained

Mn: $E^{\circ} = -1.18$ V, more negative than expected. After losing two electrons, Mn^{2+} sits at d^5, a half-filled extra-stable shell. The metal therefore “wants” to oxidise.

Zn: $E^{\circ} = -0.76$ V, more negative than expected. Zn^{2+} reaches the d^{10} noble-gas-like shell.

Cu: $E^{\circ} = +0.34$ V, the *only positive* value in the row. This is because Cu’s very high $\Delta_a H^{\circ}$ (it must vaporise) combined with a modest $\Delta_{\text{hyd}} H$ leaves the metal unwilling to ionise. This is why copper does not displace H_2 from dilute HCl or H_2SO_4.

Real-World Application

Cu’s positive E° is why the inside of a copper pot does not fizz when you put dilute vinegar in it, but a galvanised iron bucket (Zn coated, E° very negative) corrodes rapidly. It is also why copper does not release hydrogen with non-oxidising acids: only oxidising acids like hot conc. HNO_3 or hot conc. H_2SO_4 attack it.

3.6 $E^{\circ}(\text{M}^{3+}/\text{M}^{2+})$, Predicting Oxidising / Reducing Behaviour

Couple	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
$E^{\circ}(\text{M}^{3+}/\text{M}^{2+})$/V	-0.37	-0.26	-0.41	$+1.57$	$+0.77$	$+1.97$	,	,

Interpretation:

- Very *negative* E° (Ti, V, Cr) means the M^{2+} form prefers to be *oxidised* to M^{3+}, so Cr^{2+}, V^{2+}, Ti^{2+} are strong **reducing** agents and liberate H_2 from acids.
- Very *positive* E° (Mn, Co) means the M^{3+} wants to be *reduced* to M^{2+}. Mn^{3+} and Co^{3+} are therefore strong **oxidising** agents.
- Fe sits in between: Fe^{3+} is a moderate oxidant (will oxidise I^- to I_2 but not Br^-).

Quick numerical example

$$2\,\mathrm{Cr}^{2+}(\mathrm{aq}) + 2\,\mathrm{H}^+(\mathrm{aq}) \longrightarrow 2\,\mathrm{Cr}^{3+}(\mathrm{aq}) + \mathrm{H}_2(\mathrm{g})$$

The reaction is spontaneous because $E^\circ_{\text{cell}} = E^\circ(\mathrm{H}^+/\mathrm{H}_2) - E^\circ(\mathrm{Cr}^{3+}/\mathrm{Cr}^{2+}) = 0 - (-0.41) = +0.41$ V.

Mn vs Fe oxidising strength

"Why is Mn^{3+} a stronger oxidant than Fe^{3+}?" Answer: $\mathrm{Mn}^{3+}(d^4) \to \mathrm{Mn}^{2+}(d^5)$ gains a half-filled shell (large stabilisation), whereas $\mathrm{Fe}^{3+}(d^5) \to \mathrm{Fe}^{2+}(d^6)$ *loses* half-filled stability.

3.7 Stability of Higher Oxidation States

Fluorides and oxides stabilise the highest oxidation numbers:

Compound	Highest OS attained
TiX_4 (X = F, Cl, Br, I)	+4
VF_5, CrF_6	+5, +6
MnO_3F	+7 (no simple Mn halide!)
Mn_2O_7, CrO_3	+7, +6

The +1 state of copper (Cu^+) and +1 to +3 states of other late 3d metals tend to *disproportionate* in aqueous solution:

$$2\,\mathrm{Cu}^+(\mathrm{aq}) \longrightarrow \mathrm{Cu}^{2+}(\mathrm{aq}) + \mathrm{Cu}\,(\mathrm{s})$$

because the very negative $\Delta_{\text{hyd}}H$ of Cu^{2+} more than compensates for the energy needed to remove the second electron.

3.8 Chemical Reactivity

All 3d metals except copper react with dilute non-oxidising acids (1 M H^+) to liberate H_2, though some (Ti, V) are passivated by a protective oxide film and react only slowly. Copper requires an *oxidising* acid:

$$3\,\mathrm{Cu} + 8\,\mathrm{HNO_3}\,(\mathrm{dil\cdot}) \longrightarrow 3\,\mathrm{Cu(NO_3)_2} + 2\,\mathrm{NO} + 4\,\mathrm{H_2O}$$
$$\mathrm{Cu} + 2\,\mathrm{H_2SO_4}\,(\mathrm{hot, conc\cdot}) \longrightarrow \mathrm{CuSO_4} + \mathrm{SO_2} + 2\,\mathrm{H_2O}$$

3.9 Magnetic Properties, the Spin-Only Formula

When a sample is placed in a magnetic field, three outcomes are possible:

- **Diamagnetic**, all electrons paired; weakly *repelled* by the field.
- **Paramagnetic**, one or more unpaired electrons; weakly *attracted*.
- **Ferromagnetic**, bulk parallel alignment of spins; very strongly attracted (an extreme of paramagnetism). Fe, Co, Ni metals are ferromagnetic.

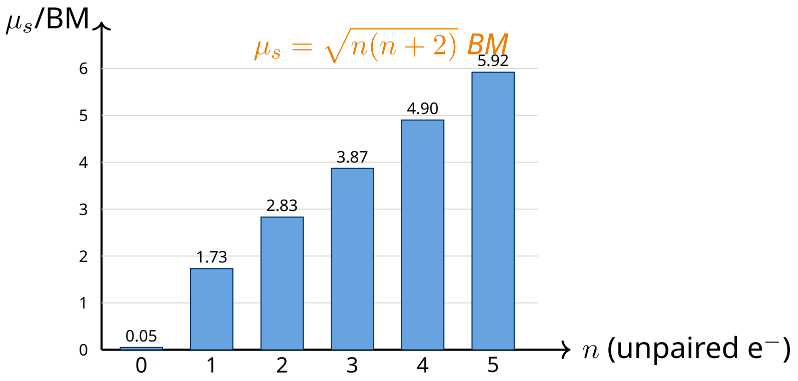
For 3d transition-metal ions, orbital angular momentum is largely “quenched” by the surrounding ligand field, so the effective magnetic moment depends only on the spin angular momentum:

Spin-only magnetic moment

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

where n is the number of unpaired electrons and 1 Bohr Magneton (BM) $= \dfrac{eh}{4\pi m_e} = 9.274 \times 10^{-24}$ J T^{-1}.

Worked example. For Mn^{2+} ($3d^5$, $n = 5$): $\mu_s = \sqrt{5(5+2)} = \sqrt{35} = 5.92$ BM (matches the observed 5.9 BM almost exactly).



Spin-only magnetic moment vs. number of unpaired electrons.

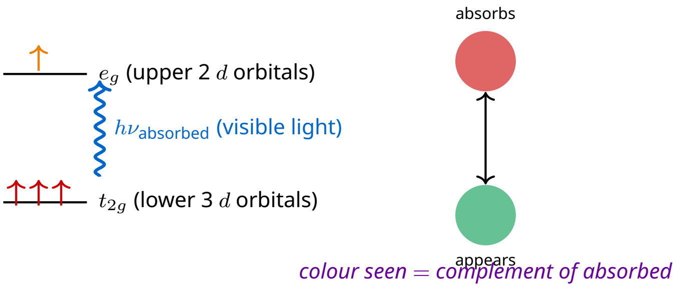
Ion	Config.	n	μ_{calc} (BM)	μ_{obs} (BM)
Sc^{3+}	$3d^0$	0	0	0
Ti^{3+}	$3d^1$	1	1.73	1.75
V^{3+}	$3d^2$	2	2.84	2.76
Cr^{3+}	$3d^3$	3	3.87	3.86
Mn^{2+}	$3d^5$	5	5.92	5.96
Fe^{2+}	$3d^6$	4	4.90	5.3–5.5
Cu^{2+}	$3d^9$	1	1.73	1.8–2.2
Zn^{2+}	$3d^{10}$	0	0	0

Common Mistake

The spin-only formula is $\sqrt{n(n+2)}$, **not** $\sqrt{n^2+2n}$ in a misremembered form. And n is the number of *unpaired* electrons, not the number of d electrons. Fe^{2+} (d^6 high-spin) has $n = 4$, not $n = 6$.

3.10 Formation of Coloured Ions

Most transition-metal ions in aqueous solution are coloured. The reason is a d–d electronic transition: an electron in a lower-energy d orbital absorbs a photon from the visible region and is promoted to a higher-energy d orbital (split by the ligand field, Unit 5). The colour we *see* is the *complementary* colour of the light that was absorbed.



A d–d transition: an electron is promoted from t_{2g} to e_g by a visible-light photon; the colour we see is the complement of the absorbed wavelength.

Fig. 4.5: Colours of some of the first row transition metal ions in aqueous solutions. From left to right: V^{4+},V^{3+},Mn^{2+},Fe^{3+},Co^{2+},Ni^{2+}and Cu^{2+} .

Source: NCERT Class 12 Chemistry Part I, Chapter 4. Fig. 4.5, Aqueous solutions of (left to right) V^{4+}, V^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}.

When is a transition-metal ion colourless?

A transition-metal ion is colourless if it has *no d–d transition available*. This happens in two cases:
(i) d^0: no d electron to promote (Sc^{3+}, Ti^{4+}, V^{5+}).
(ii) d^{10}: no empty d orbital to receive an electron (Zn^{2+}, Cu^{+}, Cd^{2+}, Hg^{2+}).

Memory Aid, coloured or not

“**Empty or Full means colourless.**” Anything between d^1 and d^9 usually shows colour. The very strong yellow of $CrO_4{}^{2-}$ and deep purple of $MnO_4{}^{-}$ are exceptions: those colours come from *ligand-to-metal charge-transfer* (LMCT) transitions, not d–d.

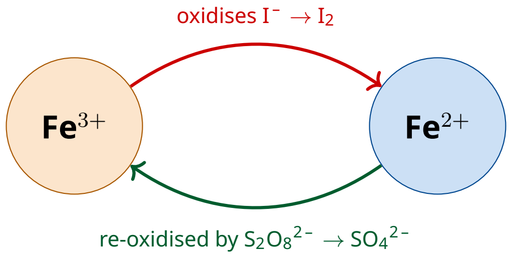
3.11 Complexes, Catalysis, Interstitial Compounds and Alloys

Complexes. Transition-metal ions are excellent complex formers because they are small, highly charged, and have vacant d orbitals for ligand donation. Examples: $[Fe(CN)_6]^{3-}$, $[Cu(NH_3)_4]^{2+}$, $[PtCl_4]^{2-}$.

Catalysis. The ability to switch between oxidation states makes transition metals (or their compounds) excellent redox catalysts. V_2O_5 catalyses $SO_2 \longrightarrow SO_3$ in the Contact process; Fe catalyses $N_2 + 3\,H_2 \longrightarrow 2\,NH_3$ (Haber); Ni catalyses fat hydrogenation; $TiCl_4 + Al(C_2H_5)_3$ forms Ziegler–Natta catalyst for polyethene; $PdCl_2$ catalyses the Wacker oxidation of ethene to acetaldehyde. The classic mechanism for the iron catalysis of $2\,I^- + S_2O_8{}^{2-} \longrightarrow I_2 + 2\,SO_4{}^{2-}$:

$$2\,Fe^{3+} + 2\,I^- \longrightarrow 2\,Fe^{2+} + I_2$$
$$2\,Fe^{2+} + S_2O_8{}^{2-} \longrightarrow 2\,Fe^{3+} + 2\,SO_4{}^{2-}$$

Catalytic cycle: variable OS regenerates the catalyst



Fe catalyses $2\,I^- + S_2O_8{}^{2-} \longrightarrow I_2 + 2\,SO_4{}^{2-}$ by cycling between Fe^{2+} and Fe^{3+}.

Interstitial compounds. Small atoms (H, C, N, B) fit into the holes of the metal lattice, giving non-stoichiometric, very hard, high-melting and metallically conducting solids: TiC, Mn_4N, Fe_3H, $VH_{0.56}$, $TiH_{1.7}$.

Alloys. Because transition metals have very similar metallic radii (within 15%), they readily form substitutional alloys. Steel = Fe + small amounts of C/Cr/Mn/Ni; stainless steel = Fe-Cr-Ni; brass = Cu-Zn; bronze = Cu-Sn; mischmetall = 95% lanthanoid + 5% Fe.

Real-World Application

The catalytic interconversion of oxidation states is the basis of biology’s most important catalyst: cytochrome P450. Its iron centre cycles between Fe(II), Fe(III) and even Fe(IV) to do the difficult chemistry of inserting an oxygen atom into an unactivated C–H bond. The same principle drives industrial catalysts and the catalytic converter in your car.

4 Important Compounds: $K_2Cr_2O_7$ and $KMnO_4$

4.1 Potassium Dichromate, $K_2Cr_2O_7$

Preparation from chromite ore ($FeCr_2O_4$). Three steps: fuse the ore with Na_2CO_3 in air, acidify, then exchange the counter-cation:

Three-step preparation of $K_2Cr_2O_7$

Step 1, alkaline air roast:

$$4\,FeCr_2O_4 + 8\,Na_2CO_3 + 7\,O_2 \longrightarrow 8\,Na_2CrO_4 + 2\,Fe_2O_3 + 8\,CO_2$$

Step 2, acidify with dilute H_2SO_4:

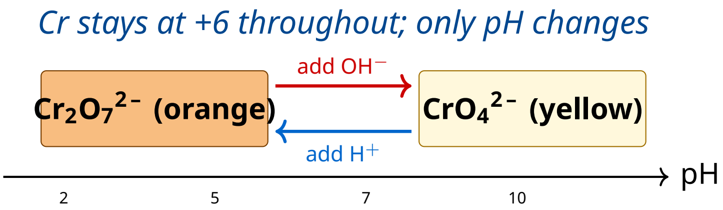
$$2\,Na_2CrO_4 + 2\,H^+ \longrightarrow Na_2Cr_2O_7 + 2\,Na^+ + H_2O$$

Step 3, swap to K^+ (less soluble $K_2Cr_2O_7$ crystallises out):

$$Na_2Cr_2O_7 + 2\,KCl \longrightarrow K_2Cr_2O_7 + 2\,NaCl$$

Chromate ⇌ dichromate equilibrium. The yellow chromate ion (CrO_4^{2-}) and the orange dichromate ion ($Cr_2O_7^{2-}$) are interconverted by pH alone, the oxidation state of Cr is +6 in both.

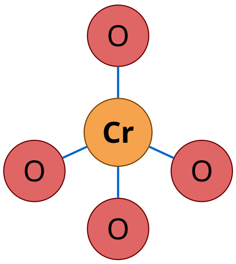
$$2\,CrO_4^{2-} + 2\,H^+ \rightleftharpoons \text{(acid forward, base reverse)}\ Cr_2O_7^{2-} + H_2O$$



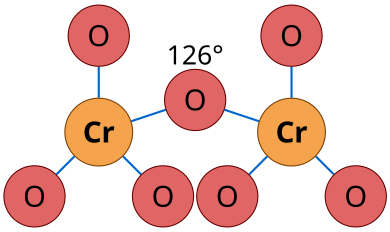
Chromate (yellow, alkaline) and dichromate (orange, acidic) interconvert by pH alone.

Structures of chromate and dichromate

Chromate CrO_4^{2-}: tetrahedral, one Cr at centre, four equivalent Cr–O bonds. **Dichromate** $Cr_2O_7^{2-}$: two corner-sharing CrO_4 tetrahedra joined by a single Cr – O – Cr bridge. The Cr–O–Cr bond angle is 126°.



Chromate $[CrO_4]^{2-}$



Dichromate $[Cr_2O_7]^{2-}$

Oxidising action. $K_2Cr_2O_7$ in acidic medium accepts six electrons:

Reduction half-reaction

$$Cr_2O_7{}^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O \qquad E^\circ = +1.33\text{ V}$$

Standard oxidations of acidified $K_2Cr_2O_7$ (orange → green chromium(III)):

$$\begin{aligned} 6\,I^- &\longrightarrow 3\,I_2 + 6\,e^- \\ 3\,H_2S &\longrightarrow 6\,H^+ + 3\,S + 6\,e^- \\ 3\,Sn^{2+} &\longrightarrow 3\,Sn^{4+} + 6\,e^- \\ 6\,Fe^{2+} &\longrightarrow 6\,Fe^{3+} + 6\,e^- \end{aligned}$$

Combined ionic equation for the $Fe^{2+}/Cr_2O_7{}^{2-}$ titration:

$$Cr_2O_7{}^{2-} + 14\,H^+ + 6\,Fe^{2+} \longrightarrow 2\,Cr^{3+} + 6\,Fe^{3+} + 7\,H_2O$$

Uses. Primary standard in volumetric analysis; chrome tanning of leather; preparation of azo dyes; lab oxidant in organic chemistry.

Real-World Application

The breathalyser test for blood-alcohol used $K_2Cr_2O_7$ for decades. Ethanol vapour reduces the orange dichromate to green Cr(III) in proportion to alcohol concentration; the colour change is read by a photometer. Modern fuel-cell breathalysers are more selective, but the chromate version is still in school chemistry kits.

4.2 Potassium Permanganate, $KMnO_4$

Preparation. From pyrolusite, MnO_2:

Two-step preparation of $KMnO_4$

Step 1, alkaline oxidative fusion (with KOH + O_2 or KNO_3):

$$2\,MnO_2 + 4\,KOH + O_2 \longrightarrow 2\,K_2MnO_4 + 2\,H_2O$$

Step 2, disproportionation (lab route) or electrolytic oxidation (industrial route) of the green manganate(VI):

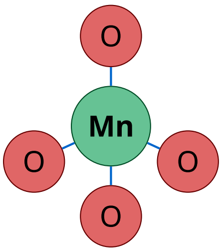
$$3\,\mathrm{MnO_4}^{2-} + 4\,\mathrm{H}^+ \longrightarrow 2\,\mathrm{MnO_4}^{-} + \mathrm{MnO_2} + 2\,\mathrm{H_2O}$$

$$\mathrm{MnO_4}^{2-} \longrightarrow \mathrm{MnO_4}^{-} + \mathrm{e}^- \quad \text{(by electrolysis in alkaline solution)}$$

A laboratory variant uses $S_2O_8^{2-}$ to oxidise Mn(II) directly to Mn(VII):

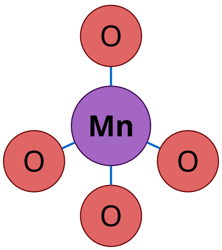
$$2\,\mathrm{Mn}^{2+} + 5\,\mathrm{S_2O_8}^{2-} + 8\,\mathrm{H_2O} \longrightarrow 2\,\mathrm{MnO_4}^{-} + 10\,\mathrm{SO_4}^{2-} + 16\,\mathrm{H}^+$$

Structures. Both MnO_4^{2-} (manganate, green) and MnO_4^- (permanganate, deep purple) are *tetrahedral*. The colour and magnetism differ:



Manganate $[MnO_4]^{2-}$

Mn(VI), d^1, paramagnetic, green



Permanganate $[MnO_4]^-$

Mn(VII), d^0, diamagnetic, deep purple

Ion	Mn OS	Config.	Unpaired	Magnetism / colour
MnO_4^{2-} (manganate)	+6	d^1	1	paramagnetic, green
MnO_4^- (permanganate)	+7	d^0	0	diamagnetic, deep purple

Why is MnO_4^- so intensely coloured if it is d^0?

The colour does *not* come from a d–d transition (impossible in d^0). It is a **ligand-to-metal charge-transfer** (LMCT) band: an electron jumps from an oxygen lone-pair orbital into an empty d orbital of Mn(VII). LMCT bands are typically very intense, which is why a trace of $KMnO_4$ colours a litre of water deep purple.

Oxidising action of $KMnO_4$. The reduction product depends on the pH:

Three reduction routes for permanganate

Acidic: $MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O \qquad E^\circ = +1.52$ V

Neutral/alkaline: $MnO_4^- + 4\,H^+ + 3\,e^- \longrightarrow MnO_2 + 2\,H_2O \qquad E^\circ = +1.69$ V

Strongly alkaline: $MnO_4^- + e^- \longrightarrow MnO_4^{2-} \qquad E^\circ = +0.56$ V

Important oxidations in acidic medium:

- **Iodide → iodine.** $10\,I^- + 2\,MnO_4^- + 16\,H^+ \longrightarrow 2\,Mn^{2+} + 8\,H_2O + 5\,I_2$
- **Iron(II) → iron(III).** $5\,Fe^{2+} + MnO_4^- + 8\,H^+ \longrightarrow Mn^{2+} + 4\,H_2O + 5\,Fe^{3+}$
- **Oxalate → CO_2** (at 333 K). $5\,C_2O_4^{2-} + 2\,MnO_4^- + 16\,H^+ \longrightarrow 2\,Mn^{2+} + 8\,H_2O + 10\,CO_2$
- **Sulphide → S.** $5\,S^{2-} + 2\,MnO_4^- + 16\,H^+ \longrightarrow 2\,Mn^{2+} + 8\,H_2O + 5\,S$
- **Sulphite/sulphurous acid → sulphate.** $5\,SO_3^{2-} + 2\,MnO_4^- + 6\,H^+ \longrightarrow 2\,Mn^{2+} + 3\,H_2O + 5\,SO_4^{2-}$
- **Nitrite → nitrate.** $5\,NO_2^- + 2\,MnO_4^- + 6\,H^+ \longrightarrow 2\,Mn^{2+} + 3\,H_2O + 5\,NO_3^-$

In neutral or faintly alkaline medium:

- Iodide → iodate: $2\,MnO_4^- + H_2O + I^- \longrightarrow 2\,MnO_2 + 2\,OH^- + IO_3^-$
- Thiosulphate → sulphate: $8\,MnO_4^- + 3\,S_2O_3^{2-} + H_2O \longrightarrow 8\,MnO_2 + 6\,SO_4^{2-} + 2\,OH^-$
- Mn(II) → MnO_2 (Zn salts catalyse): $2\,MnO_4^- + 3\,Mn^{2+} + 2\,H_2O \longrightarrow 5\,MnO_2 + 4\,H^+$

Common Mistake

Never titrate $KMnO_4$ in the presence of HCl! The chloride is oxidised to Cl_2, consuming permanganate and over-reading the titre. Use dilute H_2SO_4 as the acidifying agent.
Also: $KMnO_4$ thermally decomposes at 513 K to K_2MnO_4 + MnO_2 + O_2, so dilute solutions stored in clear glass slowly decompose under light, always store in dark bottles.

Uses. Oxidising agent in volumetric analysis and organic syntheses (e.g. side-chain oxidation of toluene to benzoic acid), bleaching agent for wool, cotton, silk and oils, and a topical disinfectant ("Condy's crystals") for skin infections.

5 The Lanthanoids (4f Series, Ce–Lu)

The lanthanoids are the 14 elements from Ce ($Z = 58$) to Lu ($Z = 71$). Lanthanum (La, $Z = 57$) is included in any discussion because it sits immediately above them.

5.1 Electronic Configurations

Lanthanoid atoms share the general form $[\text{Xe}]\,4f^n\,5d^{0\text{ or }1}\,6s^2$. The common tripositive ion Ln^{3+} has the simpler form $[\text{Xe}]\,4f^n$, with n rising from 1 (Ce^{3+}) to 14 (Lu^{3+}). Empty (f^0), half-filled (f^7) and fully-filled (f^{14}) subshells provide extra stability.

5.2 Atomic and Ionic Sizes: Lanthanoid Contraction

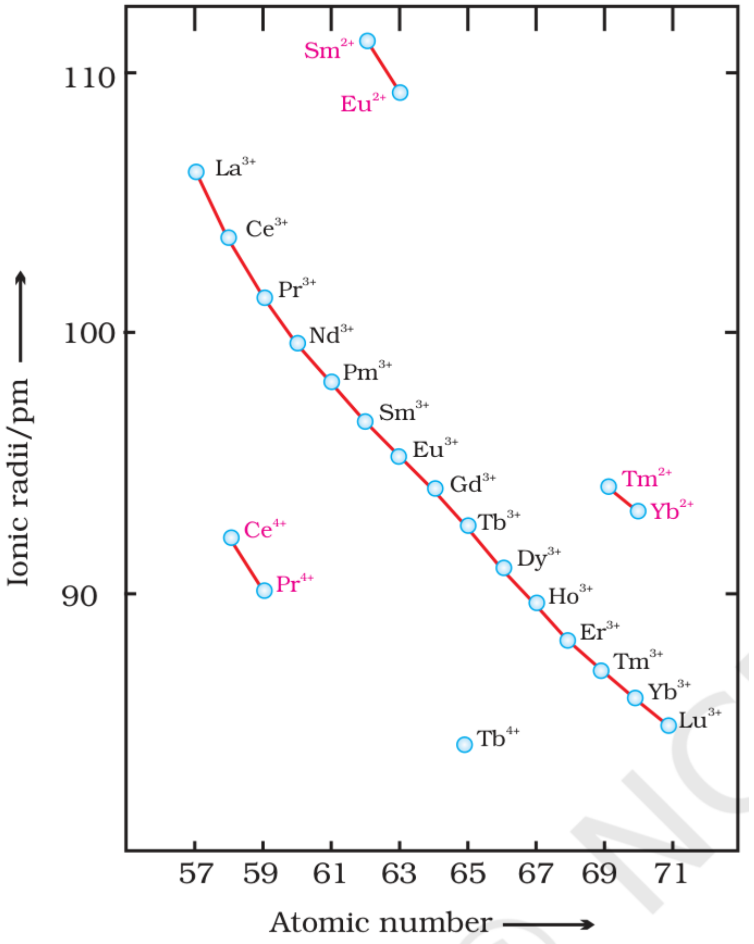
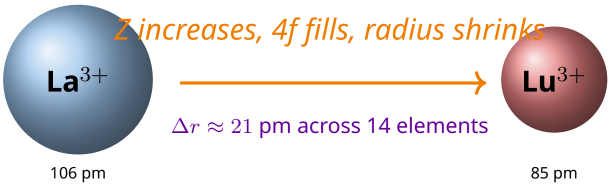


Fig. 4.6: Trends in ionic radii of lanthanoids

Source: NCERT Class 12 Chemistry Part I, Chapter 4. Fig. 4.6, Ionic radii of the lanthanoids and lanthanum, showing the steady contraction from La^{3+} to Lu^{3+}.

Why does the lanthanoid contraction happen?

A 4f electron is poor at shielding another 4f electron because the 4f orbital is buried deep inside the atom (smaller average radius than 5s or 5p) and has multiple radial nodes. So as Z rises by 1, the extra positive charge is felt almost fully by the outer 6s electrons. The whole electron cloud is pulled inward, shrinking the radius by roughly 1 pm per element across the series.



Lanthanoid contraction: ionic radius shrinks from La^{3+} (106 pm) to Lu^{3+} (85 pm).

Major consequences (already encountered for the d-block):

1. Second and third transition series are nearly identical in size (Zr/Hf, Nb/Ta, Mo/W).
2. These pairs of elements are notoriously hard to separate, Hf was discovered in zircon (a $ZrSiO_4$ mineral) only in 1923, by van Hevesy.
3. Basicity decreases from $La(OH)_3$ (most basic, ionic) to $Lu(OH)_3$ (least basic, slightly amphoteric).

5.3 Oxidation States of Lanthanoids

The *only common* oxidation state is **+3**. Two exceptions arise from extra-stable 4f configurations:

State	Ion	Stability source
+4	Ce^{4+} ($4f^0$, [Xe])	noble-gas configuration; strong oxidant ($E^\circ = +1.74$ V)
+4	Tb^{4+} ($4f^7$)	half-filled f subshell
+2	Eu^{2+} ($4f^7$)	half-filled f subshell; strong reductant
+2	Yb^{2+} ($4f^{14}$)	fully-filled f subshell

Memory Aid, non-3+ ions

"**Ce**rtain **Eu**ropean **Yb**ots can switch." Ce(+4) and Tb(+4) are stronger oxidants than O_2 in principle. Eu(+2) and Yb(+2) are stronger reductants than Zn metal in principle. Everything else is reliably +3.

5.4 General Characteristics of Lanthanoids

- Silvery-white, soft, tarnish rapidly in air.
- Melting points 1000–1200 K (Sm is anomalously high at 1623 K).
- Most Ln^{3+} ions are coloured (narrow absorption bands due to f–f transitions). La^{3+} (f^0) and Lu^{3+} (f^{14}) are colourless. Yb^{2+} and Ce^{4+} (also f^0 or f^{14}) are colourless.
- Most Ln^{3+} ions are paramagnetic, with magnetic moments not well predicted by the spin-only formula because in the lanthanoids *orbital angular momentum is not quenched*. The proper formula is $\mu = g\sqrt{J(J+1)}$.
- First IE ≈ 600 kJ/mol; second IE ≈ 1200 kJ/mol, comparable with calcium, hence highly electropositive.
- $E^\circ(Ln^{3+}/Ln) \approx -2.2$ to -2.4 V (Eu is an outlier at -2.0 V).

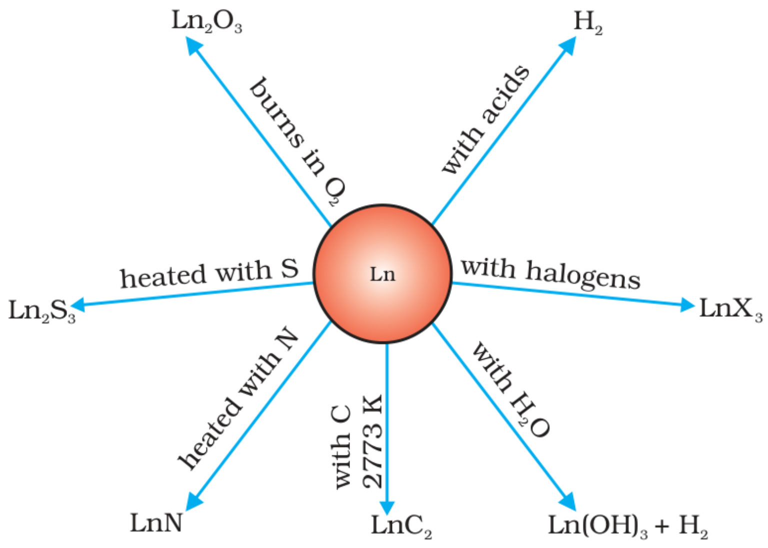


Fig 4.7: Chemical reactions of the lanthanoids.

Source: NCERT Class 12 Chemistry Part I, Chapter 4. Fig. 4.7, Chemical reactions of the lanthanoids. The metal reacts with most non-metals, water, acids, hydrogen and carbon to give the species shown.

Summary of Ln chemistry

- With water: $2\,Ln + 6\,H_2O \longrightarrow 2\,Ln(OH)_3 + 3\,H_2$
- With halogens: $2\,Ln + 3\,X_2 \longrightarrow 2\,LnX_3$
- With oxygen (on heating): $4\,Ln + 3\,O_2 \longrightarrow 2\,Ln_2O_3$
- With nitrogen (on heating): $2\,Ln + N_2 \longrightarrow 2\,LnN$
- With sulphur (on heating): $2\,Ln + 3\,S \longrightarrow Ln_2S_3$
- With carbon (at 2773 K): $Ln + 2\,C \longrightarrow LnC_2$
- With hydrogen (on heating): $Ln + H_2 \longrightarrow LnH_2$ (or LnH_3)
- With dilute acid: $2\,Ln + 6\,H^+ \longrightarrow 2\,Ln^{3+} + 3\,H_2$

5.5 Uses of Lanthanoids

- **Mischmetall** (~95% lanthanoid + ~5% Fe with traces of S, C, Ca, Al) is used in Mg-based alloys for bullets, shells and lighter flints. The famous lighter "flint" is mostly Ce-Fe alloy.
- **Petroleum cracking catalysts**: mixed Ln oxides on zeolite supports.
- **Phosphors**: Eu^{3+} (red) and Tb^{3+} (green) in fluorescent lamps, TV/LED screens, and X-ray imaging plates.
- **Strong permanent magnets**: $Nd_2Fe_{14}B$ (Neodymium magnets), $SmCo_5$.

Real-World Application

"Rare earths are everywhere". The bright red phosphor in a flat-panel TV is

> doped with Eu^{3+}; the strong magnet in a hard-disk read head is $Nd_2Fe_{14}B$; the lighter you flick uses Ce–Fe mischmetall. Despite the name, lanthanoids are not particularly rare in the earth's crust (Ce is more abundant than Cu), the name refers to the historical difficulty of separating them, a direct consequence of the lanthanoid contraction.

6 The Actinoids (5f Series, Th–Lr)

The 14 elements from thorium (Th, $Z = 90$) to lawrencium (Lr, $Z = 103$). Actinium (Ac, $Z = 89$) is included as the prototype.

6.1 Electronic Configurations and Ionic Sizes

All actinoid atoms share $7s^2$ with variable 5f and 6d occupancy. 5f orbitals are not as buried as 4f orbitals, so 5f electrons can participate in bonding to a much greater extent.

The **actinoid contraction** is the analogue of the lanthanoid contraction, a steady decrease in An^{3+} radii across the series, but is *greater per step* because 5f shielding is even poorer than 4f shielding.

6.2 Oxidation States: A Wider Range

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
	4	4	4	4	4	4	4	4						
		5	5	5	5	5								
			6	6	6	6								
				7	7									

The maximum OS climbs from +4 (Th) through +5 (Pa), +6 (U) to +7 (Np, Pu), then drops back. The most common state is **+3** for all, like the lanthanoids.

6.3 Comparison: Lanthanoids vs Actinoids

Lanthanoids (4f)	Actinoids (5f)
4f orbitals; only +3 common; +2/+4 rare.	5f orbitals; +3 to +7 all known; chemistry richer.
Non-radioactive (with traces of Pm).	All radioactive; later members made only in nanograms.
Lanthanoid contraction ≈ 11 pm.	Actinoid contraction larger per step; less regular.
Magnetic moments follow $g\sqrt{J(J+1)}$.	Magnetic behaviour more complex; lower than equivalent Ln.
Ionisation enthalpies slightly higher.	Lower IE; 5f electrons less penetrating, more available for bonding.
Compounds mostly ionic.	More covalent character; forms strong complexes (especially U, Pu).

Quick Tip

"Lanthanoid contraction is far more important than actinoid contraction", not because it is larger (it isn't) but because the elements *succeeding* the lanthanoids (the 5d series) are everyday materials (Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg), whereas the elements after the actinoids are unstable transactinides studied only in labs.

6.4 General Characteristics of Actinoids

- All silvery, highly reactive (boiling water gives oxide + hydride mix), readily attacked by dilute HCl.
- All radioactive; Th ($t_{1/2} = 1.4 \times 10^{10}$ years) and U ($t_{1/2} = 4.5 \times 10^{9}$ years) have long half-lives, but later members (Lr) have $t_{1/2} \sim$ minutes.
- Lower IE than the corresponding lanthanoid, 5f electrons are less "buried" and so more easily ionised.
- Magnetic properties more complex than the lanthanoids; spin-orbit coupling is larger.

7 Applications of d- and f-Block Elements

Iron and steel are by far the most important construction materials. Specialty alloys, catalysts, pigments, batteries, electronics and the photographic industry all depend on transition metals.

Element / compound	Use
Fe, steel alloys	Construction; stainless steel = Fe + Cr (12–18%) + Ni
TiO_2	White pigment in paint, paper, plastics, sunscreen
MnO_2	Cathode in dry battery cells; $KMnO_4$ precursor
Zn, Ni/Cd	Rechargeable battery electrodes; galvanising
V_2O_5	Catalyst for $2\,SO_2 + O_2 \longrightarrow 2\,SO_3$ in the Contact Process
Fe (finely divided)	Haber process catalyst for $N_2 + 3\,H_2 \longrightarrow 2\,NH_3$
Ni	Hydrogenation of unsaturated oils to fats (vanaspati)
$PdCl_2$	Wacker process: $C_2H_4 \longrightarrow CH_3CHO$
$TiCl_4$ / $Al(C_2H_5)_3$	Ziegler–Natta catalyst for HDPE polyethene
AgBr	Light-sensitive emulsion in classical photography
Au, Ag, Cu	Coinage metals (Cu is now only Cu-plated steel in UK 1p/2p)
$Nd_2Fe_{14}B$, $SmCo_5$	Hard-disk magnets; speakers; electric-vehicle motors
Eu^{3+}, Tb^{3+} phosphors	Red/green emitters in fluorescent and LED displays
U, Pu oxides	Nuclear-reactor fuel; Th as breeder-reactor fuel (India's three-stage programme)

8 Quick Reference Summary

Master formula list

Spin-only magnetic moment: $\mu_s = \sqrt{n(n+2)}$ BM, n = unpaired e^-

Acidic dichromate reduction: $Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O$ ($E^\circ = +1.33$ V)

Acidic permanganate reduction: $MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O$ ($E^\circ = +1.52$ V)

Neutral permanganate reduction: $MnO_4^- + 4\,H^+ + 3\,e^- \longrightarrow MnO_2 + 2\,H_2O$ ($E^\circ = +1.69$ V)

Strongly alkaline: $MnO_4^- + e^- \longrightarrow MnO_4^{2-}$ ($E^\circ = +0.56$ V)

Chromate⇌dichromate equilibrium: $2\,CrO_4^{2-} + 2\,H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$

Disproportionation of Cu^+: $2\,Cu^+ \longrightarrow Cu^{2+} + Cu$

Reduction by Cr^{2+}: $2\,Cr^{2+} + 2\,H^+ \longrightarrow 2\,Cr^{3+} + H_2$

Trends at a glance, 3d series

Atomic radius: small decrease then small rise.
Density: steadily increases (Sc 3.4 to Cu 8.9 g/cm^3).
Ionisation enthalpy: slight rise with bumps at d^5 (Cr, Mn) and d^{10} (Cu, Zn).
Melting point: maximum at d^5 (Cr, V), dip at Mn.
E°(M^{2+}/M): less negative across, but Mn and Zn (extra-stable ions) are outliers; Cu is positive.
Strongest oxidants: Mn^{3+}, Co^{3+} (M^{3+}/M^{2+} very positive).
Strongest reductants: V^{2+}, Cr^{2+}, Ti^{2+} (M^{3+}/M^{2+} very negative).
Coloured ions: all d^1 to d^9; colourless: d^0 and d^{10}.
Paramagnetic: all with unpaired d-electrons; max at d^5 (Mn^{2+}, 5.92 BM).

Key constants and bench values

1 BM $= 9.274 \times 10^{-24}$ J T^{-1}
$\Delta_{\text{hyd}}H^\circ$ values used in Born–Haber: Cu^{2+}: -2121, Ni^{2+}: -2121, Zn^{2+}: -2059 kJ/mol
$Cr_2O_7{}^{2-}$ Cr–O–Cr bridge angle: 126°
$MnO_4{}^-$ thermal decomposition starts at 513 K
Tungsten melting point: 3683 K (highest of any pure metal)

Final memory mnemonics

Cr and Cu exceptions: “Half d or full d is sweet”, 3d^5 and 3d^{10} rob from 4s.
Coloured ion test: “Empty or Full means colourless”, d^0 and d^{10}.
Lanthanoid OS exceptions: “Ce/Tb up, Eu/Yb down”, because f^0, f^7, f^{14} are extra stable.
Highest OS coincides with group number from Sc(III) to Mn(VII), then drops sharply.
Cu and HCl: “Cu refuses to fizz”, positive E°, needs an oxidising acid.

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Keep your d- and f-Block Elements prep on a single shelf:

- NCERT Solutions for Class 12 Chemistry Chapter 4 The d- and f-Block Elements
- The d- and f-Block Elements Formula Sheet (PDF)
- NCERT Exemplar Solutions Chapter 4 The d- and f-Block Elements
- Handwritten Notes for The d- and f-Block Elements
- Original NCERT Book PDF, Class 12 Chemistry Chapter 4