JEE MAIN · PAPER 1 · CHEMISTRY

11 d- & f-Block Elements

Formula & concept sheet

The d-block and f-block elements: configurations and their exceptions, trends in size, ionisation and oxidation states, why transition metals are coloured, magnetic and catalytic, then potassium dichromate and potassium permanganate (preparation, structures, reactions), and the lanthanoids and actinoids with the lanthanoid contraction. Each idea is explained first, then the tables, reactions and traps.

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READ ALONGSIDE NCERT XII · The d- and f-Block Elements

HOW TO USE THIS SHEET

1. **Skim** — Read the Key ideas, then the formula cards.
2. **Memorise** — Learn the formulas and check every Trap box.
3. **Test** — Do the worked examples, then this chapter's PYQs.
4. **Revise** — Use the last-minute checklist before the exam.

CHAPTER 11

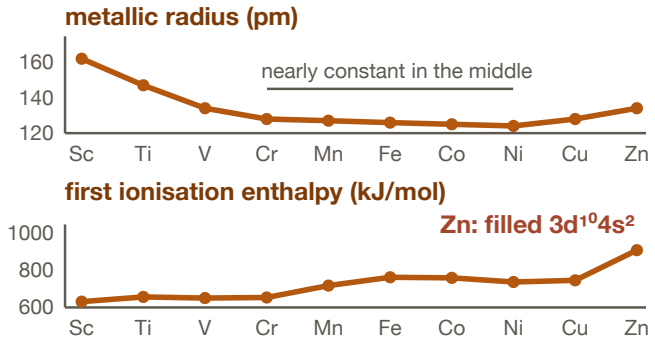
d- & f-Block Elements

NCERT XII · The d- and f-Block Elements

Covers: electronic configuration of transition elements · atomic and ionic size, ionisation enthalpy, oxidation states, electrode potentials · colour, magnetic moment, catalysis, interstitial compounds, alloys · $K_2Cr_2O_7$ and $KMnO_4$ · lanthanoids and actinoids, lanthanoid contraction.

1 Transition elements: configuration and general trends

- The **d-block** is groups 3 to 12. A **transition element** has a partly filled d subshell in the atom or in a common ion; Zn, Cd, Hg (d^{10} in both) are d-block elements but not strictly transition elements.
- General configuration $(n-1)d^{1\text{ to }10}ns^{1\text{ or }2}$. Exceptions: Cr $3d^5 4s^1$ and Cu $3d^{10}4s^1$ (half-filled and filled d are extra stable). When ions form the $4s$ electrons leave **before** $3d$: $Fe\ [Ar]3d^6 4s^2 \rightarrow Fe^{2+}\ 3d^6 \rightarrow Fe^{3+}\ 3d^5$.
- Because $(n-1)d$ and ns are close in energy, several electrons can be used and several oxidation states appear. The maximum oxidation state up to Mn equals the number of $ns + (n-1)d$ electrons: Sc +3, Ti +4, V +5, Cr +6, Mn +7; after that it falls.



radius falls, levels, then rises slightly; IE rises irregularly as 3d electrons shield poorly

SIZE AND IONISATION ENTHALPY ACROSS 3D

- Radius falls from Sc to Cr, stays nearly constant for Mn to Ni (the added $3d$ electrons shield each other poorly, so the pull and the repulsion nearly cancel), and rises for Cu and Zn.
- IE_1 rises slowly and irregularly, with the jump at Zn ($3d^{10}4s^2$).
- IE_2 peaks at Cr and Cu (the d^5 and d^{10} ion is hard to ionise; Cu is the largest, and Cr the highest from Sc to Fe); IE_3 peaks at Mn and Zn (Zn the largest).
- Cr: $IE_1 = 653 <$ Mn 717; IE_3: Cr 2987 < Mn 3248 kJ mol^{-1}.

PROPERTIES OF THE FIRST TRANSITION SERIES

PROPERTY	FACT
melting points	high (strong metallic bonding by unpaired d electrons), peaking near the middle (V, Cr); Mn and Zn are anomalously low
enthalpy of atomisation	high; 4d and 5d higher than 3d
$E^\circ(M^{2+}/M)$	negative for all except Cu (+0.34 V): Cu does not liberate H_2 from acids
$E^\circ(M^{3+}/M^{2+})$	Mn +1.57 and Co +1.97 V (strong oxidants); Cr −0.41 V (Cr^{2+} a strong reductant); Fe +0.77 V
stable ions	Mn^{2+} (d^5), Fe^{3+} (d^5), Zn^{2+} (d^{10}); $Cu^{2+}(aq)$ more stable than $Cu^+(aq)$ (high hydration enthalpy): $2\,Cu^+ \longrightarrow Cu^{2+} + Cu$
single states	Sc only +3, Zn only +2; Mn shows the most states (+2 to +7)
oxides	low oxidation state basic, high acidic: MnO basic, Mn_2O_7 acidic; CrO basic, Cr_2O_3 amphoteric, CrO_3 acidic; V_2O_5 amphoteric; mixed oxides Fe_3O_4, Mn_3O_4, Co_3O_4

KEY IDEA

The pattern is set by the d^0, d^5 and d^{10} configurations: a species that moves towards one is stable. $Mn^{3+} \rightarrow Mn^{2+}$ (d^5) makes Mn^{3+} oxidising; $Cr^{2+} \rightarrow Cr^{3+}$ (t_{2g}^3) makes Cr^{2+} reducing; Fe^{3+} (d^5) is more stable than Fe^{2+}.

QUICK CHECK

Which 3d metal has the highest IE_2 among Sc to Fe, and the spin-only moment of its M^+?

Answer: Cr: Cr^+ is $3d^5$, $n = 5$: $\mu = \sqrt{35} = 5.92 \approx 6$ BM.

2 Colour, magnetism, catalysis and special properties

- **Colour** comes from d-d transitions: a partly filled d subshell absorbs a visible colour and the ion shows the complement. d^0 (Sc^{3+}, Ti^{4+}) and d^{10} (Zn^{2+}, Cu^+) ions are colourless. MnO_4^-, $Cr_2O_7^{2-}$, CrO_4^{2-} are d^0 yet strongly coloured, by **ligand-to-metal charge transfer**, not d-d.
- **Magnetism**: unpaired electrons make an ion paramagnetic; the spin-only moment is $\mu = \sqrt{n(n+2)}$ BM, with n unpaired electrons.

SPIN-ONLY MOMENT

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

$n = 0, 1, 2, 3, 4, 5, 6, 7$ gives $0,\ 1.73,\ 2.83,\ 3.87,\ 4.90,\ 5.92,\ 6.93,\ 7.94$ BM; inverse $n = -1 + \sqrt{1+\mu^2}$

ION CONFIGURATION

remove $4s$ first, then $3d$

Fe $3d^6 4s^2$; Fe^{2+} $3d^6$; Fe^{3+} $3d^5$; Cr^{3+} $3d^3$; Cu^{2+} $3d^9$

AQUATED IONS OF THE FIRST SERIES (HIGH SPIN IN WATER)

ION	CONFIG.	UNPAIRED	μ (BM)	COLOUR
Sc^{3+}, Ti^{4+}	d^0	0	0	colourless
Ti^{3+}	d^1	1	1.73	purple
V^{3+}	d^2	2	2.83	green
V^{2+}, Cr^{3+}	d^3	3	3.87	violet
Cr^{2+}, Mn^{3+}	d^4	4	4.90	blue, violet
Mn^{2+}, Fe^{3+}	d^5	5	5.92	pale pink, yellow
Fe^{2+}	d^6	4	4.90	green
Co^{2+}	d^7	3	3.87	pink
Ni^{2+}	d^8	2	2.83	green
Cu^{2+}	d^9	1	1.73	blue
Zn^{2+}, Cu^+	d^{10}	0	0	colourless

CATALYSTS AND WHY TRANSITION METALS CATALYSE

- V_2O_5 (contact process), Fe (Haber), Ni (hydrogenation), Pt-Rh (Ostwald), $TiCl_4$ + $Al(CH_3)_3$ (Ziegler-Natta), $PdCl_2$ (Wacker), MnO_2 ($KClO_3$ decomposition).
- Reasons: variable oxidation states (intermediate compounds), a surface that adsorbs reactants, and the ability to form complexes.

INTERSTITIAL COMPOUNDS, ALLOYS, COMPLEXES

- **Interstitial** compounds (TiC, Mn_4N, Fe_3H): small atoms in the lattice holes; hard, high melting, conducting, inert, non-stoichiometric.
- **Alloys** form when radii differ by less than about 15%: brass (Cu-Zn), bronze (Cu-Sn), stainless steel (Fe-Cr-Ni).
- Transition metals form many complexes (small ions, high charge, empty d orbitals).

TRAP

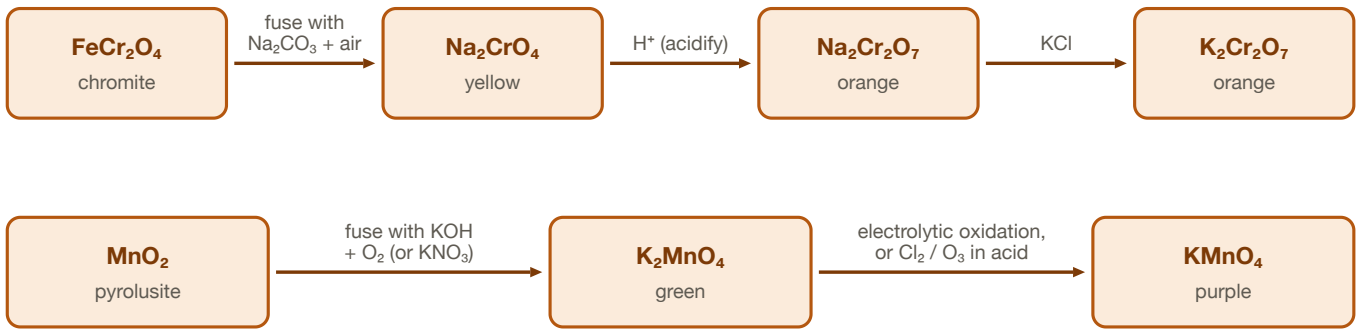
$KMnO_4$ is purple although Mn is $+7$, d^0: the colour is charge transfer. Cu^+ is d^{10} but unstable in water (disproportionates); Cu^{2+} (d^9) is stable because of its large hydration enthalpy. Zn, Cd, Hg are not strict transition elements. Zn and Al both give H_2 with acid and with alkali: $Zn + 2\,NaOH \longrightarrow Na_2ZnO_2 + H_2$.

QUICK CHECK

Number of unpaired electrons and μ for Fe^{2+} and Mn^{2+}?

Answer: Fe^{2+} $3d^6$: 4, 4.90 BM. Mn^{2+} $3d^5$: 5, 5.92 BM.

3 Potassium dichromate



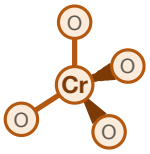
the two oxidants are made by fusion with alkali and air, then oxidation or acidification

FROM CHROMITE $4\,FeCr_2O_4 + 8\,Na_2CO_3 + 7\,O_2 \longrightarrow 8\,Na_2CrO_4 + 2\,Fe_2O_3 + 8\,CO_2$: the insoluble product is Fe_2O_3 (160 g mol^{-1}); the yellow Na_2CrO_4 is extracted, acidified to orange $Na_2Cr_2O_7$, and converted with KCl (less soluble $K_2Cr_2O_7$ crystallises).

CHROMATE AND DICHROMATE

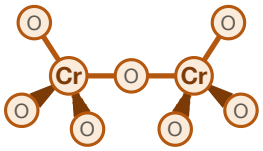
REACTION	EQUATION
acidify	$2\,Na_2CrO_4 + 2\,H^+ \longrightarrow Na_2Cr_2O_7 + 2\,Na^+ + H_2O$
with KCl	$Na_2Cr_2O_7 + 2\,KCl \longrightarrow K_2Cr_2O_7 + 2\,NaCl$
pH equilibrium	$Cr_2O_7^{2-} + 2\,OH^- \rightleftharpoons 2\,CrO_4^{2-} + H_2O$: base gives yellow chromate, acid orange dichromate; Cr is $+6$ in both
oxidant in acid	$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O$ (orange to green); $n_f = 6$
with Fe^{2+}	$Cr_2O_7^{2-} + 14\,H^+ + 6\,Fe^{2+} \longrightarrow 2\,Cr^{3+} + 6\,Fe^{3+} + 7\,H_2O$
with I^-	$Cr_2O_7^{2-} + 14\,H^+ + 6\,I^- \longrightarrow 2\,Cr^{3+} + 3\,I_2 + 7\,H_2O$
with H_2S	$Cr_2O_7^{2-} + 8\,H^+ + 3\,H_2S \longrightarrow 2\,Cr^{3+} + 3\,S + 7\,H_2O$
chromyl chloride test for Cl^-	$K_2Cr_2O_7 + 4\,NaCl + 6\,H_2SO_4 \longrightarrow 2\,CrO_2Cl_2 + 2\,KHSO_4 + 4\,NaHSO_4 + 3\,H_2O$; red-brown vapour of CrO_2Cl_2 (Cr $+6$); with NaOH: $CrO_2Cl_2 + 4\,NaOH \longrightarrow Na_2CrO_4 + 2\,NaCl + 2\,H_2O$ (yellow solution), then yellow $PbCrO_4$ with lead acetate

CrO_4^{2-}



chromate
Cr +6, yellow

$Cr_2O_7^{2-}$



dichromate
Cr +6, orange

MnO_4^-



permanganate
Mn +7, purple

MnO_4^{2-}



manganate
Mn +6, green

chromate and dichromate interconvert with pH: $2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$

WHY IT WORKS

In acid the equilibrium $2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$ moves right (two chromate tetrahedra join through a shared O). Both anions are tetrahedral at each Cr; in dichromate the Cr−O−Cr bridge angle is about 126°.

QUICK CHECK

Molar mass of the water-insoluble product from fusing chromite with Na_2CO_3 in air?

Answer: Fe_2O_3: $2 \times 56 + 3 \times 16 = 160$ g mol^{-1}.

4 Potassium permanganate

PREPARATION AND STRUCTURE

ITEM	FACT OR EQUATION
manganate from pyrolusite	$2\,MnO_2 + 4\,KOH + O_2 \longrightarrow 2\,K_2MnO_4 + 2\,H_2O$ (green K_2MnO_4)
to permanganate	electrolytic oxidation in alkali, or acid disproportionation: $3\,MnO_4^{2-} + 4\,H^+ \longrightarrow 2\,MnO_4^- + MnO_2 + 2\,H_2O$ (works in acid or neutral, not in strong alkali)
structure	MnO_4^- tetrahedral, Mn +7 (d^0, diamagnetic, purple by charge transfer); MnO_4^{2-} green, d^1, paramagnetic (1.73 BM)
heating	$2\,KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$ (about 513 K)

OXIDISING ACTION OF MnO_4^- BY MEDIUM

MEDIUM	HALF-REACTION	n_f	PRODUCT
acid	$MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O$	5	Mn^{2+} (pale pink)
neutral or weakly alkaline	$MnO_4^- + 2\,H_2O + 3\,e^- \longrightarrow MnO_2 + 4\,OH^-$	3	MnO_2 (brown)
strongly alkaline	$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$	1	MnO_4^{2-} (green)

REACTIONS IN ACID AND IN NEUTRAL SOLUTION

REDUCTANT	EQUATION
oxalate (warm, 60 to 70°C; Mn^{2+} autocatalyses)	$2\,MnO_4^- + 5\,C_2O_4^{2-} + 16\,H^+ \longrightarrow 2\,Mn^{2+} + 10\,CO_2 + 8\,H_2O$
Fe^{2+}	$MnO_4^- + 5\,Fe^{2+} + 8\,H^+ \longrightarrow Mn^{2+} + 5\,Fe^{3+} + 4\,H_2O$
I^- in acid	$2\,MnO_4^- + 10\,I^- + 16\,H^+ \longrightarrow 2\,Mn^{2+} + 5\,I_2 + 8\,H_2O$
I^- in neutral/faintly alkaline	$2\,MnO_4^- + H_2O + I^- \longrightarrow 2\,MnO_2 + 2\,OH^- + IO_3^-$
$S_2O_3^{2-}$ in neutral	$8\,MnO_4^- + 3\,S_2O_3^{2-} + H_2O \longrightarrow 8\,MnO_2 + 6\,SO_4^{2-} + 2\,OH^-$
SO_2, H_2S, H_2O_2, Sn^{2+}	oxidised in acid; $KMnO_4$ is decolourised

TRAP

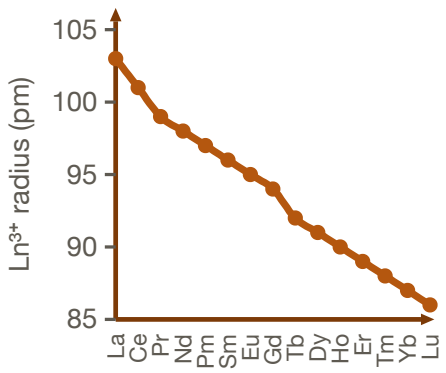
Acidify with dilute H_2SO_4 only: HCl is oxidised to Cl_2 and HNO_3 is itself an oxidant. $KMnO_4$ is purple although d^0. The disproportionation of manganate needs acid or neutral solution. In titrations the n_f depends on the medium $(5, 3, 1)$.

QUICK CHECK

Moles of H^+ needed by 1 mol MnO_4^- to oxidise oxalate?

Answer: $16/2 = 8$.

5 f-block: lanthanoids and actinoids



the lanthanoid contraction: poor $4f$ shielding, so radius falls steadily from La to Lu

- **Lanthanoids** (Ce 58 to Lu 71, La often included) fill the $4f$ subshell: $[Xe]4f^{1\text{ to }14}5d^{0\text{ or }1}6s^2$. The common state is $+3$ (Ln^{3+} has $4f^n$, $n = Z - 57$); Ce^{4+} ($4f^0$) and Tb^{4+} ($4f^7$) are oxidants, Eu^{2+} ($4f^7$) and Yb^{2+} ($4f^{14}$) reductants.
- **Lanthanoid contraction**: a steady fall in size from La to Lu, because the $4f$ electrons shield poorly while nuclear charge grows.

CONSEQUENCES OF THE CONTRACTION

- ✓ Zr (160 pm) $\approx$ Hf (159 pm), $Nb \approx Ta$, $Mo \approx W$: the second and third transition series are alike, so these pairs are hard to separate.
- ✓ Separation of the lanthanoids themselves is difficult; basicity falls: $La(OH)_3 > \cdots > Lu(OH)_3$.
- ✓ $5d$ elements have higher ionisation enthalpy and density than the $4d$ ones.

PROPERTIES OF LANTHANOIDS

- ✓ Silvery, reactive metals (react with water giving H_2); Ln^{3+} colours arise from f-f transitions.
- ✓ Diamagnetic ions: La^{3+} ($4f^0$), Ce^{4+} ($4f^0$), Yb^{2+} ($4f^{14}$), Lu^{3+} ($4f^{14}$); colourless: La^{3+}, Lu^{3+}.
- ✓ Uses: mischmetal (Fe + about 95% lanthanoids) in lighter flints and alloys.

LANTHANOIDS AND ACTINOIDS COMPARED

PROPERTY	LANTHANOIDS ($4f$)	ACTINOIDS ($5f$)
configuration	$[Xe]4f^{1\text{ to }14}5d^{0,1}6s^2$	$[Rn]5f^{1\text{ to }14}6d^{0,1}7s^2$
oxidation states	mainly $+3$ ($+2$, $+4$ in a few)	a wide range ($+3$ to $+7$): $5f$, $6d$, $7s$ are close in energy; Th $+4$, U up to $+6$, Np and Pu up to $+7$
contraction	lanthanoid contraction	actinoid contraction, larger (5f shields even worse)
radioactivity	only Pm is radioactive	all radioactive; Np and heavier are synthetic (Th, Pa, U occur naturally)
compounds	less complex-forming	more complexing and basic character varies with state

TRAP

Count carefully: Cm is an actinoid; Eu, Er, Tb, Yb, Lu are lanthanoids. The lanthanoid contraction is a decrease in **ionic radius** (Ln^{3+}), with a gradual atomic-radius fall also. It explains why the $4d$ and $5d$ elements of a group are similar, not why La is the biggest.

QUICK CHECK

Which of La^{3+}, Ce^{4+}, Eu^{3+}, Yb^{2+}, Lu^{3+} are diamagnetic?

Answer: La^{3+} (f^0), Ce^{4+} (f^0), Yb^{2+} (f^{14}), Lu^{3+} (f^{14}); Eu^{3+} is f^6, paramagnetic.

6 Worked examples

MAGNETIC MOMENT

μ of Cr^{3+}, Co^{2+} (high spin) and Ni^{2+}?

Cr^{3+} $3d^3$: $\sqrt{15} = 3.87$; Co^{2+} $3d^7$: 3 unpaired, 3.87; Ni^{2+} $3d^8$: 2, $\sqrt{8} = 2.83$ BM

UNPAIRED FROM μ

A complex ion has $\mu = 4.90$ BM. Unpaired electrons?

$n = -1 + \sqrt{1 + 24.0} = -1 + 5 = 4$

ORDER OF μ

Order the spin-only moments of Ti^{2+}, V^{2+}, Ti^{3+}, Sc^{3+}.

Ti^{2+} d^2: 2.83; V^{2+} d^3: 3.87; Ti^{3+} d^1: 1.73; Sc^{3+}: 0; so $V^{2+} > Ti^{2+} > Ti^{3+} > Sc^{3+}$

CHROMYL CHLORIDE

NaCl with conc. H_2SO_4 and $K_2Cr_2O_7$ gives red fumes B, which on NaOH give a yellow solution C. Identify B and C.

B: CrO_2Cl_2 (chromyl chloride); C: Na_2CrO_4

REDOX TITRATION

20 mL of 0.05 M $K_2Cr_2O_7$ (acid) oxidises Fe^{2+}. Volume of 0.1 M Fe^{2+} consumed?

$Cr_2O_7^{2-}$ takes 6 Fe^{2+}: $0.02 \times 0.05 \times 6 = 6 \times 10^{-3}$ mol; $V = \dfrac{6 \times 10^{-3}}{0.1} = 60$ mL

COLOURLESS IONS

Which are colourless: Ti^{4+}, Cu^{+}, Zn^{2+}, Cu^{2+}, Sc^{3+}?

d^0 or d^{10}: Ti^{4+}, Cu^{+}, Zn^{2+}, Sc^{3+}; Cu^{2+} (d^9) is blue

7 Last-minute checklist

BEFORE YOU ANSWER

Write the ion's configuration with $4s$ out first, count unpaired electrons, then use $\sqrt{n(n+2)}$. Is the colour d-d or charge transfer? Which medium does the oxidant act in?

- Cr $3d^5 4s^1$, Cu $3d^{10} 4s^1$; ions lose $4s$ first; maximum state Sc $+3$ to Mn $+7$; IE_2 highest for Cr, Cu; Mn $+2$ to $+7$; Sc $+3$, Zn $+2$ only.
- $\mu = \sqrt{n(n+2)}$: 1.73, 2.83, 3.87, 4.90, 5.92; d^0, d^{10} colourless; MnO_4^-, CrO_4^{2-}, $Cr_2O_7^{2-}$ coloured by charge transfer; Cu^{2+} more stable than Cu^+ in water.
- $K_2Cr_2O_7$: chromite fusion gives Na_2CrO_4 (and Fe_2O_3, 160); $CrO_4^{2-} \rightleftharpoons Cr_2O_7^{2-}$ with pH; $n_f = 6$; chromyl chloride test; Cr always $+6$.
- $KMnO_4$: $MnO_2 \rightarrow K_2MnO_4 \rightarrow KMnO_4$; n_f: 5 (acid), 3 (neutral), 1 (alkaline); acidify only with dilute H_2SO_4; $2\,KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$.
- Lanthanoids: $+3$ common, contraction from poor $4f$ shielding, Zr $\approx$ Hf; diamagnetic ions La^{3+}, Ce^{4+}, Yb^{2+}, Lu^{3+}; actinoids show many states and are radioactive.

Now test it. Practise this chapter with past-paper and bank questions on Prep Vault. **Practice this chapter →**