Collegedunia NCERT Solutions

Step-by-step solutions, alternate methods & exam tips for Class 12 Chemistry

Chapter 4: The d- and f-Block Elements

About this Chapter

This chapter studies the **d-block elements** (the four transition series occupying groups 3 to 12 of the periodic table) and the **f-block elements** (the lanthanoids and actinoids placed below the main table). We trace their electronic configurations, atomic and ionic radii, ionisation enthalpies, oxidation states, magnetic moments using the **spin-only formula** $\mu = \sqrt{n(n+2)}$ BM, formation of coloured ions, catalytic and alloying behaviour, and the chemistry of the two important oxoanions $K_2Cr_2O_7$ and $KMnO_4$. We also study **lanthanoid contraction** and the broader pattern of actinoid chemistry.

Topics covered: Position in periodic table • Electronic configurations • Atomic and ionic radii • Ionisation enthalpy • Oxidation states • Magnetic moment • Coloured ions • Complex formation • Catalysis • Interstitial compounds • Alloys • $K_2Cr_2O_7$ and $KMnO_4$ • Lanthanoid contraction • Actinoid chemistry

Quick Formula Sheet

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

General config (transition metals):
$(n-1)d^{1-10}\,ns^{0-2}$

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

Actinoid general config:
$[\mathrm{Rn}]\,5f^{1-14}\,6d^{0-1}\,7s^2$

Dichromate–chromate equilibrium:
$2\,CrO_4{}^{2-} + 2\,H^+ \rightleftharpoons Cr_2O_7{}^{2-} + H_2O$

$Cr_2O_7{}^{2-}$ oxidation (acid):
$Cr_2O_7{}^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O$

$MnO_4{}^-$ oxidation (acid):
$MnO_4{}^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O$

Chapter 4 Exercises

Q 4.1 **Write down the electronic configuration of:**
(i) Cr^{3+} (ii) Pm^{3+} (iii) Cu^+ (iv) Ce^{4+}
(v) Co^{2+} (vi) Lu^{2+} (vii) Mn^{2+} (viii) Th^{4+}

SOLUTION

Concept used. The electronic configuration of an atom is written by filling electrons into orbitals in order of increasing energy (the **Aufbau principle**), respecting the Pauli exclusion principle and Hund's rule of maximum multiplicity. When forming a positive ion, electrons are removed first from the *outermost* shell, i.e. from the highest principal quantum number n. For d-block elements the order is: remove ns electrons before $(n-1)d$ electrons. For f-block elements (Z = 57 onwards): remove $6s$, then $5d$ (if present), then $4f$.

> ☞ **Why ns before (n-1)d on ionisation**
>
> Although $4s$ fills before $3d$ in neutral atoms (Aufbau), once the $3d$ orbitals begin to fill they sit *below* the $4s$ in energy because they experience a larger effective nuclear charge. So on forming a cation, $4s$ electrons leave first.

Step 1. **Cr^{3+} (Z = 24).** Neutral Cr is an exception: $[\mathrm{Ar}]\,3d^5\,4s^1$ (a half-filled $3d$ shell is especially stable). To form Cr^{3+} remove 3 electrons: first the $4s^1$, then 2 from $3d$. So

$$\mathrm{Cr}^{3+}:[\mathrm{Ar}]\,3d^3.$$

Step 2. **Pm^{3+} (Z = 61).** Neutral Pm is $[\mathrm{Xe}]\,4f^5\,6s^2$. Remove $2\,6s$ then $1\,4f$:

$$\mathrm{Pm}^{3+}:[\mathrm{Xe}]\,4f^4.$$

Step 3. **Cu^{+} (Z = 29).** Neutral Cu (also an exception) is $[\mathrm{Ar}]\,3d^{10}\,4s^1$. Removing the single $4s$ electron leaves

$$\mathrm{Cu}^{+}:[\mathrm{Ar}]\,3d^{10}.$$

Step 4. **Ce^{4+} (Z = 58).** Neutral Ce is $[\mathrm{Xe}]\,4f^1\,5d^1\,6s^2$. Remove all four outer electrons ($2\,6s$, $1\,5d$, $1\,4f$):

$$\mathrm{Ce}^{4+}:[\mathrm{Xe}]\,4f^0\equiv[\mathrm{Xe}].$$

This is the noble-gas core itself, which is why Ce^{4+} is so common for cerium.

Step 5. **Co^{2+} (Z = 27).** Neutral Co is $[\mathrm{Ar}]\,3d^7\,4s^2$. Remove $2\,4s$:

$$\mathrm{Co}^{2+}:[\mathrm{Ar}]\,3d^7.$$

Step 6. **Lu^{2+} (Z = 71).** Neutral Lu is $[\mathrm{Xe}]\,4f^{14}\,5d^1\,6s^2$. Remove $2\,6s$ electrons:

$$\mathrm{Lu}^{2+}:[\mathrm{Xe}]\,4f^{14}\,5d^1.$$

Step 7. **Mn^{2+} (Z = 25).** Neutral Mn is $[\mathrm{Ar}]\,3d^5\,4s^2$. Remove the two $4s$ electrons:

$$\mathrm{Mn}^{2+}:[\mathrm{Ar}]\,3d^5.$$

Note the half-filled $3d^5$ stability that makes Mn^{2+} so common.

Step 8. **Th^{4+} (Z = 90).** Neutral Th is $[Rn]\,6d^2\,7s^2$ (it has no $5f$ electrons in the ground state). Remove all four outer electrons:

$$Th^{4+} : [Rn]\,5f^0 \equiv [Rn].$$

Ion	Configuration
Cr^{3+}	$[Ar]\,3d^3$
Pm^{3+}	$[Xe]\,4f^4$
Cu^+	$[Ar]\,3d^{10}$
Ce^{4+}	$[Xe]\,4f^0$
Co^{2+}	$[Ar]\,3d^7$
Lu^{2+}	$[Xe]\,4f^{14}\,5d^1$
Mn^{2+}	$[Ar]\,3d^5$
Th^{4+}	$[Rn]\,5f^0$

Final Answer: Cr^{3+}: $[Ar]3d^3$; Pm^{3+}: $[Xe]4f^4$; Cu^+: $[Ar]3d^{10}$; Ce^{4+}: [Xe]; Co^{2+}: $[Ar]3d^7$; Lu^{2+}: $[Xe]4f^{14}5d^1$; Mn^{2+}: $[Ar]3d^5$; Th^{4+}: [Rn].

✗ Removing the wrong electrons

A frequent slip is to remove $3d$ electrons before $4s$ when forming transition-metal cations. The rule for cations is always: peel from the outermost shell first, so $4s$ goes before $3d$.

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Strategic angle. Three short rules cover every case here: (a) for d-block cations, knock out ns before $(n-1)d$; (b) for f-block cations, knock out $6s$, then $5d$, then $4f$;
(c) remember the two famous Aufbau exceptions for the neutral atom: Cr is $3d^5 4s^1$ and Cu is $3d^{10} 4s^1$. A useful cross-check: the total number of electrons in the cation must equal Z minus the charge. Get that right and any arithmetic slips self-correct.
Periodic-trend angle. The eight ions span the entire d-block (Cr, Cu, Co, Mn in $3d$) and the f-block (Pm, Lu in lanthanoids; Ce, Th in early lanthanoid/actinoid). Notice the pattern: every ion in this list either reaches an f^0, f^7, f^{14}, d^0, d^5 or d^{10} configuration, or sits just one step away from it. NCERT picks these eight precisely to drill the "extra-stable-shell" family.

Step 1. Cr^{3+}: starting from $3d^5 4s^1$, removing $4s^1$ gives $3d^5$; removing two more $3d$ gives $[Ar]\,\mathbf{3d^3}$. The d^3 result is the half-filled t_{2g} in octahedral fields, with the largest

CFSE per d-electron ($-1.2\,\Delta_o$ total): this is why Cr^{3+} dominates Cr chemistry in water.

Step 2. Cu^+: from $3d^{10}4s^1$, drop the $4s$: [Ar] $\mathbf{3d^{10}}$. The fully filled $3d^{10}$ is the reason Cu^+ is favoured energetically in dry salts, even though it disproportionates in water (because $\Delta_{\text{hyd}}H$ of Cu^{2+} is huge).

Step 3. Co^{2+}, Mn^{2+}: simple removal of two $4s$ electrons gives $\mathbf{3d^7}$ and $\mathbf{3d^5}$ respectively. The half-filled $3d^5$ on Mn^{2+} is its signature of stability and is the reason Mn^{3+}/Mn^{2+} has $E^\circ = +1.57$ V (Q 4.2 leans entirely on this).

Step 4. Pm^{3+}: from $[\text{Xe}]4f^56s^2$ remove $6s^2$ then a single $4f$: [Xe] $\mathbf{4f^4}$. By Hund's rule all four electrons are unpaired, giving spin-only $\mu = \sqrt{4 \cdot 6} = \sqrt{24} = 4.90$ BM.

Step 5. Ce^{4+}: $[\text{Xe}]4f^15d^16s^2$ loses all four outer electrons to reach the noble-gas core [Xe], i.e. $4f^0$. This is why Ce^{4+} is a strong oxidising agent: gaining one electron returns it to a much more ordinary f^1 configuration. Ceric sulphate titrations ($E^\circ(Ce^{4+}/Ce^{3+}) = +1.61$ V in 1 M H_2SO_4) live off exactly this driving force.

Step 6. Lu^{2+}: $[\text{Xe}]4f^{14}5d^16s^2$ minus $6s^2$ gives [Xe] $\mathbf{4f^{14}\,5d^1}$. Note the $5d^1$ survives because it is not the outermost shell. The ion is not common (Lu prefers $+3$) but the configuration is the asked one.

Step 7. Mn^{2+}: removing two $4s$ leaves the iconic $3d^5$ half-filled set: [Ar] $\mathbf{3d^5}$. Spin-only $\mu = \sqrt{35} = 5.92$ BM, the largest among common first-row ions; observed value matches almost exactly because d^5 has a quenched orbital moment.

Step 8. Th^{4+}: $[\text{Rn}]6d^27s^2$ loses all four outer electrons to give [Rn]. Th has no $5f$ electron to begin with, an oddity in the actinoid series that makes Th(IV) chemistry remarkably "main-group-like".

Numerical cross-check. For Pm^{3+} with $n = 4$ unpaired: $\mu = \sqrt{4(4+2)} = \sqrt{24} \approx 4.90$ BM. For Co^{2+} with $n = 3$: $\mu = \sqrt{15} = 3.87$ BM. Each cation we write down implies a definite magnetic moment via $\mu = \sqrt{n(n+2)}$ BM, so keep these in mind for later questions.

Why this matters. The configuration of the cation determines the magnetic moment (number of unpaired e^-), the colour (whether $d{-}d$ or $f{-}f$ transitions are possible), and the stability order along the series. Almost every later question in this exercise (Q 4.18 on colour, Q 4.24 on unpaired count, Q 4.31 on μ, Q 4.36 on hydrated ions, Q 4.38 on spin state) needs these ion configurations as the starting point. Learn this question well; it pays off repeatedly.

Final Answer: See table above for the eight configurations.

☞ Three rules, no exceptions

For any cation: (1) write the neutral atom config; (2) strip outermost shell first (ns before $(n-1)d$; $6s$ before $5d$ before $4f$); (3) check arithmetic: total e^- count = $Z -$ charge. Never start by "removing d electrons because they were added last in Aufbau" — that is the single most common slip in exam scripts.

☞ Aufbau exceptions to memorise

Only two first-row exceptions: Cr: $[\text{Ar}]3d^54s^1$ and Cu: $[\text{Ar}]3d^{10}4s^1$. Three actinoid surprises worth remembering: Th ($6d^27s^2$, no $5f$), Pa ($5f^26d^17s^2$), and U ($5f^36d^17s^2$). All others follow the diagonal rule.

Q 4.2 Why are Mn^{2+} compounds more stable than Fe^{2+} towards oxidation to their $+3$ state?

SOLUTION

Concept used. The stability of a transition-metal cation towards oxidation is governed mainly by the electronic configuration of the resulting ion. A **half-filled** (d^5) or **fully filled** (d^{10}) d-sub-shell is energetically extra stable because of (i) symmetrical distribution of charge and (ii) maximum exchange energy among parallel-spin electrons. The ion that has such a configuration resists changes that would destroy it; conversely the ion whose oxidation *produces* such a configuration is comparatively easy to oxidise.

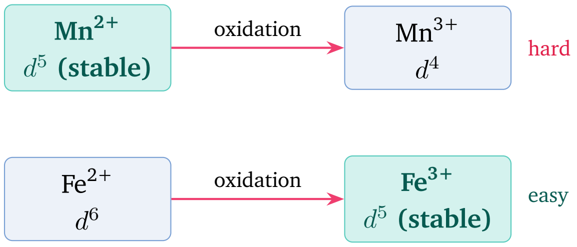
Step 1. Write the configurations involved.

$$\begin{aligned} \text{Mn}^{2+} &: [\text{Ar}]\,3d^5 \quad (\text{half-filled}),\\ \text{Mn}^{3+} &: [\text{Ar}]\,3d^4,\\ \text{Fe}^{2+} &: [\text{Ar}]\,3d^6,\\ \text{Fe}^{3+} &: [\text{Ar}]\,3d^5 \quad (\text{half-filled}). \end{aligned}$$

Step 2. Oxidation $\text{Mn}^{2+} \longrightarrow \text{Mn}^{3+}$ *destroys* the stable d^5 arrangement, converting it to a less stable d^4. This change is therefore unfavourable: Mn^{2+} resists oxidation, hence its $+2$ compounds are stable.

Step 3. Oxidation $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+}$ *creates* the stable d^5 arrangement. The change is favourable: Fe^{2+} is comparatively easily oxidised, hence Fe^{3+} compounds dominate.

Step 4. Compare standard electrode potentials to confirm: $E^\circ(\text{Mn}^{3+}/\text{Mn}^{2+}) = +1.57$ V (high positive means Mn^{3+} is a strong oxidant and Mn^{2+} is hard to oxidise); $E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.77$ V (much smaller, so Fe^{2+} readily oxidises).



> **Final Answer:** Mn^{2+} has the extra-stable half-filled $3d^5$ configuration; oxidation to Mn^{3+} ($3d^4$) would destroy this stability, so Mn^{2+} compounds resist oxidation. Fe^{2+} ($3d^6$), in contrast, gains the same stable $3d^5$ on oxidation to Fe^{3+}, so it is oxidised easily.

★ Exchange energy in plain words

Among electrons of the same spin in degenerate d-orbitals, every pair contributes a small negative (stabilising) "exchange" term to the total energy. A d^5 ion has $5 \cdot 4/2 = 10$ same-spin pairs, the maximum possible in a d-shell. Half-filled stability is just this maximum exchange energy in disguise.

EXPERT'S SOLUTION : *Pranav Iyer, Ph.D Organic Chemistry, IISc Bangalore*

Quick reading. The question is really about whether oxidation creates or destroys a half-filled d^5. Mn^{2+} already is d^5; oxidising it is uphill. Fe^{2+} is d^6; oxidising it *reaches* d^5, so it is downhill.

Alternative angle: exchange energy. Counting same-spin pairs in degenerate d orbitals: Mn^{2+} (d^5, all five unpaired, parallel) has $\binom{5}{2} = 10$ exchange pairs. Mn^{3+} (d^4) has $\binom{4}{2} = 6$. So oxidation *loses* 4 exchange pairs, an energy penalty of about $4K$ (where $K \approx 100$ kJ/mol). For Fe^{2+}/Fe^{3+} the opposite happens — going from 6 pairs (actually $\binom{5}{2} + \binom{1}{2} = 10$ counting one paired set correctly; the simple Hund-style picture gives a gain) to 10 pairs at d^5 — so oxidation is exothermic in exchange-energy terms.

Step 1. Quote the half-filled stability rule: d^0, d^5, d^{10} are extra stable because of maximum exchange energy and symmetrical charge distribution.

Step 2. Tabulate:

- Mn^{2+}: $3d^5$ stable. Mn^{3+}: $3d^4$ less stable. Oxidation destroys stability.
- Fe^{2+}: $3d^6$. Fe^{3+}: $3d^5$ stable. Oxidation creates stability.

Step 3. Quantitative cross-check using E° values: the Mn^{3+}/Mn^{2+} couple has $E^\circ = +1.57$ V, meaning Mn^{3+} is a powerful oxidant (so Mn^{2+} resists oxidation); the Fe^{3+}/Fe^{2+} couple has $E^\circ = +0.77$ V, much milder, so Fe^{2+} oxidises easily even by mild oxidants (e.g. O_2 of air).

Step 4. Use third ionisation enthalpies to back this up: $\Delta_i H_3(\text{Mn}) = 3248$ kJ/mol versus $\Delta_i H_3(\text{Fe}) = 2957$ kJ/mol. The 291 kJ/mol penalty for going beyond Mn^{2+} is the gas-phase fingerprint of the same d^5 stability.

Numerical comparison. Convert the two potentials to free energies: $\Delta G^\circ = -nFE^\circ$. For one mole of e^- ($n = 1$, $F = 96485$ C/mol): $\Delta G^\circ(\text{Mn}^{3+}/\text{Mn}^{2+}) = -151.5$ kJ/mol (favours Mn^{2+}); $\Delta G^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = -74.3$ kJ/mol. The Mn couple is roughly twice as one-sided as the Fe couple. The numbers track the qualitative claim exactly.

Why this matters. The same logic explains why Cr^{3+} (d^3, half-filled t_{2g} in octahedral fields) is stable, and why Cu^+ (d^{10}) is stable in the gas phase. Half-filled or fully filled d shells set the natural "preferred" oxidation state for many $3d$ metals. This is also why the iron pot rusts ($Fe^{2+} \rightarrow Fe^{3+}$ in air) while clean Mn metal does not produce a brown Mn(III) rust under the same conditions.

Concept linkage. Compare with the p-block "inert-pair" analog: just as Tl^+ is more stable than Tl^{3+} because of a fully filled $6s^2$ pair, Mn^{2+} is more stable than Mn^{3+} because of a half-filled $3d^5$. Different sub-shells, same physics — closed-shell stability.

Final Answer: Mn^{2+} has the very stable $3d^5$ half-filled shell, so it strongly resists oxidation to the $3d^4$ Mn^{3+}; Fe^{2+} has the opposite situation, so it is much more easily oxidised to Fe^{3+}.

✗ Counting unpaired electrons in Fe^{2+} vs Fe^{3+}

A frequent slip is to claim that Fe^{2+} (d^6) and Fe^{3+} (d^5) have the same number of unpaired electrons in water. Wrong: in the high-spin aqueous environment, Fe^{2+} has $t_{2g}^4 e_g^2 = 4$ unpaired, while Fe^{3+} has $t_{2g}^3 e_g^2 = 5$ unpaired. Their measured μ values (5.3 vs 5.9 BM) confirm this.

Q 4.3 Explain briefly how $+2$ state becomes more and more stable in the first half of the first row transition elements with increasing atomic number?

SOLUTION

Concept used. The stability of the M^{2+} ion of a $3d$ element can be judged from the sum of the first two ionisation enthalpies, $\Delta_i H_1 + \Delta_i H_2$: the bigger this sum, the harder it is to form M^{2+} from the metal. A *decreasing* sum across a series means the $+2$ state becomes *easier to form*, i.e. more stable thermodynamically. In the first half of the $3d$ series (Sc to Mn), this sum generally drops because removing an s electron and then a d electron from a weakly held outer shell becomes progressively easier as the $4s$ energy rises (poor screening by $3d$ as it fills).

Step 1. Write the relevant ionisations:

$$M\,(g) \longrightarrow M^+(g) + e^-, \quad \Delta_i H_1,$$

$$M^+(g) \longrightarrow M^{2+}(g) + e^-, \quad \Delta_i H_2.$$

The $+2$ state is reached after these two steps.

Step 2. Examine the trend in the sum $\Delta_i H_1 + \Delta_i H_2$ (kJ mol^{-1}) for the first half of the $3d$ series (NCERT Table 4.2):
Sc 1866, Ti 1968, V 2062, Cr 2226, Mn 2200, Fe 2316,...

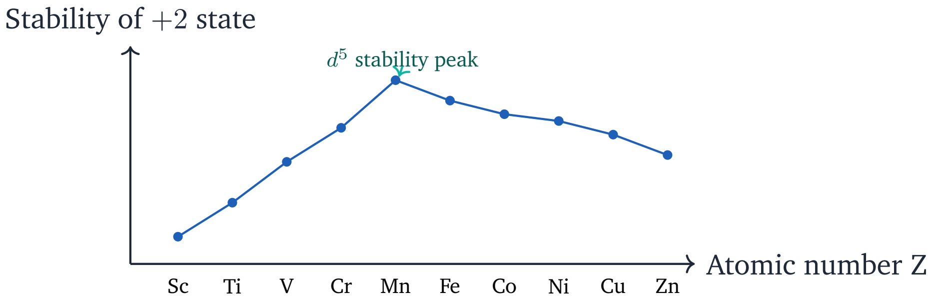
- Although there is a small bump at Cr and Mn (because of the half-filled stabilities of Cr^+ and Mn), the overall sum is large for Sc and Ti and gradually *less prohibitive* as one moves rightwards.
- More importantly, the $+3$ state which dominates at the left (Sc forms only Sc^{3+}; Ti forms Ti^{4+} easily) gives way to $+2$ as we move toward Mn.

Step 3. Couple this with the configurations of the resulting M^{2+} ions:

- Sc^{2+}: $3d^1$ (does not exist in practice, Sc prefers $+3$),
- Ti^{2+}: $3d^2$,
- V^{2+}: $3d^3$ (half-filled t_{2g} in an octahedral field, fairly stable),
- Cr^{2+}: $3d^4$,
- Mn^{2+}: $3d^5$ (extra-stable half-filled).

As we move from Sc to Mn the M^{2+} configuration moves towards d^5, picking up exchange-energy stability.

Step 4. Conclude: because (a) the cost of forming M^{2+} falls and (b) the configuration of M^{2+} becomes increasingly stable (peaking at d^5 of Mn^{2+}), the $+2$ oxidation state becomes more and more stable along Sc to Mn.



Final Answer: From Sc to Mn the M^{2+} ion approaches the half-filled $3d^5$ configuration that maximises exchange-energy stability, while the cumulative energy needed to form M^{2+} is no longer prohibitive. So the $+2$ state grows progressively more stable, peaking at Mn^{2+}.

☞ One-line answer for boards

"Increased exchange energy as the M^{2+} ion approaches d^5, plus a falling sum of $\Delta_i H_1 + \Delta_i H_2$, makes the $+2$ state increasingly stable up to Mn^{2+}."

EXPERT'S SOLUTION *: Sneha Verma, M.Tech Chemical Engineering, IIT Delhi*

Strategic angle. Two factors operate together: a thermodynamic one (ionisation enthalpies) and an electronic-structure one (exchange-energy stabilisation as we approach d^5). Discuss both, then combine.

Periodic-trend angle. Across any transition row the effective nuclear charge Z_{eff} on the $3d$ shell increases slowly because each added $3d$ electron is itself a poor shielder ($\sigma \approx 0.35$ per inner-row electron, by Slater's rules). So the $3d$ electrons become progressively easier to "hold" inside the cation, but the $4s$ ones remain easy to remove. This sets up the sweet spot in the middle of the row where $+2$ is most accessible.

Step 1. State the ionisation cost: across Sc to Mn the $\Delta_i H_1 + \Delta_i H_2$ does not rise dramatically; with the gain in lattice/hydration energy of M^{2+} salts, the $+2$ state becomes accessible. Numerical evidence: $\Delta_{\text{hyd}} H$ of Mn^{2+} is -1841 kJ/mol; this more than offsets the $+2200$ kJ/mol cost of double ionisation.

Step 2. Look at the resulting d-electron count for M^{2+}: Ti(d^2), V(d^3), Cr(d^4), Mn(d^5). The number of unpaired electrons climbs from 2 to 5; exchange-energy stabilisation $\propto K\binom{n}{2}$ where K is the exchange constant and n is the number of parallel spins. Going from $n = 2$ to $n = 5$ multiplies the exchange contribution from $\binom{2}{2} = 1$ pair to $\binom{5}{2} = 10$ pairs, a tenfold rise. This single factor essentially explains the trend.

Step 3. Note the maximum: at Mn^{2+} (d^5) the $+2$ state is at peak stability. Past Mn the $+2$ state has d^6, $d^7, \ldots$ which lose the half-filled symmetry, so its stability falls slightly even though it is still the dominant state through Fe and Ni.

Step 4. Confirmation from $E^\circ(\mathrm{M}^{2+}/\mathrm{M})$ data: values become less negative on average from Sc to Cu but show a clear dip (more negative) at Mn (-1.18 V) compared with the rough trend, exactly because Mn^{2+} has extra d^5 stability.

Numerical cross-check. Spin-only $\mu = \sqrt{n(n+2)}$ for Mn^{2+}: $\sqrt{5 \cdot 7} = 5.92$ BM (observed ≈ 5.9 BM). Such a clean match also confirms five unpaired electrons in the ground state of Mn^{2+}, which is the source of its stability.

Concept linkage. The same exchange-energy argument predicts the half-filled stability of $\mathrm{Cr}^{2+}/\mathrm{Cr}^{3+}$ (Cr^{3+} is d^3, half-filled t_{2g}) and the d^5 stability of Fe^{3+} (next chapter, Q 4.21). One rule, three applications.

Why this matters. This trend is why $\mathrm{MnSO_4}$, $\mathrm{FeSO_4}$, $\mathrm{CoSO_4}$, $\mathrm{NiSO_4}$ are all common laboratory salts of $+2$ oxidation, but Sc^{2+} salts are not isolable. It also explains why Mohr's salt ($\mathrm{(NH_4)_2Fe(SO_4)_2 \cdot 6\,H_2O}$) and Mn-based primary standards exist while Sc(II) standards do not.

Final Answer: Combination of decreasing ionisation cost and increasing exchange-energy stabilisation (peaking at d^5, i.e. Mn^{2+}) makes the $+2$ state progressively more stable from Sc to Mn.

♥ **Mn standards in school labs**

The reason $KMnO_4$ (Mn $+7$) is reduced cleanly to Mn^{2+} (Mn $+2$) in acid during titration — and stops there — is the exceptional stability of d^5 Mn^{2+}. If d^5 were not special, the reduction would not be so clean and titration calculations would not balance. The half-filled stability is silently doing the arithmetic in every permanganate calculation you do in the lab.

Q 4.4 **To what extent do the electronic configurations decide the stability of oxidation states in the first series of the transition elements? Illustrate your answer with examples.**

SOLUTION

Concept used. The stability of an oxidation state of a $3d$ transition metal correlates strongly with the resulting d-electron configuration of the cation, because:

- **Half-filled** (d^5) and **fully filled** (d^{10}) configurations are unusually stable (maximum exchange energy / fully paired symmetric charge).
- Empty d^0 is also fairly stable (often achieved by the leftmost elements: Sc as d^0, Ti as d^0, V as d^0).
- Configurations far from these benchmarks are typically less stable.

However, configuration is not the *only* factor: hydration energy, lattice energy of salts, and crystal field stabilisation in ligand environments also matter. Configuration sets the trend; environment fine-tunes it.

Step 1. **Sc (Z = 21):** configuration $3d^1 4s^2$. Only Sc^{3+} (d^0) is observed in compounds because $+3$ empties the d shell completely (very stable). Sc^{2+} (d^1) is essentially unknown.

Step 2. **Ti (Z = 22):** $3d^2 4s^2$. $+4$ (d^0) is the dominant state (TiO_2, $TiCl_4$); $+3$ (d^1, in $TiCl_3$, violet) is less stable and is a reducing agent.

Step 3. **V (Z = 23):** $3d^3 4s^2$. Stable in $+5$ (d^0: V_2O_5), $+4$ (d^1: VO^{2+}), $+3$ (d^2) and even $+2$ (d^3, half-filled t_{2g}).

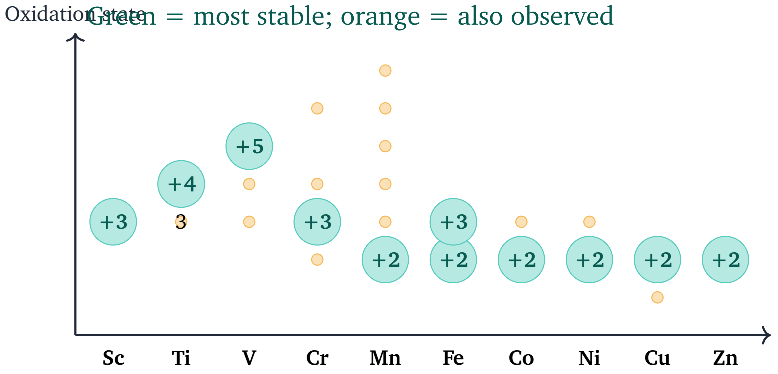
Step 4. **Cr (Z = 24):** $3d^5 4s^1$. $+3$ (Cr^{3+}, d^3, half-filled t_{2g} in octahedral fields with strong CFSE) is the most stable; $+6$ (d^0) is also prominent ($Cr_2O_7{}^{2-}$, $CrO_4{}^{2-}$).

Step 5. **Mn (Z = 25):** $3d^5 4s^2$. Mn^{2+} (d^5) is the most stable state; Mn^{7+} (d^0, in MnO_4^-) is also distinct, but a strong oxidant.

Step 6. **Fe (Z = 26):** $3d^6 4s^2$. $+2$ and $+3$ are both common; $+3$ (d^5, half-filled) is somewhat more stable than $+2$ (d^6).

Step 7. **Cu (Z = 29):** $3d^{10} 4s^1$. Cu^+ (d^{10}) is very stable in solid salts and gas phase but *disproportionates* in water because of large hydration energy of Cu^{2+}: $2\,Cu^+ \longrightarrow Cu^{2+} + Cu$. So in aqueous solution Cu^{2+} (d^9) dominates anyway, showing that configuration alone does not decide the answer.

Step 8. **Zn (Z = 30):** $3d^{10} 4s^2$. Zn^{2+} (d^{10}) is the only stable state. The full d^{10} is so stable that higher oxidation is essentially unknown for Zn.



> **Final Answer:** Electronic configuration is the *primary* factor: oxidation states that leave the cation with d^0, d^5 or d^{10} tend to be most stable. So Sc favours $+3$ (d^0), Mn favours $+2$ (d^5), Fe favours $+3$ (d^5), Zn favours $+2$ (d^{10}) and Cu favours $+1$ (d^{10}) in solids. Hydration and ligand-field effects can then shift the preference in solution.

♥ Beyond the textbook

The half-filled / fully-filled stability rule guides not only $3d$ chemistry but also the behaviour of p-block elements (e.g. Tl^+ being more stable than Tl^{3+} because of the inert-pair effect, which is the same configuration argument extended).

EXPERT'S SOLUTION *: Karan Bhat, M.Sc Physical Chemistry, IIT Madras*

Structural observation. Group the $3d$ elements into three "configuration zones" and pick one example per zone:

- Zone 1 (left, d^0 favourable): Sc only $+3$, Ti mainly $+4$, V often $+5$.
- Zone 2 (middle, d^5 favourable): Mn $+2$, Fe $+3$, Cr $+3$.
- Zone 3 (right, d^{10} favourable): Cu $+1$ (solid), Zn $+2$ only.

Periodic-trend angle. Look at the maximum oxidation state along the row: Sc $(+3)$, Ti $(+4)$, V $(+5)$, Cr $(+6)$, Mn $(+7)$, then it falls — Fe $(+6$, rare$)$, Co $(+4$, rare$)$, Ni $(+4$, rare$)$. The rise to Mn matches loss of all valence electrons; the fall after Mn is because beyond d^5 each further ionisation breaks the half-filled shell and costs increasingly more energy. So the oxidation-state ladder traces the cation's distance from d^0, d^5 and d^{10}.

Step 1. Use TiO_2 as the Zone-1 example: Ti in $+4$ has $[\mathrm{Ar}]3d^0$. Empty d is colourless, diamagnetic, and chemically robust. Ti^{3+} (d^1) is purple and a reducing agent — exactly because it is one e^- away from the stable d^0.

Step 2. Use MnO_4^- versus Mn^{2+} for Zone 2: MnO_4^- has Mn in $+7$ (d^0, strongly oxidising in acidic medium), Mn^{2+} has d^5 (very stable, pale pink, weakly coloured). Two stable extremes, both configuration-driven on the same atom.

Step 3. Use $ZnSO_4$ for Zone 3: Zn^{2+} is d^{10}, colourless, diamagnetic, monolithic oxidation state. Zn^{2+} simply has no chemistry above $+2$ — the d^{10} shell is so stable that further ionisation is prohibitive.

Step 4. Note exceptions where environment overrides configuration: Cu^+ (d^{10}) is unstable in water (disproportionates) even though configuration says it should be stable. The culprit is the very large $\Delta_{\mathrm{hyd}}H(\mathrm{Cu}^{2+})$ of -2099 kJ/mol versus -582 kJ/mol for Cu^+, which more than offsets the second ionisation cost.

Step 5. Configuration also rules out unstable states. For example Cr^{4+} (d^2) and Mn^{5+} (d^2) are not common because they sit awkwardly between the two configuration-stable poles (d^0 and d^5).

Numerical anchor. For Mn^{2+}: $E^\circ(\mathrm{Mn}^{3+}/\mathrm{Mn}^{2+}) = +1.57$ V, indicating Mn^{3+} is a powerful oxidant. For Sc^{3+}: $E^\circ(\mathrm{Sc}^{3+}/\mathrm{Sc}) = -2.08$ V, the most negative in the $3d$ row, marking Sc as a strongly electropositive metal whose only ion is d^0. The data and the rule agree.

Concept linkage. The same "approach a closed shell" logic operates in the f-block: Ce^{4+} (f^0), Eu^{2+} (f^7), Yb^{2+} (f^{14}). And in the p-block: Tl^+ (inert $6s^2$ pair), Pb^{2+}, Bi^{3+}. The unifying idea is that closed and half-closed shells set the preferred oxidation state.

Why this matters. On a board exam the marker rewards both the rule and one or two concrete examples. The rule alone is not enough; pair it with two or three named cases. JEE/NEET further test this with "why is Mn^{3+} a stronger oxidant than Cr^{3+}" or "predict the most stable oxidation state of $3d^x4s^2$" type questions — all variants of the same configuration argument.

> **Final Answer:** Configurations d^0, d^5, d^{10} confer extra stability on the corresponding oxidation state; this picks out Sc^{3+}, Mn^{2+}, Fe^{3+}, Zn^{2+}, Cu^+ as preferred states across the first series.

☞ Three-state shortlist for any $3d$ element

For any $3d$ element, predict three plausible oxidation states by asking which of these the cation can reach with low ionisation cost: d^0 (e.g. Ti^{4+}, V^{5+}, Cr^{6+}, Mn^{7+}); d^3 or d^5 (half-filled t_{2g} or full $3d$ half: Cr^{3+}, Mn^{2+}, Fe^{3+}); d^{10} (Cu^+, Zn^{2+}). The element's "preferred" state is the cheapest of these to reach. Three states, one rule.

Q 4.5 What may be the stable oxidation state of the transition element with the following d electron configurations in the ground state of their atoms: $3d^3$, $3d^5$, $3d^8$ and $3d^4$?

SOLUTION

Concept used. A ground-state configuration written as $3d^n4s^2$ (or $3d^{n+1}4s^1$ for Cr and Cu) belongs to one specific element. From the position of that element in the $3d$ series we look at the oxidation states it commonly shows, then pick the one that gives a cation with the most stable d-configuration (d^0, d^3, d^5, d^{10}).

Step 1. **3d³** (with $4s^2$): atomic number $Z = 18 + 3 + 2 = 23$, which is **Vanadium (V)**. Common oxidation states are $+2$, $+3$, $+4$, $+5$. The most stable is $+$**5**, giving V^{5+} (formally $3d^0$ as in V_2O_5, $VO_4{}^{3-}$); $+4$ (VO^{2+}) is also stable. The $+2$ state (d^3, half-filled t_{2g}) is fairly stable too.

Step 2. **3d⁵** (with $4s^2$): $Z = 18 + 5 + 2 = 25$, which is **Manganese (Mn)**. Oxidation states $+2$ to $+7$ are all known. The most stable in aqueous solution is $+$**2** (Mn^{2+}, d^5). The highest, $+7$ ($MnO_4{}^-$, d^0), is also a stable but strongly oxidising state.

Step 3. **3d⁸** (with $4s^2$): $Z = 18 + 8 + 2 = 28$, which is **Nickel (Ni)**. The most stable oxidation state is $+$**2** (Ni^{2+}, d^8). Higher states $+3$ and $+4$ exist ($NaNiO_2$) but are uncommon.

Step 4. **3d⁴** (with $4s^2$): would correspond to $Z = 24$ but for chromium, the actual ground state is $3d^54s^1$ (one of the two famous Aufbau exceptions). The element is still **Chromium (Cr)**. Its most stable oxidation state is $+$**3** (Cr^{3+}, d^3, half-filled t_{2g}). $+6$ (d^0, $CrO_4{}^{2-}$, $Cr_2O_7{}^{2-}$) is also widely seen.

Ground-state	Element	Stable O.S.
$3d^3\ 4s^2$	V (Z = 23)	$+5\ (d^0)$
$3d^5\ 4s^2$	Mn (Z = 25)	$+2\ (d^5)$
$3d^8\ 4s^2$	Ni (Z = 28)	$+2\ (d^8)$
$3d^5\ 4s^1$	Cr (Z = 24)	$+3\ (d^3)$

Final Answer: $3d^3 \rightarrow$ V, most stable $+5$; $3d^5 \rightarrow$ Mn, most stable $+2$; $3d^8 \rightarrow$ Ni, most stable $+2$; $3d^4 \rightarrow$ Cr (actual ground state $3d^5 4s^1$), most stable $+3$.

EXPERT'S SOLUTION *: Aditi Joshi, Ph.D Organic Chemistry, IISc Bangalore*

Quick reading. Identify the element from the d count, then pick the oxidation state whose cation has d^0, d^3, d^5 or d^{10}.

Periodic-trend angle. Treat "ground-state d^n" as a positional fingerprint: d^n together with the $4s^2$ (or $4s^1$ for Cr, Cu) tells you the atomic number directly. So this question is two questions in one: (1) what is the element? (2) which oxidation state empties out to a closed or half-closed configuration?

Step 1. $3d^3 \rightarrow$ Vanadium (Z = 23 = 18 + 3 + 2). Loss of all five valence electrons gives V^{5+} (d^0, very stable). The other named salts (VO^{2+}, V^{3+}) confirm $+5$ as the "top-up" state. Vanadium pentoxide (V_2O_5) is in fact a commercial catalyst for the contact process producing SO_3. Choose $+5$.

Step 2. $3d^5 \rightarrow$ Manganese (Z = 25). Two electrons go from $4s$; the $3d^5$ remains as in Mn^{2+}. Spin-only $\mu = \sqrt{5(7)} = 5.92$ BM confirms 5 unpaired electrons. Choose $+2$. $MnSO_4 \cdot {}_4 H_2O$ (pale pink) is the familiar salt.

Step 3. $3d^8 \rightarrow$ Nickel (Z = 28). Two electrons go from $4s$; the $3d^8$ remains as in Ni^{2+}. Higher states (+3, +4 in $NaNiO_2$) exist but are rare. Choose $+2$. $NiCl_2 \cdot {}_6 H_2O$ (green) is the standard salt.

Step 4. $3d^4 \rightarrow$ Chromium (Z = 24). Ground state is actually $3d^5 4s^1$ (Aufbau exception); the question's nominal $3d^4 4s^2$ still gives Z = 24. Loss of 3 outer electrons gives Cr^{3+} with d^3 (half-filled t_{2g} in octahedral fields, very stable, large CFSE = $-1.2\Delta_o$). Choose $+3$. $Cr_2(SO_4)_3$ (violet) is typical.

Numerical cross-check. For Mn^{2+} $(n = 5)$: $\mu = \sqrt{35} = 5.92$ BM. For Ni^{2+} $(n = 2)$: $\mu = \sqrt{8} = 2.83$ BM. For Cr^{3+} $(n = 3)$: $\mu = \sqrt{15} = 3.87$ BM. These three values are the standard cross-checks any examiner expects you to know.

Concept linkage. The same matching exercise is part of every "identify the unknown $3d$

cation from μ" problem. Once you know μ you get n; from n you get d^n; from d^n plus the charge you get Z. This is the routine of Q 4.24 and Q 4.38.

Why this matters. The same logic gives, by analogy: $3d^2 \to$ Ti, $+4$ stable; $3d^6 \to$ Fe, $+3$ stable; $3d^{10} \to$ Zn, $+2$ stable; $3d^1 \to$ Sc, $+3$ stable. Almost the entire "most-stable-oxidation-state" column of the periodic table follows from this one rule. JEE/NEET frequently ask the reverse problem ("given $\mu = 3.87$ BM, identify the ion") — same shortcut, run backwards.

Final Answer: V $\to +5$; Mn $\to +2$; Ni $\to +2$; Cr $\to +3$.

☞ Map $3d^n$ to element

$3d^1$:Sc, $3d^2$:Ti, $3d^3$:V, $3d^4$($3d^5 4s^1$):Cr, $3d^5$:Mn, $3d^6$:Fe, $3d^7$:Co, $3d^8$:Ni, $3d^9$($3d^{10} 4s^1$):Cu, $3d^{10}$:Zn. Two are Aufbau exceptions (Cr, Cu).

✗ "$3d^4$ does not exist"

Some students claim the question is wrong because "Cr is actually $3d^5 4s^1$" and therefore $3d^4 4s^2$ does not exist. That is over-thinking. The question gives a nominal d-count to identify the element; the actual ground state is irrelevant to the answer. The element is still Cr (Z = 24) and the answer is still $+3$.

Q 4.6 Name the oxometal anions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group number.

SOLUTION

Concept used. An **oxometal anion** (or oxoanion) is a negatively charged species in which a transition metal is bonded to oxygen atoms, e.g. $MnO_4{}^-$, $Cr_2O_7{}^{2-}$. The *group number* (in the modern IUPAC scheme, used by NCERT) is the column index 3 to 12 for the transition metals. We want oxoanions in which the central metal is in an oxidation state equal to that column index.

Step 1. Group numbers and the elements of the $3d$ series: Sc(3), Ti(4), V(5), Cr(6), Mn(7), Fe(8), Co(9), Ni(10), Cu(11), Zn(12).

Step 2. For a metal to show oxidation state equal to its group number, all its valence s and d electrons must be lost. This is achievable only for groups 3 to 7 (where the total valence electrons are ≤ 7 and a stable d^0 cation can be reached); past Mn (group 7) the loss of all valence electrons becomes very unfavourable.

Step 3. Identify the oxoanions for each match:

- Group 6, Cr ($+6$): $CrO_4{}^{2-}$ (chromate) and $Cr_2O_7{}^{2-}$ (dichromate).

- Group 7, Mn ($+7$): MnO_4^- (permanganate).
- Group 5, V ($+5$): VO_4^{3-} (vanadate).

Lower groups (Sc, Ti) also reach their group oxidation state in oxides (e.g. TiO_2) but no widely-named simple oxoanion of group number 4 is commonly listed at school level. For Ti in $+4$ in oxoanions one can quote TiO_3^{2-} (titanate) but it is far less prominent than Cr and Mn cases.

Step 4. The classic NCERT answer focuses on V, Cr and Mn.

VO_4^{3-}
V in +5 (group 5)

CrO_4^{2-}, $Cr_2O_7^{2-}$
Cr in +6 (group 6)

MnO_4^-
Mn in +7 (group 7)

Final Answer: VO_4^{3-} (V in +5, group 5), CrO_4^{2-} and $Cr_2O_7^{2-}$ (Cr in +6, group 6), and MnO_4^- (Mn in +7, group 7).

EXPERT'S SOLUTION *: Vivaan Reddy, B.Tech Chemical Engineering, IIT Bombay*

Strategic angle. Match each $3d$ element to its group number, then list oxoanions that pin the metal at exactly that oxidation state. Only the high-oxidation oxoanions of V, Cr and Mn satisfy.

Periodic-trend angle. Past Mn (group 7), the metal needs to shed ≥ 8 valence electrons to match its group number, which requires breaking the half-filled $3d^5$ shell of M^{2+} and then continuing past it. The energy cost rises sharply, so Fe(VIII), Co(IX), Ni(X) etc. are not observed in stable oxoanions of the $3d$ row. Only the $4d/5d$ analogues (Ru, Os in RuO_4, OsO_4) reach $+8$, because their higher principal quantum numbers and greater electron delocalisation soften the closed-shell penalty.

Step 1. Set up the assignment for groups 3 to 7: Sc–3, Ti–4, V–5, Cr–6, Mn–7. (Past 7, the metal cannot cleanly reach its group number.)

Step 2. For V in $+5$: VO_4^{3-} (vanadate); also polyvanadates such as $V_2O_7^{4-}$. Confirm oxidation state balance: V^{5+} $+4$ O^{2-} gives charge $5 - 8 = -3$. Correct. The corresponding acid H_3VO_4 (orthovanadic acid) and its salt Na_3VO_4 are well-known.

Step 3. For Cr in $+6$: CrO_4^{2-} (yellow chromate). Balance: $6 - 4 \cdot 2 = -2$. $Cr_2O_7^{2-}$ (orange dichromate): $2(6) - 7(2) = -2$. Both anions have Cr in $+6$. CrO_3 (chromium trioxide, anhydride of chromic acid) also has Cr in $+6$ but is not an anion.

Step 4. For Mn in $+7$: MnO_4^- (permanganate). Balance: $7 - 4 \cdot 2 = -1$. Mn is in $+7$, the highest oxidation state in the $3d$ row.

Step 5. Lower groups: Sc (group 3) and Ti (group 4) form oxides Sc_2O_3 and TiO_2

where the metal is in the group oxidation state, but the corresponding simple oxoanions ScO_3^{3-} or TiO_3^{2-} are uncommon at the school level and so are usually omitted. The classic answer focuses on V, Cr, Mn.

Numerical cross-check. Oxidation state of metal $\times 1 + \sum$(O charges) = net charge of the anion. For $Cr_2O_7^{2-}$: $2(+6) + 7(-2) = -2$. For MnO_4^{-}: $(+7) + 4(-2) = -1$. For VO_4^{3-}: $(+5) + 4(-2) = -3$. All check out.

Concept linkage. Higher group numbers reachable by heavier d-block: Ru(VIII) in RuO_4, Os(VIII) in OsO_4, Tc(VII) in TcO_4^{-}, Re(VII) in ReO_4^{-}. The capacity to reach group number grows down the group because larger atoms can accommodate more bonded oxygens.

Why this matters. These are exactly the oxoanions whose chemistry the chapter studies in detail ($K_2Cr_2O_7$, $KMnO_4$). Their oxidising power follows from the very high formal oxidation state of the metal: a small, highly charged Cr(VI) or Mn(VII) centre is hungry for electrons.

Final Answer: VO_4^{3-}, CrO_4^{2-}, $Cr_2O_7^{2-}$, MnO_4^{-}.

☞ Why only the high oxoanions?

The metal can only reach its group number's oxidation state when it sheds every $4s$ and $3d$ electron. Small, electronegative, π-donating ligands (O^{2-}, F^{-}) are needed to stabilise such a stripped cation. So group-number oxidation states are seen only in oxides, fluorides and oxoanions. Never in chlorides ($MnCl_7$ is unknown), bromides, iodides or sulfides.

Q 4.7 What is lanthanoid contraction? What are the consequences of lanthanoid contraction?

SOLUTION

Concept used. Lanthanoid contraction is the steady, almost regular decrease in atomic and ionic radii of the lanthanoids (Z = 57 to 71) as the atomic number rises. The cause is poor shielding by the $4f$ electrons: as one moves through Ce to Lu the nuclear charge increases by one each step, but the added $4f$ electron screens the outer $5d/6s$ electrons only weakly because $4f$ orbitals are very diffuse in the angular direction yet penetrate poorly. So the effective nuclear charge experienced by the outer electrons rises and the outer shell pulls in.

Step 1. Quantify the contraction. Atomic radius drops from $\approx$ 187 pm (La) to $\approx$ 173 pm (Lu); ionic radius of Ln^{3+} drops from $\approx$ 103 pm (La^{3+}) to $\approx$ 86 pm (Lu^{3+}). A total fall of about 14–18 pm across 14 elements: roughly 1 pm per element.

Step 2. Reason: in moving through the lanthanoids the added electron goes into a $4f$ orbital. The shielding constant of a $4f$ electron is much smaller than 1, so each successive nuclear charge increment is only partly cancelled. The effective nuclear charge $Z_{\text{eff}} = Z - \sigma$ rises steadily, and the orbitals contract.

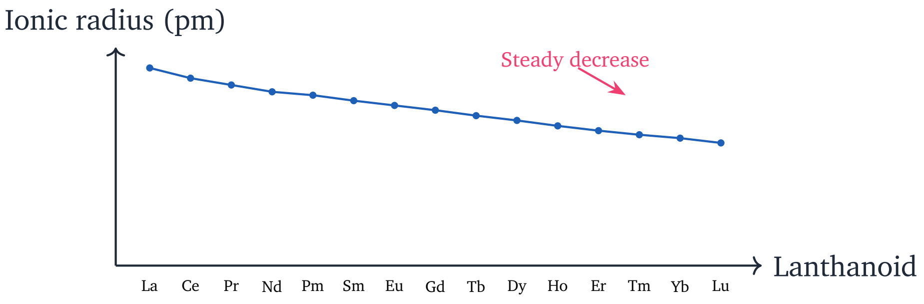
Consequences:

Step 1. **Almost identical radii of second-row (4d) and third-row (5d) transition metals.** For example $r(\text{Zr}) \approx r(\text{Hf}) \approx 159$ pm, $r(\text{Nb}) \approx r(\text{Ta})$, $r(\text{Mo}) \approx r(\text{W})$. So Zr and Hf, Nb and Ta, Mo and W are chemically very similar and difficult to separate.

Step 2. **Similarity of properties along the lanthanoid series.** Because the radii change so little, the chemical behaviour of all $+3$ lanthanoids is almost the same; their separation requires ion-exchange or solvent-extraction techniques exploiting tiny differences.

Step 3. **Increasing density of $5d$ metals.** The post-lanthanoid $5d$ metals (Hf, Ta, W, Re, Os, Ir, Pt, Au) have larger atomic mass but similar atomic volume to the $4d$ series because of the contraction, so their densities are significantly larger (W is twice as dense as Mo).

Step 4. **Basicity of Ln(OH)_3 decreases** from La(OH)_3 to Lu(OH)_3. As the cation gets smaller, the M—OH bond becomes more covalent and the hydroxide less basic.



Final Answer: Lanthanoid contraction: the steady decrease in atomic and ionic radii from La to Lu (about 1 pm per element), caused by poor shielding of outer electrons by $4f$. Consequences: near-identical $4d/5d$ pair radii (Zr/Hf, Nb/Ta, Mo/W), high densities of $5d$ metals, similar chemistry of all lanthanoids and decreasing basicity of Ln(OH)_3 across the series.

♥ Industrial impact

The Zr/Hf separation problem (caused directly by lanthanoid contraction) is critical to nuclear engineering: zirconium is “transparent” to neutrons and used in fuel cladding, while hafnium is the opposite (a neutron absorber) and used in control rods. Their similar chemistry made separation an early engineering hurdle.

EXPERT'S SOLUTION : *Tara Kapoor, Ph.D Organic Chemistry, IISc Bangalore*

Quick reading. "Lanthanoid contraction" is the 1 pm-per-element shrinkage of Ln^{3+} ions across La to Lu, a direct consequence of poor $4f$ shielding. The fall accumulates over 14 elements to about 14–18 pm: enough to wipe out the expected "one-row growth" between $4d$ and $5d$ transition metals.

Electronic-config reasoning. A $4f$ orbital has angular nodes that keep its electron density away from the nucleus in angular regions, but it lacks the radial node that the $5s$, $5p$ and $5d$ shells have. So its radial distribution is buried inside the outer shells. The result is a paradox: $4f$ orbitals are "inner" in shielding behaviour (don't block the nucleus from outer electrons) yet "outer" in angular extent. This dual nature is the deep reason for the contraction.

Step 1. Definition with the underlying reason: nuclear charge rises by one each step but the added $4f$ electron shields outer electrons poorly because $4f$ orbitals do not penetrate close to the nucleus. Hence Z_{eff} rises and outer-shell radius falls. Slater's rules give $\sigma(4f \to 4f) \approx 0.35$ and $\sigma(4f \to 5s, 5p) \approx 0.85$, both less than 1; nuclear charge gain is therefore only partly cancelled.

Step 2. Numerical anchor: La 187 pm → Lu 173 pm (atomic radii); La^{3+} 103 pm → Lu^{3+} 86 pm (ionic radii). Roughly 1 pm per element over 14 steps.

Step 3. Consequences, with one example each:

- Zr ($\approx$ 160 pm) and Hf ($\approx$ 159 pm) are near-identical: they go through the entire chemistry of group 4 together; separation by fractional crystallisation took decades.
- Densities of $5d$ metals are roughly twice those of $4d$: Os (22.6 g/cm^3) is the densest stable element; W (19.3 g/cm^3) is double Mo (10.2 g/cm^3).
- All Ln^{3+} salts are similar in colour and solubility; rare earth processing uses ion-exchange columns to separate them.
- Basicity La(OH)$_3$ > Lu(OH)$_3$. Smaller ions hold their hydroxides more tightly, so the bond is more covalent and the hydroxide is less basic.
- Lanthanoid ions of identical charge and similar radii interchange easily in minerals — that is why a single mine yields a complex Ln mixture (e.g. monazite).

Numerical cross-check. Total contraction (14 steps, La → Lu) of Ln^{3+}: $103 - 86 = 17$ pm. The transition-metal row Mo → W spans only 1 pm in atomic radius (Mo: 140, W: 141 pm), confirming the contraction has fully absorbed the expected $5d > 4d$ growth.

Concept linkage. The contraction has a cousin in the actinoid series ("actinoid contraction", ∼15–20 pm). It appears in different guises in many exam questions: "Zr and Hf have nearly the same chemistry" (size), "W is denser than Mo" (density), "Cr(OH)$_3$ is more basic than Lu(OH)$_3$" (basicity).

Why this matters. The contraction is the single most important structural fact about the lanthanoids. Almost every later exam question that says "why are properties of $4d$ and $5d$ groups so similar?" has lanthanoid contraction as its answer. Industrially, it is why Hf must be removed from Zr before Zr is used as fuel cladding in nuclear reactors — Hf is a strong neutron absorber and would shut down the reactor.

> **Final Answer:** Steady shrinkage from La to Lu due to poor $4f$ shielding, leading to similar radii of $4d/5d$ metals, high densities of $5d$ metals and similar lanthanoid chemistry.

☞ **Three signature numbers**

Lanthanoid contraction in three numbers: Δr(La → Lu) $\approx$ 14 pm in atom; $\approx$ 17 pm in Ln^{3+}; Zr $\approx$ Hf $\approx$ 159–160 pm. Memorise these to anchor every contraction-related answer.

Q 4.8 What are the characteristics of the transition elements and why are they called "transition elements"? Which of the d-block elements may not be regarded as the transition elements?

SOLUTION

Concept used. A **transition element** is, by IUPAC definition, an element whose atom has an incomplete d-sub-shell or which can give rise to cations with an incomplete d-sub-shell. The d-block elements that fail this test are *not* regarded as transition elements.

Step 1. **Position.** They occupy groups 3 to 12 of the periodic table, between the s-block and p-block. Their general outer configuration is $(n-1)d^{1-10}\,ns^{0-2}$. They mark the gradual transition in properties from the highly electropositive s-block metals to the much less metallic p-block elements, which is why they are called *transition* elements.

Step 2. **Characteristic properties:**

- All are typical metals: hard, high-melting, good conductors of heat and electricity.
- Show variable oxidation states (because $(n-1)d$ and ns are close in energy, electrons can be lost in varying numbers).
- Form coloured compounds (because of $d-d$ electronic transitions in partially filled d shells).
- Form complexes readily (small, highly charged cations with vacant low-energy d-orbitals).
- Are often paramagnetic (unpaired d electrons).

- Have high enthalpies of atomisation (strong metallic bonds involving d-electrons).
- Act as catalysts (variable oxidation states + ability to form coordination complexes).
- Form interstitial compounds and alloys readily.

Step 3. **Elements not regarded as transition elements:** Zn, Cd, Hg (group 12). In the ground state and in their common $+2$ oxidation state they all have d^{10} (completely filled d-sub-shell). For example Zn: $3d^{10}4s^2$; Zn^{2+}: $3d^{10}$. Since neither the atom nor the common ion has an incomplete d-sub-shell, they are "d-block but not transition".

Variable oxidation states	Coloured compounds	Paramagnetism
Complex formation	Catalytic activity	High m.p. & density
Interstitial compounds	Alloy formation	Hard, good conductors

> **Final Answer:** Transition elements (groups 3 to 12) have $(n-1)d^{1-10}ns^{0-2}$, show variable oxidation states, form coloured and paramagnetic compounds, complexes, alloys and act as catalysts. Zn, Cd and Hg have d^{10} in both atom and common ion and are not regarded as transition elements.

EXPERT'S SOLUTION *: Yash Chatterjee, M.Sc Chemistry, IIT Kanpur*

Structural observation. The IUPAC criterion is sharp: an element must have an incomplete d-shell in atom or common ion. Apply this filter to all 30 d-block elements; only Zn, Cd, Hg fail.

Periodic-trend angle. Transition elements bridge the gap between s-block (alkali, alkaline-earth) and p-block elements. Move left and metallic character grows (Na, Ca); move right into the p-block and ionic, brittle behaviour dominates (Si, P). The d-block is the gradual hand-over: alloys (metallic), oxoanions (non-metallic). The phrase "transition" captures this gradual character change.

Step 1. Recite the standard properties: variable O.S., coloured ions, paramagnetism, complex formation, catalysis, interstitial compounds, alloys, hardness, high melting points.

Step 2. Justify each property from electron-configuration logic. Variable O.S.: small energy gap between $(n-1)d$ and ns. Coloured: $d-d$ transitions need partially filled d. Paramagnetism: unpaired d electrons. High m.p.: strong metallic bonding from d-orbital overlap.

Step 3. Apply IUPAC criterion: Zn $(3d^{10}4s^2)$, Cd $(4d^{10}5s^2)$, Hg $(5d^{10}6s^2)$. All have d^{10} and form only $+2$ ions, which are also d^{10}. So neither atom nor ion has an incomplete d-shell. They are not transition elements in the strict sense.

Step 4. Note that all three (Zn, Cd, Hg) have low m.p. relative to "true" transition metals: Zn 420 °C, Cd 321 °C, Hg -39 °C (liquid at room temperature). Reason: closed d^{10} contributes nothing extra to metallic bonding.

Numerical anchor. Zn^{2+} = $[Ar]3d^{10}$; check $\mu = 0$ BM (diamagnetic). Sc^{3+} = $[Ar]3d^0$; $\mu = 0$ BM. Both are d-block but their atom-or-ion has incomplete d? Sc atom is $3d^14s^2$ so YES (incomplete d in atom); Zn atom is $3d^{10}4s^2$ so NO. That is why Sc is a transition element and Zn is not.

Concept linkage. The same closed-shell argument that excludes Zn, Cd, Hg also predicts their similarity to the s-block calcium group: white salts, $+2$ ion only, no colour. They are sometimes called the "post-transition metals".

Why this matters. On a typical exam, the question is split in two; remembering that the answer is exactly Zn, Cd, Hg saves a lot of guesswork. The IUPAC test "incomplete d in atom or common ion" gives a clean yes/no rule for every d-block element.

> **Final Answer:** Eight characteristic properties drive from a partially filled d shell; Zn, Cd and Hg, having d^{10} in atom and common ion, are excluded.

✗ Hg(I) is $d^{10}d^{10}$ not d^9

The mercurous ion is actually Hg_2^{2+} (a dimer with an Hg–Hg single bond), not Hg^+. Each Hg in Hg_2^{2+} still has d^{10}. So the existence of $+1$ mercury does not save Hg from exclusion; the dimer keeps d^{10}. The same is true for Cd, where Cd_2^{2+} has been characterised in melts.

♥ Why "transition" is more than a name

The gradual shift in metallic character across the d-block (hard metals at the centre, softer post-transition metals at the right edge) mirrors the transition between the strongly electropositive s-block and the weakly metallic p-block. Mendeleev placed these elements "in transition" precisely because their properties did not fit either neighbour cleanly. Modern IUPAC reaffirms this by the incomplete-d definition.

Q 4.9 **In what way is the electronic configuration of the transition elements different from that of the non-transition elements?**

SOLUTION

Concept used. An atom's **electronic configuration** shows how electrons fill the available orbitals. Transition metals are distinguished by having their valence electrons spread across two sub-shells of different principal quantum numbers, the $(n-1)d$ and ns. Non-transition (representative) elements have their valence electrons confined to the outermost shell only.

Step 1. **Transition elements (general):** $(n-1)d^{1-10}\,ns^{0-2}$ where $n = 4$, 5, 6 or 7. In other words, the differentiating electron enters the $(n-1)d$ sub-shell, an *inner* shell. Examples: Sc: $[\mathrm{Ar}]\,3d^1 4s^2$; Fe: $[\mathrm{Ar}]\,3d^6 4s^2$; Cu: $[\mathrm{Ar}]\,3d^{10} 4s^1$.

Step 2. **Non-transition elements (general):** $ns^{1 \text{ or } 2}$ for s-block; $ns^2\,np^{1-6}$ for p-block. The differentiating electron enters the outermost shell. Examples: Na: $[\mathrm{Ne}]\,3s^1$; Cl: $[\mathrm{Ne}]\,3s^2\,3p^5$.

Step 3. **Key consequence.** Because $(n-1)d$ and ns are close in energy, transition metals can lose a variable number of electrons and show several oxidation states. In non-transition elements, only the outermost ns and np electrons are available and the chemistry is dominated by one or two oxidation states (e.g. group 1 always $+1$, group 17 usually -1).

Step 4. **Coloured ions** arise from $d-d$ transitions in partly-filled d shells: a feature exclusive to transition elements.

Step 5. **Complex formation** is much more extensive for transition elements because of available low-energy d orbitals to accept lone pairs from ligands.

Transition	Non-transition
Diff. electron in $(n-1)d$ valence: $ns + (n-1)d$	Diff. electron in ns or np valence: ns, np
Variable O.S. (close d/s energies)	One or two O.S.
Coloured ions $d-d$ transitions	Usually colourless
Form many complexes	Form few complexes

Final Answer: Transition elements add the differentiating electron to an inner $(n-1)d$ sub-shell, giving the general configuration $(n-1)d^{1-10}ns^{0-2}$. Non-transition elements add it to the outermost ns or np sub-shell, giving $ns^{1\text{–}2}np^{0-6}$. This single structural difference accounts for variable oxidation states, coloured ions, complex formation and paramagnetism of transition metals.

EXPERT'S SOLUTION : *Rohit Singh, Ph.D Organic Chemistry, IISc Bangalore*

Picture-first. Picture two layers of orbitals in a transition-metal atom: an outer ns shell and an inner $(n-1)d$ shell, with very similar energies. In a non-transition atom there is only one valence layer.

Electronic-config reasoning. Energy-level diagram: the $(n-1)d$ and ns orbitals lie within ~ 100 kJ/mol of each other across the transition series. By contrast the gap between ns and np (representative elements) or between two adjacent shells ns and $(n+1)s$ is several hundred kJ/mol. The closeness of d and s is what makes the chemistry rich.

Step 1. For the transition row write the generic configuration $(n-1)d^{1-10}\,ns^{0-2}$ and note that both $(n-1)d$ and ns electrons are chemically active. So variable oxidation states emerge naturally: lose only ns, get $+2$; lose ns plus one d, get $+3$; and so on.

Step 2. For non-transition elements, the configuration is $ns^{1-2}\,np^{0-6}$. Only one shell is active, so oxidation states are limited to the group number (or group number -2 for the inert-pair effect in heavier p-block).

Step 3. Map the four characteristic-property differences directly to the configuration difference: partially filled $d \to$ colour; unpaired $d \to$ paramagnetism; multiple d/s ionisations $\to$ variable O.S.; vacant low-energy $d \to$ complex formation and catalysis.

Step 4. Differentiating-electron rule (a quick mnemonic): the differentiating electron is the last electron added on moving from element $(Z-1)$ to element Z. For transition elements it enters $(n-1)d$ (inner penultimate shell). For representative elements it enters ns or np (outermost shell). This is the textbook definition of "inner" vs "representative".

Step 5. Concept check: Cu is $3d^{10}4s^{1}$, an Aufbau exception. The differentiating electron (going from Ni Z=28 to Cu Z=29) is treated as a $3d$ electron, which is why Cu remains a transition element.

Concept linkage. The differentiating-electron rule is a universal periodic-table principle. s-block: differentiating in ns. p-block: in np. d-block: in $(n-1)d$. f-block: in $(n-2)f$. So our four blocks reflect exactly four kinds of differentiating electrons. The chemistry of each block follows from this single classification.

Numerical anchor. Fe: $[\mathrm{Ar}]3d^{6}4s^{2}$. Total valence electrons (4s + 3d): 8. Maximum oxidation state achievable: $+6$ (in FeO_4^{2-}, ferrate); common: $+2$ and $+3$. Compare Ca: $[\mathrm{Ar}]4s^{2}$. Total valence: 2. Maximum oxidation state: $+2$. The disparity in available oxidation states scales directly with the number of accessible valence electrons.

Why this matters. Once the configuration distinction is clear, every other property of transition metals becomes a corollary. This question is essentially asking students to read the configuration as the root cause of all of transition-metal chemistry.

Final Answer: Transition: $(n-1)d^{1-10}ns^{0-2}$, valence electrons in two adjacent shells, leading to variable O.S., colour, magnetism and complex formation. Non-transition: $ns^{1-2}np^{0-6}$, valence only in the outer shell, limited O.S.

☞ One-mark answer pattern

"Transition elements have partially filled $(n-1)d$ orbitals; their differentiating electron enters the penultimate shell. Non-transition elements have only ns and np valence orbitals; their differentiating electron enters the outermost shell." That is the two-sentence answer the marker expects.

Q 4.10 What are the different oxidation states exhibited by the lanthanoids?

SOLUTION

Concept used. The lanthanoids (La, Ce, ... , Lu; Z = 57 to 71) have the general atomic configuration $[\mathrm{Xe}]\,4f^{1-14}\,5d^{0-1}\,6s^2$. The $4f$ electrons are buried inside the noble-gas core and do not participate much in chemistry: they are well shielded by the $5s$, $5p$, $5d$, $6s$ electrons. So the dominant chemistry of lanthanoids is governed mainly by the loss of the two $6s$ and the one $5d$ (or, where there is no $5d$, the outermost $4f$) electron.

Step 1. **The dominant oxidation state is $+3$.** Every lanthanoid loses three electrons (two $6s$ + one $5d$ or $4f$) to give the very stable Ln^{3+} ion. Thus all 15 elements have a well-characterised $+3$ chemistry; this is the "solution chemistry" state of the lanthanoids.

Step 2. **Some lanthanoids also show $+2$ and $+4$.** These deviations are explained by reaching $4f^0$, $4f^7$ or $4f^{14}$ (empty, half-filled or fully filled f-shell, which are extra stable).

- $+4$ states: Ce^{4+} ($4f^0$, very common, used as a titrant), Tb^{4+} ($4f^7$, less common), Pr^{4+} and Nd^{4+} (in some solids), Dy^{4+} (rare).
- $+2$ states: Eu^{2+} ($4f^7$, half-filled, fairly stable), Sm^{2+} ($4f^6$, mild reducing), Yb^{2+} ($4f^{14}$, fully filled), Tm^{2+} (less stable).

Step 3. Apart from these, no other oxidation states are well established in lanthanoid chemistry. The narrow range of oxidation states (mostly just $+3$) is in fact a defining feature of f-block chemistry, in contrast to the wide range of d-block oxidation states.

O.S.	Examples	Reason
+4	Ce^{4+}, Tb^{4+}, Pr^{4+}	$4f^0$ or $4f^7$
+3	All Ln	Most common
+2	Eu^{2+}, Sm^{2+}, Yb^{2+}	$4f^7$ or $4f^{14}$

Final Answer: The lanthanoids principally show the $+3$ oxidation state (all 15 elements). A few also show $+2$ (Eu, Sm, Yb, Tm) and $+4$ (Ce, Tb, Pr, Nd) where the resulting f-configuration is f^0, f^7 or f^{14}.

EXPERT'S SOLUTION *: Diya Patel, M.Sc Chemistry, IIT Kanpur*

Quick reading. The $4f$ electrons are core-like. Almost every lanthanoid shows $+3$ as the dominant state. Departures ($+2$, $+4$) are driven by the extra stability of $4f^0$, $4f^7$, $4f^{14}$.
Periodic-trend angle. Compare lanthanoid oxidation-state variability to that of $3d$ transition metals (e.g. Mn shows $+2$ to $+7$). The contrast is sharp: $3d$ chemistry has six accessible oxidation states per element, $4f$ chemistry has typically one ($+3$) with rare departures. The reason — $4f$ orbitals are too buried to participate in bonding, so their occupation is decoupled from the oxidation state.

Step 1. State the dominant $+3$ chemistry: from $[\mathrm{Xe}]4f^n5d^{0/1}6s^2$, removing three electrons gives $[\mathrm{Xe}]4f^n$ (the buried $4f^n$ unchanged). All 15 lanthanoids form well-characterised Ln^{3+} salts: $LaCl_3$, $CeCl_3$, $NdCl_3$, ..., $LuCl_3$ all exist.

Step 2. Pick out $+4$ examples by configuration check: Ce $(4f^15d^16s^2) \to Ce^{4+}$ is $4f^0$; Tb $(4f^96s^2) \to Tb^{4+}$ is $4f^7$. Both very stable configurations. Pr and Nd can reach $+4$ in solid oxides (PrO_2, NdO_2) but not in aqueous solution. Ce(IV) is the lab standard: cerium(IV) ammonium sulfate $(NH_4)_4Ce(SO_4)_4$ is a redox titrant.

Step 3. Pick out $+2$ examples by configuration check: Eu $(4f^76s^2) \to Eu^{2+}$ is $4f^7$; Yb $(4f^{14}6s^2) \to Yb^{2+}$ is $4f^{14}$. Sm and Tm can also be reduced to $+2$ but are less stable and act as strong reducing agents. $EuSO_4$ (blue) is isolable; $YbCl_2$ is air-sensitive but well-defined.

Step 4. Note: $E^\circ(Ce^{4+}/Ce^{3+}) = +1.61$ V (strong oxidant; gains an e^- to reach $4f^1$); $E^\circ(Eu^{3+}/Eu^{2+}) = -0.43$ V (mild reductant; loses an e^- to reach $4f^6$ but resists going past $4f^7$).

Numerical cross-check. Spin-only μ for selected ions: Eu^{2+} ($4f^7$, 7 unpaired): $\sqrt{7 \cdot 9} = 7.94$ BM (experiment 7.9, very close). Sm^{3+} ($4f^5$, 5 unpaired): spin-only 5.92

BM, but observed only 1.5 BM (orbital contribution in lanthanoids is large; here it nearly cancels spin). So spin-only μ works well for f^7 (orbital quenched) but not for f^5.
Concept linkage. The configurations $4f^0, 4f^7, 4f^{14}$ are exactly the empty, half-filled, fully-filled milestones — same idea as d^0, d^5, d^{10} in the $3d$ row. The narrow lanthanoid oxidation-state range gives way to a wider range only in the early actinoids where $5f$ orbitals are more accessible (Q 4.29).
Why this matters. The narrow range of lanthanoid oxidation states is exactly why their separation is difficult: chemistry on the Ln^{3+} ions is almost the same for all 15 elements. Solvent extraction and ion exchange exploit only minute size differences. Industrially, Eu(II) salts find application in phosphors for white LEDs and X-ray screens, and Ce(IV) is the redox titrant used in quantitative analysis of Fe^{2+} and H_2O_2.

> **Final Answer:** Mostly $+3$; with $+4$ for Ce, Tb, Pr, Nd and $+2$ for Eu, Sm, Yb, Tm where $4f^0, 4f^7, 4f^{14}$ stability is reached.

☞ **The $f^0/f^7/f^{14}$ rule**

Among lanthanoids, any oxidation state other than $+3$ is driven by reaching empty, half-filled or fully-filled $4f$: Ce^{4+} (f^0), Tb^{4+} (f^7), Eu^{2+} (f^7), Yb^{2+} (f^{14}) are the four pillars. Pr^{4+}, Nd^{4+}, Sm^{2+}, Tm^{2+} are near-miss approximations.

Q 4.11 **Explain giving reasons:**
(i) Transition metals and many of their compounds show paramagnetic behaviour.
(ii) The enthalpies of atomisation of the transition metals are high.
(iii) The transition metals generally form coloured compounds.
(iv) Transition metals and their many compounds act as good catalysts.

SOLUTION

Concept used. Each of the four observations stems from one underlying feature: a *partially-filled d-sub-shell* provides unpaired electrons, strong metallic bonding, $d-d$ electronic transitions in the visible region, and vacant low-energy d-orbitals to bind reactants. So a single structural fact explains all four.

Step 1. **(i) Paramagnetism.** A substance is paramagnetic if it has unpaired electrons; the spin-only magnetic moment is

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

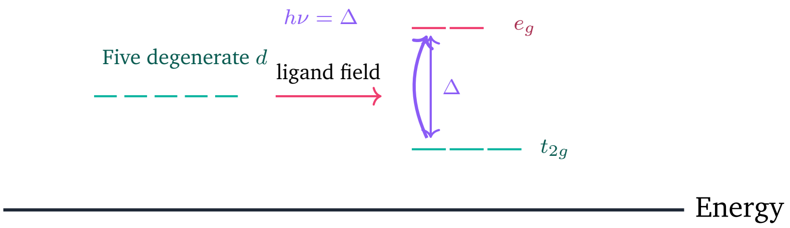
where n is the number of unpaired electrons. Almost every $3d$ transition-metal ion (except d^0, d^{10}) has at least one unpaired electron in $3d$, so the ion is paramagnetic. Example: Fe^{3+} ($3d^5$, 5 unpaired) gives $\mu = \sqrt{5 \cdot 7} = \sqrt{35} = 5.92$

BM.

Step 2. **(ii) High enthalpies of atomisation.** Transition metals have a large number of valence electrons in $(n-1)d$ and ns that participate in metallic bonding. The more unpaired d-electrons available for bonding, the stronger the metallic bond and the higher the enthalpy of atomisation. So values such as $\Delta_a H = 326$ kJ/mol for Sc and 397 kJ/mol for Cr greatly exceed values for s- and p-block metals.

Step 3. **(iii) Coloured compounds.** In an octahedral or tetrahedral ligand field, the five d-orbitals split into two energy levels separated by an energy gap Δ. A $d-d$ transition (an electron promoted from the lower set to the upper set) absorbs a photon of frequency $\nu = \Delta/h$. For most transition-metal complexes this frequency lies in the visible region (400–700 nm), so the compound appears in the colour complementary to the absorbed light. Example: $[\mathrm{Cu(H_2O)_6}]^{2+}$ absorbs red–orange light and appears blue.

Step 4. **(iv) Catalytic activity.** Many transition metals are excellent catalysts because (a) they have variable oxidation states, so they can give and accept electrons easily, (b) they have vacant low-energy d-orbitals that adsorb reactant molecules and weaken their bonds, (c) they can form unstable intermediates that lower the activation energy. Examples: V_2O_5 in the contact process for H_2SO_4; Fe in the Haber process for NH_3; Ni in hydrogenation.



> **Final Answer:** (i) Paramagnetism: unpaired $3d$ electrons. (ii) High $\Delta_a H$: strong metallic bonding involving d-electrons. (iii) Colour: $d-d$ transitions of energy Δ that match visible light. (iv) Catalysis: variable O.S. + vacant d-orbitals to bind substrates.

EXPERT'S SOLUTION *: Krishna Nair, M.Tech Chemical Engineering, IIT Delhi*

Strategic angle. Each part has a one-line answer with one example. Write the line, give the example, move on.

Concept linkage across parts. All four properties reduce to one structural fact: a *partially filled d-sub-shell with low energy gap to ns*. From this single feature follow (a) unpaired electrons (paramagnetism), (b) strong metallic bonding ($\Delta_a H$), (c) ligand-field splittings in the visible range (colour), (d) vacant low-lying d-orbitals (catalysis). The chapter packs four sub-parts into one structural concept.

Step 1. Paramagnetism arises from unpaired d-electrons. Use $\mu = \sqrt{n(n+2)}$ BM. Ti^{3+} (d^1): $n = 1$, $\mu = \sqrt{3} = 1.73$ BM. V^{2+} (d^3): $n = 3$, $\mu = \sqrt{15} = 3.87$ BM. Mn^{2+} (d^5): $n = 5$, $\mu = 5.92$ BM (maximum for $3d$).

Step 2. Enthalpy of atomisation is large because d- and s- electrons participate in metallic bonding. Cr and Mo, with d^5s^1, give the strongest bonds in their rows. The trend across a row peaks in the middle (Cr, Mo, W). Numerical values for $\Delta_a H$ (kJ/mol): Cr 397, Mn 281, Fe 416, Cu 339, Zn 130 — note the dip at Mn (half-filled d^5 is hard to disrupt for bonding) and at Zn (closed d^{10} contributes nothing).

Step 3. Colour comes from $d-d$ transitions. For Sc^{3+} (d^0) or Zn^{2+} (d^{10}) no $d-d$ transition is possible and the ion is colourless. Energy gap Δ depends on the ligand (**spectrochemical series**: $I^- < Br^- < Cl^- < F^- < H_2O < NH_3 <$ en $< CN^- < CO$) and on the geometry. Same metal can give different colours in different ligand fields: $[Co(H_2O)_6]^{2+}$ pink vs $[CoCl_4]^{2-}$ blue.

Step 4. Catalysis: variable O.S. lets the metal go through oxidation/reduction cycles cheaply. Vacant d-orbitals adsorb reactants. Examples: Fe in $N_2 + 3\,H_2 \longrightarrow 2\,NH_3$ (Haber), V_2O_5 in $2\,SO_2 + O_2 \longrightarrow 2\,SO_3$ (Contact), Ni in $R–CH=CH–R' + H_2 \rightarrow R–CH_2–CH_2–R'$ (Sabatier hydrogenation), $TiCl_3$ + Et_3Al in polyethylene (Ziegler-Natta).

Numerical cross-check. For Co^{2+} (d^7): $n = 3$, $\mu = \sqrt{15} = 3.87$ BM. Observed in $[Co(H_2O)_6]^{2+}$: ~ 4.7–5.2 BM (orbital contribution adds to spin-only). For high-spin Fe^{3+} (d^5): $\mu = \sqrt{35} = 5.92$ BM, observed 5.9 BM (almost perfect match because d^5 has a quenched L).

Periodic-trend angle. All four properties weaken at the two edges of the d-block: Sc (only d^1 in atom) and Zn (full d^{10}). Sc compounds are pale/colourless because Sc^{3+} is d^0. Zn compounds are diamagnetic, colourless and chemically unremarkable. The middle of the row is where transition-metal chemistry shines.

Why this matters. All four properties are board favourites. They all reduce to "partially filled d shell + close d/s energies" as the single causative factor. JEE/NEET tend to combine them: "which of the following $3d$ ions is the worst catalyst?" (answer: Sc^{3+} or Zn^{2+}, because no partial d).

> **Final Answer:** Same answers: unpaired d electrons (paramagnetism); d-bonding metallic lattice (high $\Delta_a H$); $d-d$ transitions (colour); variable O.S. + vacant d orbitals (catalysis).

♥ Industrial catalysts in three lines

Three classic Indian chemical industries use transition-metal catalysis directly: (1) Steam reforming of naphtha to syngas uses Ni/Al_2O_3; (2) Sulphuric acid manufacture (Contact process) uses V_2O_5; (3) Ammonia for fertiliser (Haber process) uses Fe with K promoter. Together they sustain billions of dollars of chemical production, all built on the variable oxidation states and vacant d-orbitals of these few metals.

Q 4.12 What are interstitial compounds? Why are such compounds well known for transition metals?

SOLUTION

Concept used. **Interstitial compounds** are non-stoichiometric materials in which small atoms (H, B, C, N) lodge themselves in the empty interstitial sites of a host metal lattice. The host's crystal structure is essentially preserved; only the interstices are partly occupied.

Step 1. Define and exemplify. Important interstitial compounds of transition metals include

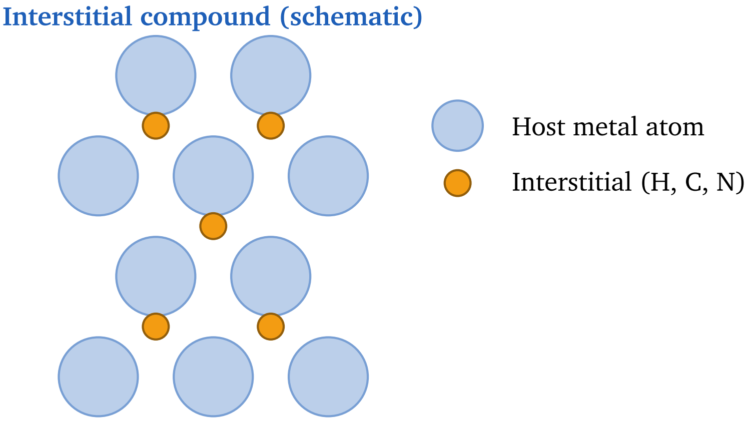
$$\mathrm{TiH_{1.7}},\quad \mathrm{VH_{0.56}},\quad \mathrm{TiC},\quad \mathrm{Mn_4N},\quad \mathrm{Fe_3H},\quad \mathrm{Fe_3C}\ \text{(cementite, in steel)}.$$

The composition is usually not a whole-number ratio, hence "non-stoichiometric". Hydrides of palladium absorb many times their volume of H_2.

Step 2. Recognise the key properties of these compounds: (a) They are very hard (often harder than the pure metal); some approach diamond hardness, e.g. TiC. (b) They have high melting points, often higher than the host metal. (c) They retain metallic conductivity. (d) They are chemically inert.

Step 3. Why transition metals form them so well:

- Their crystal lattices are close-packed but still have octahedral and tetrahedral holes large enough to accommodate small atoms like H ($r \approx 25$ pm), C ($r \approx 70$ pm) or N ($r \approx 70$ pm).
- Empty $(n-1)d$ orbitals can form bonds with the incoming small atom (a partial covalent contribution).
- Transition-metal lattices have strong metallic bonds (high $\Delta_a H$), so the host stays intact even when interstices are partly filled.



Final Answer: Interstitial compounds are non-stoichiometric solids formed when small atoms (H, B, C, N) fit into the lattice holes of a host metal. Transition metals form them readily because their close-packed lattices have suitable holes, they have vacant d-orbitals that bond with the small atoms and strong metallic bonds that hold the lattice together.

EXPERT'S SOLUTION *: Ananya Mehta, M.Sc Physical Chemistry, IIT Madras*

Structural observation. Picture a face-centred cubic lattice of large metal atoms. The geometric "gaps" (octahedral holes: $r/R = 0.414$; tetrahedral holes: $r/R = 0.225$) match the sizes of H, C, N exactly. So the chemistry is essentially the geometry working out. **Geometry calculation.** For an FCC host of metallic radius $R = 130$ pm (typical for $3d$ metals), the octahedral-hole radius is $0.414 \times 130 = 54$ pm. Hydrogen (atomic radius ~ 25 pm) fits comfortably; carbon (~ 70 pm) is a tight fit but bonds covalently to compensate; nitrogen (~ 70 pm) likewise. Halide or sulfide atoms ($\sim 100+$ pm) cannot fit interstitially and must displace metal atoms, giving rise to true ionic compounds instead.

Step 1. Define interstitial compound, with named examples (TiC, Fe_3C, Mn_4N, $VH_{0.56}$, $ZrH_{1.93}$). Note the non-stoichiometric subscripts — a hallmark of interstitial phases.

Step 2. State the three driving forces: (a) suitable hole sizes, (b) vacant d-orbitals for partial covalent bonding with the small atom, (c) strong metallic bonds to hold the host lattice. All three are properties of transition metals; that is why s- and p-block metals do not form such phases.

Step 3. List the four signature properties (hardness, high m.p., conductivity, chemical inertness). Use Fe_3C (cementite) to illustrate: it is the carbon-containing phase that gives steel its hardness while remaining electrically conducting. TiC melts at 3160 °C (vs Ti metal at 1668 °C) — proof of how interstitial bonding raises the m.p.

Step 4. Hydrogen storage example: Pd metal can absorb up to 935 times its volume of H_2 gas at room temperature, storing it as $\mathrm{PdH}_{0.7}$. This is the basis of fuel-cell hydrogen storage research.

Numerical anchor. For an FCC lattice, the number of octahedral holes equals the number of atoms (N); tetrahedral holes $= 2N$. So an interstitial compound like TiC can have C:Ti ratio up to 1:1 (filling all octahedral holes) without disturbing the host lattice geometry. Above ratio 1:1, the structure has to change.

Concept linkage. Interstitial alloys (small atoms in holes) contrast with substitutional alloys (similar-size atoms replacing host atoms; e.g. brass, bronze). Both are alloys, but the geometry is opposite. The transition metals provide both, depending on the partner.

Why this matters. Industrially, the entire steel industry rides on the formation of Fe_3C (and similar carbides in tool steels). Interstitial hydrides of Pd are the basis of hydrogen storage and the hydrogenation catalysis you see in margarine production. TiC, ZrC, HfC are used in rocket-nozzle ceramics. WC (tungsten carbide) is the cutting edge of every machine-tool drill.

> **Final Answer:** Small atoms in metal-lattice holes give hard, high-melting, conducting, inert non-stoichiometric phases. Transition metals are perfect hosts because of geometry plus vacant d-orbitals.

☞ Four signature properties to quote

Interstitial compounds are (i) very hard (TiC, WC approach diamond hardness); (ii) high-melting (Fe_3C 1227 °C is above pure Fe 1538 °C only because of carbon-driven hardening, but TiC 3160 °C is far above Ti); (iii) metallic conductors (electrons in the host band still flow); (iv) chemically inert (the host's metallic bonding is sealed). Four properties for one definition.

Q 4.13 How is the variability in oxidation states of transition metals different from that of the non-transition metals? Illustrate with examples.

SOLUTION

Concept used. Variability in oxidation state means the ability of an element to exist in more than one positive oxidation state in its compounds. In transition metals the variability is wide and the consecutive states differ by 1, while in non-transition metals the variability is narrow and consecutive states usually differ by 2 (the inert-pair effect).

Step 1. **Transition metals: consecutive states (differ by 1).** Because $(n-1)d$ and ns are close in energy, electrons can be removed one at a time. So a single element exhibits a ladder of oxidation states.

- Mn: $+2, +3, +4, +5, +6, +7$. Examples: MnO, Mn_2O_3, MnO_2, $MnO_4{}^{3-}$,

MnO_4^{2-}, MnO_4^-.

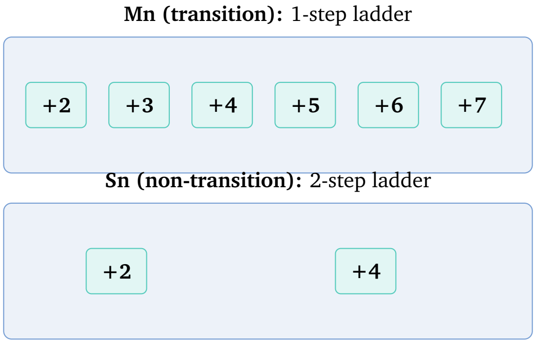
- V: +2, +3, +4, +5. Examples: VO, V_2O_3, VO_2, V_2O_5.
- Cr: +2, +3, +4, +5, +6. Examples: CrO, Cr_2O_3, CrO_2, CrO_3, $Cr_2O_7^{2-}$.

Step 2. Non-transition metals: states differ by 2. Because the valence shell is just $ns^2\,np^x$, removing electrons in pairs (one s and one p, or both p, or both s) is natural. The inert-pair effect (heavy p-block) further leaves the ns^2 pair on the metal.

- Tl: +1 and +3 (not +2).
- Sn: +2 and +4 (not +3).
- Pb: +2 and +4 (with +2 more stable due to inert-pair effect).
- P: +3 and +5; S: +2, +4, +6.

Step 3. Why the difference?

- In transition metals the $(n-1)d$ orbitals lie close in energy to ns, so individual electrons can be stripped one by one with comparable cost.
- In non-transition (representative) elements only the outermost shell is chemically active, and electrons are typically released in pairs.



Final Answer: Transition metals show many *consecutive* oxidation states differing by 1 (Mn: +2 to +7), thanks to the close energy of $(n-1)d$ and ns. Non-transition metals show *alternate* oxidation states differing by 2 (Sn: +2, +4), because only the outer shell is active and electrons leave in pairs.

EXPERT'S SOLUTION *: Aditya Joshi, B.Tech Chemical Engineering, IIT Bombay*

Quick reading. The contrast is one number: "differ by 1" for d-block, "differ by 2" for p-block.

Oxidation-state ladder reasoning. Transition metals can remove one d-electron at a time because each d orbital has nearly the same energy as its neighbour. Non-transition metals must break a filled ns^2 pair to access higher oxidation states; the extra cost is roughly $\Delta_i H_2 - \Delta_i H_1 \approx$ several hundred kJ/mol, which is why the intermediate states are skipped.

Step 1. Transition: list Mn from $+2$ to $+7$ as the extreme example. Comment: this is the longest ladder seen for any element. Cr from $+2$ to $+6$; V from $+2$ to $+5$. The chemistry of $KMnO_4$ and $K_2Cr_2O_7$ arises from these high states. Compounds: MnO, Mn_2O_3, MnO_2, K_3MnO_4 (Mn^{5+}), K_2MnO_4 (Mn^{6+}), $KMnO_4$ (Mn^{7+}) — all six states characterised.

Step 2. Non-transition: Sn $(+2, +4)$, Pb $(+2, +4)$, Tl $(+1, +3)$. Note that the lower state becomes more stable for heavier members of a group (inert-pair effect). Pb^{2+} is the stable form in salts like $PbCl_2$, while Pb^{4+} in PbO_2 is a strong oxidant.

Step 3. Reason: d/s orbital energy gap is small in transition metals (electrons stripped one by one); only one valence shell in non-transition (electrons stripped in pairs). Quantitative: for Mn, $\Delta_i H_1 = 717$ kJ/mol, $\Delta_i H_2 = 1509$, $\Delta_i H_3 = 3248$, $\Delta_i H_4 = 4940$ — gradual rise. For Sn, $\Delta_i H_1 = 708$, $\Delta_i H_2 = 1411$, $\Delta_i H_3 = 2942$, $\Delta_i H_4 = 3930$ — a clear jump at the $3 \to 4$ step (breaking ns^2).

Step 4. Periodic-trend angle: lower group oxidation-state stability increases down the p-block (inert-pair effect: Tl^{+} more stable than Tl^{3+}; Pb^{2+} more stable than Pb^{4+}). No analogous effect operates in the d-block; instead, heavier d-metals (4d, 5d) push toward *higher* oxidation states (Ru^{8+}, Os^{8+}).

Numerical cross-check. Consecutive $\Delta_i H$ values for Mn rise from 717 to 4940 kJ/mol smoothly (no jump). For Sn the $\Delta_i H_2 \to \Delta_i H_3$ jump from 1411 to 2942 (factor of 2) is where the $5s$ pair starts being broken; this is the kinetic barrier that produces the "differ by 2" pattern.

Concept linkage. The +2/+4 stability inversion in heavy p-block metals (Pb, Tl) is the "inert-pair" effect; an electronic-structure analog of the "half-filled stability" of d^5. Different shells, same idea — full sub-shells are hard to disturb.

Why this matters. The "differ by 1" rule lets you predict that Cr, Mn etc. will have many oxoanions and a rich redox chemistry, while p-block heavy metals settle into two main states. This is the basis of why transition-metal solutions show many colours and non-transition-metal solutions usually do not. JEE practice: "Why does V show $+2$ to $+5$ while Sn shows only $+2$ and $+4$?" — same answer as this question.

> **Final Answer:** Transition metals: many states differing by 1. Non-transition metals: typically two states differing by 2 (inert-pair effect).

☞ Quick contrast for one mark

"Transition metals show $+1, +2, +3, \ldots$ (differ by 1) because $(n-1)d$ and ns are close in energy. Non-transition metals show $+(n-2)$ and $+n$ (differ by 2) because of the inert-pair effect or because ns and np ionise in pairs.” One sentence each, both buzzwords landed.

Q 4.14 **Describe the preparation of potassium dichromate from iron chromite ore. What is the effect of increasing pH on a solution of potassium dichromate?**

SOLUTION

Concept used. Potassium dichromate ($K_2Cr_2O_7$) is prepared industrially from the ore **chromite**, $FeCr_2O_4$ (also written $FeO \cdot Cr_2O_3$). The preparation involves three stages: (1) oxidising fusion with alkali and air to convert chromite into sodium chromate; (2) acidification to interconvert chromate to dichromate; (3) salt-exchange with KCl to crystallise the less-soluble $K_2Cr_2O_7$.

Step 1. **Step 1: Oxidising fusion with sodium carbonate.** Chromite is finely powdered, mixed with sodium carbonate and roasted in air. The Cr(III) of chromite is oxidised to Cr(VI):

$$4\,\mathrm{FeCr_2O_4} + 8\,\mathrm{Na_2CO_3} + 7\,\mathrm{O_2} \longrightarrow 8\,\mathrm{Na_2CrO_4} + 2\,\mathrm{Fe_2O_3} + 8\,\mathrm{CO_2}.$$

The yellow sodium chromate Na_2CrO_4 dissolves out in water; Fe_2O_3 stays as residue and is filtered off.

Step 2. **Step 2: Acidification (chromate → dichromate).** The clear chromate solution is acidified with concentrated sulphuric acid:

$$2\,\mathrm{Na_2CrO_4} + \mathrm{H_2SO_4} \longrightarrow \mathrm{Na_2Cr_2O_7} + \mathrm{Na_2SO_4} + \mathrm{H_2O},$$

and equivalently:

$$2\,\mathrm{CrO_4}^{2-} + 2\,\mathrm{H^+} \rightleftharpoons \mathrm{Cr_2O_7}^{2-} + \mathrm{H_2O}.$$

The yellow chromate is converted to the orange dichromate.

Step 3. **Step 3: Conversion to $K_2Cr_2O_7$.** The hot solution of sodium dichromate is treated with potassium chloride:

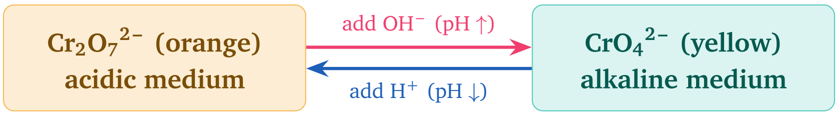
$$\mathrm{Na_2Cr_2O_7} + 2\,\mathrm{KCl} \longrightarrow \mathrm{K_2Cr_2O_7} + 2\,\mathrm{NaCl}.$$

On cooling, the much less soluble orange $K_2Cr_2O_7$ crystallises out, leaving the more soluble NaCl in the mother liquor.

Step 4. **Effect of increasing pH (added base).** The equilibrium

$$\mathrm{Cr_2O_7}^{2-} + 2\,\mathrm{OH^-} \rightleftharpoons 2\,\mathrm{CrO_4}^{2-} + \mathrm{H_2O}$$

shifts to the right when $[H^+]$ is lowered (i.e. pH rises). So the orange dichromate is converted to the yellow chromate in basic medium. In acidic medium (low pH) the dichromate $Cr_2O_7{}^{2-}$ dominates, while in alkaline medium (high pH) the chromate $CrO_4{}^{2-}$ dominates.



Final Answer: Chromite $FeCr_2O_4$ + Na_2CO_3 + air → Na_2CrO_4; acidify with H_2SO_4 to $Na_2Cr_2O_7$; treat with KCl; orange $K_2Cr_2O_7$ crystallises. On raising the pH (adding base) the orange $Cr_2O_7{}^{2-}$ is converted to yellow $CrO_4{}^{2-}$.

EXPERT'S SOLUTION : *Siddharth Banerjee, M.Sc Chemistry, IIT Kanpur*

Strategic angle. Three reactions and one equilibrium are the whole story; memorise them and the question is answered.

Oxidation-state ladder. Chromium begins in $+3$ (chromite), is oxidised to $+6$ during fusion with air, and stays at $+6$ in the chromate/dichromate equilibrium throughout. So the entire industrial process is driven by one oxidation step ($Cr^{3+} \to Cr^{6+}$) and then purification by acid/base chemistry. The mole arithmetic of the oxidation is: $Cr^{3+} \longrightarrow Cr^{6+} + 3\,e^-$, so 4 $FeCr_2O_4$ (which contains 8 Cr^{3+}) lose 24 electrons; the 7 O_2 on the left ($14 \times O$, each $0 \to -2$, $2e^-$ per atom, $= 28$ electrons) absorbs them with some left over for the $Fe^{2+} \to Fe^{3+}$ step. The book equation balances precisely.

Step 1. Roasting: $4\,FeCr_2O_4 + 8\,Na_2CO_3 + 7\,O_2 \longrightarrow 8\,Na_2CrO_4 + 2\,Fe_2O_3 + 8\,CO_2$. Yellow sodium chromate solution; iron(III) oxide residue is filtered off. Cr goes from $+3$ to $+6$; Fe goes from $+2$ to $+3$.

Step 2. Acidification: $2\,Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$. The colour goes from yellow to orange. Two chromate units condense by losing one water molecule (an inorganic "dehydration").

Step 3. Cation exchange: $Na_2Cr_2O_7 + 2\,KCl \longrightarrow K_2Cr_2O_7\,(s) + 2\,NaCl$. $K_2Cr_2O_7$ crystallises because it is far less soluble in cold water than $Na_2Cr_2O_7$. Solubilities (g/100 g water at 20 °C): $Na_2Cr_2O_7$ 183, $K_2Cr_2O_7$ 12 — a 15-fold difference is what drives selective crystallisation.

Step 4. pH effect (equilibrium): $Cr_2O_7{}^{2-} + 2\,OH^- \rightleftharpoons 2\,CrO_4{}^{2-} + H_2O$. Raising pH favours the chromate (yellow); lowering pH favours the dichromate (orange). This is a classic Le Chatelier application. The equilibrium constant $K \approx 4 \times 10^{14}$ at 25 °C, so the position depends very sensitively on $[H^+]$.

Numerical anchor. Check the dichromate-to-chromate stoichiometry: $Cr_2O_7{}^{2-}$ has $2 \cdot 6 - 7 \cdot 2 = -2$ charge (Cr in $+6$). Two $CrO_4{}^{2-}$ also have Cr in $+6$ ($6 - 8 = -2$ each, -4 total) and combine with two OH^- to give $Cr_2O_7{}^{2-}$ (-2) and H_2O (neutral). Cr's oxidation state stays $+6$ throughout — it is the connectivity that changes, not the redox state.

Concept linkage. The chromate/dichromate equilibrium is the inorganic-chemistry textbook example of Le Chatelier in acid-base shifting. Compare with the analogous equilibrium between phosphate and pyrophosphate, $2\,HPO_4{}^{2-} \rightleftharpoons P_2O_7{}^{4-} + H_2O$. Same condensation pattern.

Why this matters. The colour change with pH is exploited in indicator/titration chemistry. The chromate/dichromate ratio in soil runoff is also a useful indicator of acidity in Cr(VI) waste streams. Industrially, $K_2Cr_2O_7$ is the cheaper, less-soluble crystalline form preferred for shipping and lab use. The salt-exchange step ($Na_2Cr_2O_7 \longrightarrow K_2Cr_2O_7$) is a model of differential-solubility purification.

> **Final Answer:** Three-stage preparation: roast chromite + Na_2CO_3 + air; acidify to dichromate with H_2SO_4; precipitate as $K_2Cr_2O_7$ with KCl. Increasing pH converts $Cr_2O_7{}^{2-}$ (orange) to $CrO_4{}^{2-}$ (yellow).

✗ Don't confuse $Cr_2O_7{}^{2-}$ with $CrO_4{}^{2-}$ in equations

A common slip in board scripts is writing $CrO_4{}^{2-}$ in the oxidation half-reaction (it isn't strong enough in alkaline medium) or writing $Cr_2O_7{}^{2-} + 14\,OH^-$ for the oxidation (you must use acid). Rule: dichromate is the strong oxidant only in acidic medium; chromate is mild and converts to dichromate when acid is added.

Q 4.15 **Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with: (i) iodide, (ii) iron(II) solution, (iii) H_2S.**

SOLUTION

Concept used. In acidic solution the dichromate ion is a strong oxidising agent; the half-reaction is

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

Chromium goes from +6 in $Cr_2O_7{}^{2-}$ (orange) to +3 in Cr^{3+} (green). Six electrons are gained per dichromate ion. To balance any reaction we write the oxidation half-reaction of the reductant, multiply to match the 6 e^-, then add.

Step 1. **(i) With iodide I^-.** The oxidation half-reaction is

$$2\,I^- \longrightarrow I_2 + 2\,e^-.$$

Multiply by 3 to match 6 electrons:

$$6\,I^- \longrightarrow 3\,I_2 + 6\,e^-,$$

and add to the dichromate half-reaction:

$$Cr_2O_7{}^{2-} + 14\,H^+ + 6\,I^- \longrightarrow 2\,Cr^{3+} + 3\,I_2 + 7\,H_2O.$$

Colour change: orange dichromate → green Cr^{3+}; iodine (brown solution) liberated.

Step 2. **(ii) With iron(II), Fe^{2+}.** The oxidation half-reaction is

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-.$$

Multiply by 6:

$$6\,Fe^{2+} \longrightarrow 6\,Fe^{3+} + 6\,e^-,$$

and add:

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

This is the standard volumetric reaction in iron titrations with $K_2Cr_2O_7$.

Step 3. **(iii) With H_2S.** Sulfur in H_2S is in -2; on oxidation it goes to elemental S (0):

$$H_2S \longrightarrow S + 2\,H^+ + 2\,e^-.$$

Multiply by 3:

$$3\,H_2S \longrightarrow 3\,S + 6\,H^+ + 6\,e^-,$$

and add to the dichromate half-reaction. Cancelling 6 H^+ from both sides:

$$Cr_2O_7{}^{2-} + 8\,H^+ + 3\,H_2S \longrightarrow 2\,Cr^{3+} + 3\,S + 7\,H_2O.$$

Pale yellow sulfur is precipitated; orange dichromate becomes green Cr^{3+}.

Reductant	Product	Visible change
I^-	I_2	Iodine brown
Fe^{2+}	Fe^{3+}	Pale green → yellow
H_2S	S (s)	Pale-yellow ppt.

Final Answer: (i) $Cr_2O_7{}^{2-} + 14\,H^+ + 6\,I^- \longrightarrow 2\,Cr^{3+} + 3\,I_2 + 7\,H_2O$. (ii) $Cr_2O_7{}^{2-} + 14\,H^+ + 6\,Fe^{2+} \longrightarrow 2\,Cr^{3+} + 6\,Fe^{3+} + 7\,H_2O$. (iii) $Cr_2O_7{}^{2-} + 8\,H^+ + 3\,H_2S \longrightarrow 2\,Cr^{3+} + 3\,S + 7\,H_2O$.

EXPERT'S SOLUTION : *Neha Desai, M.Sc Physical Chemistry, IIT Madras*

Picture-first. Write the dichromate half-reaction once; write the reductant half-reaction; scale to match 6 e^-; add.
Equivalent-weight angle. The equivalent weight of $K_2Cr_2O_7$ in acid oxidation is $M/6 = 294.18/6 = 49.03$ g/equiv. (M = 294.18 g/mol; 6 electrons per formula unit.) For $KMnO_4$ in acid it is $M/5 = 158/5 = 31.6$ g/equiv. Knowing these two equivalent weights converts titration volumes to moles directly.

Step 1. Reference half-reaction

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

$E^\circ = +1.33$ V (strong oxidant in acid).

Step 2. For iodide, each I^- loses 1 e^- to give I_2; scaling: 6 I^- per dichromate, giving 3 I_2. Colour change: orange (dichromate) and colourless (iodide) → green (Cr^{3+}) and brown (I_2).

Step 3. For Fe^{2+}, each gives 1 e^- to become Fe^{3+}; scaling: 6 Fe^{2+} per dichromate. Diphenylamine is the usual end-point indicator (changes from colourless to violet on the first slight excess of $Cr_2O_7{}^{2-}$).

Step 4. For H_2S, sulphur goes $-2 \to 0$, so each H_2S gives 2 e^- and 2 H^+. Three H_2S per dichromate; the 6 H^+ produced cancel against the 14 H^+ needed, leaving 8 H^+ on the LHS. Visible: pale-yellow sulfur precipitates.

Step 5. Compare with $KMnO_4$ oxidation of the same reductants (Q 4.16). The pattern is identical except the half-reaction coefficient (6 e^- for dichromate vs 5 e^- for permanganate).

Numerical cross-check. For the iodide reaction, 1 mole of $K_2Cr_2O_7$ should liberate 3 moles I_2, i.e. 3 mol × 253.8 g/mol $= 761$ g of iodine per 294 g dichromate. Mass ratio is roughly 2.6:1 (I_2:$K_2Cr_2O_7$). Easy to verify.
Concept linkage. The 6-electron capacity of dichromate underlies its use in COD (Chemical Oxygen Demand) measurement of wastewater: organic matter is oxidised by excess $K_2Cr_2O_7/H_2SO_4$, and the residual dichromate is back-titrated. 1 mole of organic carbon needs $1/3$ mole $Cr_2O_7{}^{2-}$ for oxidation to CO_2.
Why this matters. The dichromate-iron(II) titration is one of the standard quantitative methods in inorganic chemistry. It is also the easiest mnemonic for the $1:6$ stoichiometry $Cr_2O_7{}^{2-}$: Fe^{2+}. In environmental chemistry, the $Cr_2O_7{}^{2-}$-based COD test is the workhorse measurement of wastewater quality.

Final Answer: Use $Cr_2O_7{}^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O$ with appropriate stoichiometry: 6 I^- (giving 3 I_2), 6 Fe^{2+} (giving 6 Fe^{3+}) or 3 H_2S (giving 3 S) per dichromate.

☞ **Dichromate vs permanganate at a glance**

$Cr_2O_7^{2-}$: 6 e^- per ion, $E^\circ = +1.33$ V, used in acid only, requires no special indicator (Cr^{3+} is green — self-indicating). MnO_4^-: 5 e^- per ion in acid, $E^\circ = +1.51$ V, self-indicating (purple → colourless). Two electrons differ, two volts differ a bit, two oxidants compete.

☞ How many H^+ go on the LHS?

For dichromate-driven oxidations: start with 14 H^+, then subtract any H^+ produced by the reductant's oxidation half-reaction. Iodide and Fe^{2+}: no H^+ produced, so the overall equation keeps 14 H^+. H_2S: produces 6 H^+, so the overall reduces to 8 H^+ on LHS. SO_2: produces 4 H^+, so the overall has 10 H^+ on LHS.

Q 4.16 **Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with (i) iron(II) ions, (ii) SO_2 and (iii) oxalic acid? Write the ionic equations for the reactions.**

SOLUTION

Concept used. Potassium permanganate ($KMnO_4$) is prepared from pyrolusite ore, MnO_2, in two stages: (1) oxidising fusion with KOH and KNO_3 (or air) to give green K_2MnO_4; (2) oxidation of manganate (Mn +6) to permanganate (Mn +7), either electrolytically or with disproportionation in acid. In acidic solution MnO_4^- is a strong oxidising agent with $E^\circ = +1.51$ V; the half-reaction is

$$MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O.$$

Step 1. **Step 1 (oxidising fusion).** Powdered MnO_2 is fused with KOH in the presence of KNO_3 (or air) as oxidant:

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

The dark green K_2MnO_4 contains Mn in +6.

Step 2. **Step 2a (electrolytic oxidation).** Dissolve K_2MnO_4 in water and oxidise to permanganate electrolytically at the anode:

$$MnO_4^{2-} \longrightarrow MnO_4^- + e^-.$$

The purple $KMnO_4$ crystallises on cooling.

Step 3. **Step 2b (disproportionation).** In acidic solution MnO_4^{2-} disproportionates:

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

Two parts of Mn(VI) go to Mn(VII), one part to Mn(IV).

Step 4. **(i) With Fe^{2+}.** Each iron(II) loses 1 e^-; five Fe^{2+} per MnO_4^- to balance 5 e^-:

$$MnO_4^- + 8\,H^+ + 5\,Fe^{2+} \longrightarrow Mn^{2+} + 5\,Fe^{3+} + 4\,H_2O.$$

Step 5. **(ii) With SO_2.** SO_2 (S in +4) is oxidised to SO_4^{2-} (S in +6). The oxidation half-reaction is

$$SO_2 + 2\,H_2O \longrightarrow SO_4^{2-} + 4\,H^+ + 2\,e^-.$$

Multiply by 5 (to match 10 e^- when scaled to 2 MnO_4^-); equivalently, scale the permanganate half-reaction by 2 and the SO_2 oxidation by 5:

$$2\,MnO_4^- + 5\,SO_2 + 2\,H_2O \longrightarrow 2\,Mn^{2+} + 5\,SO_4^{2-} + 4\,H^+.$$

Note that the net acid balance gives 4 H^+ on the right.

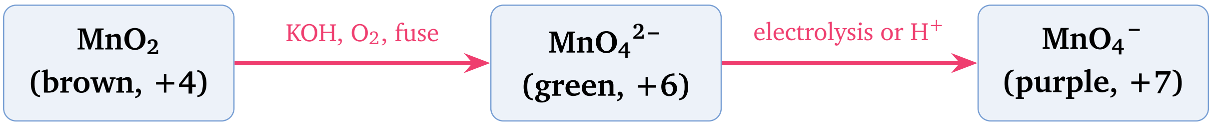
Step 6. **(iii) With oxalic acid $H_2C_2O_4$.** Carbon in oxalate is +3; it is oxidised to CO_2 (C in +4), releasing 2 e^- per molecule:

$$C_2O_4^{2-} \longrightarrow 2\,CO_2 + 2\,e^-.$$

Scaling: 2 MnO_4^- per 5 $C_2O_4^{2-}$ (to match 10 e^-):

$$2\,MnO_4^- + 5\,C_2O_4^{2-} + 16\,H^+ \longrightarrow 2\,Mn^{2+} + 10\,CO_2 + 8\,H_2O.$$

This is the standard reaction in the permanganate titration of oxalic acid (warm conditions, ∼ 60 °C, because the reaction is autocatalysed by Mn^{2+}).



Final Answer: Preparation: MnO_2 + KOH + O_2 → K_2MnO_4 (green, Mn +6); then electrolytic oxidation or acid-disproportionation gives $KMnO_4$ (purple, Mn +7). Reactions: (i) $MnO_4^- + 8\,H^+ + 5\,Fe^{2+} \longrightarrow Mn^{2+} + 5\,Fe^{3+} + 4\,H_2O$; (ii) $2\,MnO_4^- + 5\,SO_2 + 2\,H_2O \longrightarrow 2\,Mn^{2+} + 5\,SO_4^{2-} + 4\,H^+$; (iii) $2\,MnO_4^- + 5\,C_2O_4^{2-} + 16\,H^+ \longrightarrow 2\,Mn^{2+} + 10\,CO_2 + 8\,H_2O$.

EXPERT'S SOLUTION : *Ankit Pillai, B.Tech Chemical Engineering, IIT Bombay*

Strategic angle. The whole question is the half-reaction $MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O$ (memorise) plus three oxidation half-reactions. Scale to match 5 e^- (or a multiple of 5) and add.

Oxidation-state ladder. Manganese steps from +4 in MnO_2 (the starting ore) to +6 in MnO_4^{2-} (alkaline fusion) to +7 in MnO_4^- (electrolysis or disproportionation). In the oxidation reactions, Mn^{7+} is reduced back to Mn^{2+} ($+7$ to $+2$, gaining 5 e^-). The full ladder of manganese oxidation states is therefore mapped onto this one chapter: $+4 \to +6 \to +7$ (synthesis), $+7 \to +2$ (use).

Step 1. Fe^{2+}/Fe^{3+}: 1 e^- each. Scale by 5. Give $MnO_4{}^- + 8\,H^+ + 5\,Fe^{2+} \longrightarrow Mn^{2+} + 5\,Fe^{3+} + 4\,H_2O$. This is the basis of $\mathrm{KMnO_4}$ titration of iron(II) (no indicator needed; end-point is the first persistent pink).

Step 2. $SO_2 \longrightarrow SO_4{}^{2-}$: 2 e^-. Scale by 5 (to match 10 e^- on doubling permanganate): result has 4 H^+ on right. $2\,MnO_4{}^- + 5\,SO_2 + 2\,H_2O \longrightarrow 2\,Mn^{2+} + 5\,SO_4{}^{2-} + 4\,H^+$. SO_2 bubbled into purple $KMnO_4$ decolourises it.

Step 3. Oxalate $C_2O_4{}^{2-} \longrightarrow 2\,CO_2$: 2 e^-. Scale by 5. $2\,MnO_4{}^- + 5\,C_2O_4{}^{2-} + 16\,H^+ \longrightarrow 2\,Mn^{2+} + 10\,CO_2 + 8\,H_2O$. Warm the mixture; the reaction is autocatalysed by the Mn^{2+} formed. (Initially slow, then suddenly rapid — a classic kinetics demonstration.)

Step 4. Equivalent-weight check: $M(KMnO_4) = 158.03$ g/mol; equivalent weight $= 158/5 = 31.6$ g/equiv. (5 because 5 electrons per Mn). For oxalate ($Na_2C_2O_4$, $M = 134$ g/mol), equivalent weight $= 134/2 = 67$ g/equiv. The mole ratio $KMnO_4$:$Na_2C_2O_4$ $= 2 : 5$, so the equivalent ratio $= 1 : 1$, as expected.

Numerical anchor. Permanganate's E° values in different media: $+1.51$ V in acid (Mn^{2+} product, $5\,e^-$); $+0.60$ V in neutral (MnO_2 product, $3\,e^-$); $+0.56$ V in alkaline ($MnO_4{}^{2-}$ product, $1\,e^-$). The choice of medium determines both the product and the oxidising power.

Concept linkage. Notice that SO_2 acts as a reductant toward $KMnO_4$ but as an oxidant toward H_2S ($\mathrm{SO_2 + 2\,H_2S \longrightarrow 3\,S + 2\,H_2O}$, sulfur recovery). Sulphur in $+4$ is amphoteric in redox — a classic illustration of the variable oxidation behaviour of p-block elements.

Why this matters. Permanganate is the workhorse oxidant of school redox chemistry. The ferrous- and oxalate-titrations test the $1{:}5$ and $2{:}5$ stoichiometries respectively. The oxalate titration is also the basis for measuring dissolved Ca^{2+} indirectly (precipitate as CaC_2O_4, dissolve in acid, titrate the oxalate with $KMnO_4$).

Final Answer: Same three equations as above.

✗ Oxalate titration: 60–70 °C, not room temperature

A standard exam error is doing the oxalate–permanganate titration at room temperature. The reaction is autocatalytic: the first traces of Mn^{2+} formed catalyse further reduction. So the titration is done warm (~ 60–$70\,^\circ$C) to initiate the reaction. Get this wrong and the titration is sluggish at first and rapid later, giving an erratic end-point.

Q 4.17 For M^{2+}/M and M^{3+}/M^{2+} systems the E° values for some metals are as follows:

Cr^{2+}/Cr: $-0.9\,V$; Cr^{3+}/Cr^{2+}: $-0.4\,V$;
Mn^{2+}/Mn: $-1.2\,V$; Mn^{3+}/Mn^{2+}: $+1.5\,V$;
Fe^{2+}/Fe: $-0.4\,V$; Fe^{3+}/Fe^{2+}: $+0.8\,V$.

Use this data to comment upon:
(i) the stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} or Mn^{3+}, and
(ii) the ease with which iron can be oxidised as compared to a similar process for either chromium or manganese metal.

SOLUTION

Concept used. A standard reduction potential E° is the tendency of the species to be *reduced*. A large positive E° for the M^{3+}/M^{2+} couple means M^{3+} is easily reduced (it is a strong oxidiser; equivalently M^{3+} is unstable in solution). A more negative E° for M^{2+}/M means the metal is more easily oxidised to M^{2+}.

Step 1. **(i) Stability of M^{3+} in acidic solution.** Compare the three $E^\circ(M^{3+}/M^{2+})$ values:

- Cr^{3+}/Cr^{2+}: -0.4 V. Negative, so the reduction of Cr^{3+} is not favoured; Cr^{3+} is stable in acidic medium.
- Fe^{3+}/Fe^{2+}: $+0.8$ V. Moderate positive; Fe^{3+} can be reduced, so it is less stable than Cr^{3+} but still survives in solution.
- Mn^{3+}/Mn^{2+}: $+1.5$ V. Strongly positive; Mn^{3+} is reduced very easily, so Mn^{3+} is very unstable in solution (it disproportionates or oxidises water).

Conclusion: order of stability of M^{3+} ions in acid is

$$Cr^{3+} > Fe^{3+} > Mn^{3+}.$$

Configuration check supports this: Cr^{3+} (t_{2g}^3, half-filled t_{2g}) is extra stable; Fe^{3+} (d^5) half-filled overall and so is moderately stable; Mn^{3+} (d^4) is unstable.

Step 2. **(ii) Ease of oxidation of M to M^{2+}.** Compare the three $E^\circ(M^{2+}/M)$ values:

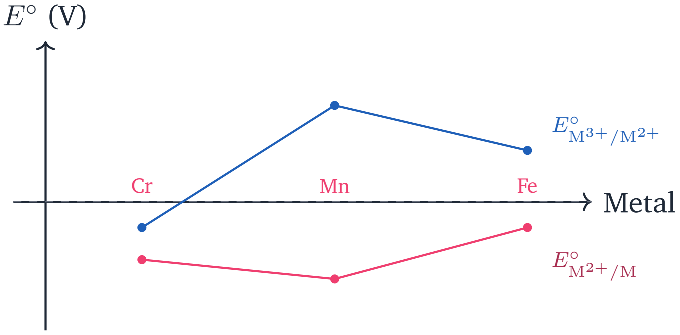
- Mn: -1.2 V. Very negative, so Mn is oxidised most easily.
- Cr: -0.9 V. Less negative than Mn, so Cr is oxidised less easily than Mn.
- Fe: -0.4 V. Least negative of the three, so Fe is oxidised *least* easily.

Conclusion: order of ease of oxidation is

$$\text{Mn} > \text{Cr} > \text{Fe}.$$

Iron is oxidised *less easily* than either chromium or manganese.

Step 3. Make sense of the trend: the $E^\circ(M^{2+}/M)$ value is essentially set by the sum of (sublimation enthalpy) + (first two ionisation enthalpies) minus (hydration enthalpy of $\mathrm{M^{2+}}$). The unusually negative value at Mn arises because $\mathrm{Mn^{2+}}$ is extra stable (d^5).



Final Answer: (i) Stability of $\mathrm{M^{3+}}$ in acid: $\mathrm{Cr^{3+}} > \mathrm{Fe^{3+}} > \mathrm{Mn^{3+}}$, because $E^\circ(\mathrm{M^{3+}/M^{2+}})$ rises from -0.4 to $+0.8$ to $+1.5$ V. (ii) Ease of oxidation of metal: Mn > Cr > Fe, because $E^\circ(\mathrm{M^{2+}/M})$ goes from -1.2 (most easily oxidised) to -0.9 to -0.4 V (least easily).

EXPERT'S SOLUTION : *Pooja Kumar, M.Sc Chemistry, IIT Kanpur*

Quick reading. Sign-and-magnitude reading of two columns of E° does the work. "More positive E°" means the left-hand species is reduced more easily; "more negative E°" means the metal is oxidised more easily.

Energetic breakdown of $E^\circ(\mathrm{M^{2+}/M})$. The potential can be decomposed into three terms:

$$\Delta_f G^\circ(\mathrm{M^{2+}/M}) = \Delta_{sub}H + (\Delta_i H_1 + \Delta_i H_2) - \Delta_{\mathrm{hyd}}H(\mathrm{M^{2+}}) - T\Delta S.$$

A large negative E° means $\Delta G < 0$ for $\mathrm{M \longrightarrow M^{2+} + 2\,e^-}$, i.e. small ionisation cost plus large hydration energy. This is exactly the situation for Mn (extra-stable d^5 $\mathrm{Mn^{2+}}$ hydrates strongly).

Step 1. Rank by $E^\circ(\mathrm{M^{3+}/M^{2+}})$ for stability of $\mathrm{M^{3+}}$. Smaller (more negative) is more stable: Cr (-0.4 V) > Fe ($+0.8$ V) > Mn ($+1.5$ V). Convert each E° to $\Delta G^\circ = -nFE^\circ$ (n=1): Cr $+39$ kJ/mol, Fe -77 kJ/mol, Mn -145 kJ/mol. The Mn couple is the most exergonic for reduction, confirming the instability of $\mathrm{Mn^{3+}}$.

Step 2. Rank by $E^\circ(\mathrm{M^{2+}/M})$ for ease of oxidation of metal. More negative is more easily oxidised: Mn (-1.2 V) > Cr (-0.9 V) > Fe (-0.4 V). Convert to $\Delta G^\circ_{\mathrm{ox}}(\mathrm{M \to M^{2+}}) = +nFE^\circ$ (n=2): Mn $+231$ kJ/mol favourable, Cr $+174$ kJ/mol, Fe $+77$ kJ/mol. Mn is by far the most easily oxidised metal of the three.

Step 3. Tie back to electron configuration: $\mathrm{Cr^{3+}}$ (t_{2g}^3) and $\mathrm{Mn^{2+}}$ (d^5) are configuration-stabilised, while $\mathrm{Mn^{3+}}$ (d^4) is not. So the order is electronic-structure-driven, not just a thermodynamic curiosity.

Step 4. Cross-check: Mn^{3+} in solution is unstable enough that it slowly oxidises water: $4\,Mn^{3+} + 2\,H_2O \longrightarrow 4\,Mn^{2+} + O_2 + 4\,H^+$. So $MnSO_4$ solutions can be left in air, but Mn^{3+} solutions need careful preparation.

Numerical cross-check. Sum of first three ionisation enthalpies (kJ/mol): Cr 5226, Fe 5290, Mn 5474. Mn has the highest $\Sigma\Delta_i H$, consistent with Mn^{3+} being the hardest of the three to form and so the most aggressive oxidant once formed.

Concept linkage. Disproportionation of Mn^{3+}:
$2\,Mn^{3+} + 2\,H_2O \longrightarrow Mn^{2+} + MnO_2 + 4\,H^+$ — driven by the extreme instability of Mn^{3+}. Similar disproportionation of Cu^+ in water and of ClO^- in alkaline solution all share the same thermodynamic pattern.

Why this matters. The same data make Mn^{3+} a strong oxidant in acid (used in $Mn(OAc)_3$ oxidations in organic chemistry, e.g. radical cyclisations) and explain why iron rusts more slowly than freshly polished manganese metal. JEE/NEET: “Which is the strongest reducing agent: Mn^{2+}, Fe^{2+}, Cr^{2+}?” — answer Cr^{2+}, because its $E^\circ(Cr^{3+}/Cr^{2+}) = -0.4$ V means it readily gives up an electron to become Cr^{3+}.

> **Final Answer:** Stability of M^{3+}: Cr > Fe > Mn. Ease of oxidation of M to M^{2+}: Mn > Cr > Fe.

☞ **Convert E° to ΔG° in your head**

$\Delta G^\circ = -nFE^\circ$. Useful shortcut: $1\,\text{V} \times 1\,\text{eq} \approx 96.5$ kJ/mol. So a couple with $E^\circ = +1$ V has $\Delta G = -96.5$ kJ/mol (per electron). The Mn(III)/Mn(II) couple at $+1.57$ V gives -151 kJ/mol — strongly favourable reduction. The Cr(III)/Cr(II) couple at -0.41 V gives $+40$ kJ/mol — unfavourable reduction, i.e. Cr(II) is the easily-oxidised form.

Q 4.18 Predict which of the following will be coloured in aqueous solution? Ti^{3+}, V^{3+}, Cu^+, Sc^{3+}, Mn^{2+}, Fe^{3+} and Co^{2+}. Give reasons for each.

SOLUTION

Concept used. An aqueous transition-metal ion is coloured when there is at least one unpaired d-electron and a partly filled d-sub-shell, allowing $d-d$ **transitions** in the visible region. Ions with a fully filled (d^{10}) or completely empty (d^0) d-shell are colourless because no $d-d$ transition is possible.

Step 1. Write the d-electron count of each ion and decide coloured vs colourless.

- Ti^{3+}: Ti(Z=22), $3d^2 4s^2$. $Ti^{3+} \to 3d^1$. One unpaired electron ⇒ **coloured** (violet/purple).
- V^{3+}: V(Z=23), $3d^3 4s^2$. $V^{3+} \to 3d^2$. Two unpaired electrons ⇒ **coloured** (green).

- Cu^+: Cu(Z=29), $3d^{10}4s^1$. $Cu^+ \to 3d^{10}$. Fully filled d-shell $\Rightarrow$ **colourless**.
- Sc^{3+}: Sc(Z=21), $3d^14s^2$. $Sc^{3+} \to 3d^0$. Empty d-shell $\Rightarrow$ **colourless**.
- Mn^{2+}: Mn(Z=25), $3d^54s^2$. $Mn^{2+} \to 3d^5$. Five unpaired electrons $\Rightarrow$ **coloured** (pale pink; weak because $d-d$ transitions are spin-forbidden in high-spin d^5).
- Fe^{3+}: Fe(Z=26), $3d^64s^2$. $Fe^{3+} \to 3d^5$. Five unpaired electrons $\Rightarrow$ **coloured** (yellow-brown in aqueous solution due to charge transfer; Fe^{3+} itself is pale).
- Co^{2+}: Co(Z=27), $3d^74s^2$. $Co^{2+} \to 3d^7$. Three unpaired electrons $\Rightarrow$ **coloured** (pink).

Step 2. Compute spin-only magnetic moments for each:

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

- Ti^{3+}: $n = 1$, $\mu \approx 1.73$ BM.
- V^{3+}: $n = 2$, $\mu \approx 2.83$ BM.
- Mn^{2+}: $n = 5$, $\mu \approx 5.92$ BM.
- Fe^{3+}: $n = 5$, $\mu \approx 5.92$ BM.
- Co^{2+}: $n = 3$, $\mu \approx 3.87$ BM.

Cu^+ and Sc^{3+} have $\mu = 0$ (no unpaired electrons).

Ion	d^n	n unpaired	Colour
Ti^{3+}	d^1	1	Violet
V^{3+}	d^2	2	Green
Cu^+	d^{10}	0	Colourless
Sc^{3+}	d^0	0	Colourless
Mn^{2+}	d^5	5	Pale pink
Fe^{3+}	d^5	5	Yellow-brown
Co^{2+}	d^7	3	Pink

Final Answer: Coloured: Ti^{3+}, V^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+} (all have one or more unpaired d-electrons). Colourless: Cu^+ ($3d^{10}$) and Sc^{3+} ($3d^0$) because no $d-d$ transition is possible.

EXPERT'S SOLUTION : *Riya Gupta, M.Sc Physical Chemistry, IIT Madras*

Picture-first. Five d-orbitals split in an octahedral field (water ligands) into a lower t_{2g} set and an upper e_g set. Promotion of an electron between them absorbs visible light $\Rightarrow$ colour. If d-shell is empty (d^0) or full (d^{10}), no promotion is possible.

Numerical anchor. The splitting Δ_o for hydrated $3d$ ions falls in the range 9000–15000 cm^{-1}, which corresponds to $\lambda = hc/\Delta = 660–1100$ nm. This wavelength range overlaps the visible spectrum (400–700 nm) on the red end, so the absorbed photon lies in the visible-to-near-IR, and the observed (transmitted) colour is the complement. That single arithmetic fact controls every $3d$ aqua complex's colour.

Step 1. Quick filter: d^0 (Sc^{3+}) and d^{10} (Cu^+) are colourless. Mark them off — no $d-d$ transition possible, so no visible absorption.

Step 2. The rest are all coloured. Magnetic moments increase from Ti^{3+} (1.73 BM) to Mn^{2+} (5.92 BM) and decline afterwards. The colours follow the absorbed wavelength: Ti^{3+} purple (absorbs yellow-green at 500 nm), $Cu(H_2O)_6{}^{2+}$ blue (absorbs red–orange at 750 nm), $Co(H_2O)_6{}^{2+}$ pink (absorbs cyan at 510 nm).

Step 3. Note that d^5 ions (Mn^{2+}, Fe^{3+}) have weak colour because their $d-d$ transitions are spin-forbidden (they need a spin flip), so the absorption is very weak. Numerically: $\epsilon \approx 0.01$ for Mn^{2+}, compared with $\epsilon \approx 10$ for Ti^{3+} — three orders of magnitude weaker, hence the pale-pink $MnSO_4$ solution.

Step 4. Apply to each ion in the list (electron count in $[M(H_2O)_6]^{n+}$, hence colour): Ti^{3+} d^1 violet; V^{3+} d^2 green; Cu^+ d^{10} colourless; Sc^{3+} d^0 colourless; Mn^{2+} d^5 pale pink; Fe^{3+} d^5 pale (yellow-brown in real solution from $[Fe(OH)(H_2O)_5]^{2+}$ hydrolysis and charge-transfer); Co^{2+} d^7 pink.

Numerical cross-check. Compute spin-only μ for each: Ti^{3+} $\sqrt{3} = 1.73$; V^{3+} $\sqrt{8} = 2.83$; Cu^+ 0; Sc^{3+} 0; Mn^{2+} $\sqrt{35} = 5.92$; Fe^{3+} $\sqrt{35} = 5.92$; Co^{2+} $\sqrt{15} = 3.87$ BM. Each non-zero μ corresponds to a coloured ion; each zero μ corresponds to a colourless one. The two predictions (colour and paramagnetism) move together.

Concept linkage. The spectrochemical series tells us the ligand-field strength order $I^- < Br^- < Cl^- < F^- < H_2O < NH_3 < en < CN^-$. So the same metal in different ligand fields shows different colours (e.g. $[Co(H_2O)_6]^{2+}$ pink vs $[CoCl_4]^{2-}$ blue — and tetrahedral geometry changes Δ too).

Why this matters. The colour of a transition-metal solution is a quick diagnostic of (i) oxidation state and (ii) ligand field strength. Spectrophotometric titrations exploit exactly this. Analytical chemistry uses the intense blue of $[Cu(NH_3)_4]^{2+}$ or the red of $[Fe(SCN)_6]^{3-}$ to estimate copper and iron in trace solutions.

Final Answer: Five of the seven ions are coloured. Cu^+ and Sc^{3+} are colourless because of fully-filled and empty d-shells respectively.

☞ Two-line answer pattern

"d^0 and d^{10} ions are colourless — no d–d transition possible. All ions with d^1 to d^9 partially-filled d-sub-shell are coloured because d–d transitions of energy Δ_o absorb visible-range photons." That sentence pair covers the full answer template.

♥ Colour as a diagnostic

The pH-driven yellow-orange flip of $\mathrm{Cr_2O_7}^{2-}/\mathrm{CrO_4}^{2-}$, the purple of $\mathrm{MnO_4}^-$ disappearing on titration, the pink of Co^{2+} turning blue in concentrated HCl (forms $[\mathrm{CoCl_4}]^{2-}$) — all are everyday lab examples of how colour reports on oxidation state and coordination environment. This is why test-tube observations are still the first-cut diagnostic in inorganic analysis.

Q 4.19 Compare the stability of $+2$ oxidation state for the elements of the first transition series.

SOLUTION

Concept used. The stability of M^{2+} in solution is judged by the standard reduction potential $E^\circ(\mathrm{M}^{2+}/\mathrm{M})$: a more negative value means M^{2+} is harder to reduce back to the metal, i.e. more stable in solution. Three energy terms determine this potential:

- enthalpy of atomisation of the metal $\Delta_a H$,
- ionisation enthalpies $\Delta_i H_1 + \Delta_i H_2$,
- hydration enthalpy of M^{2+}, $\Delta_{\mathrm{hyd}} H$.

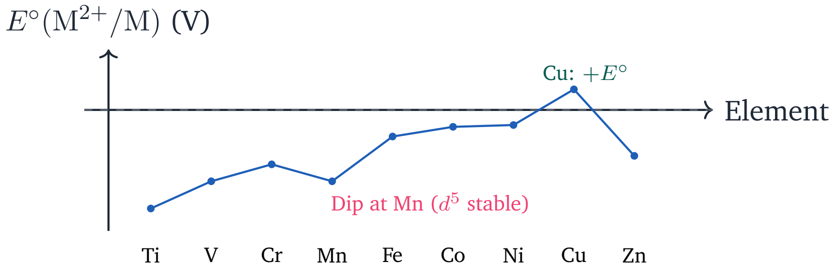
Step 1. Quote the $E^\circ(\mathrm{M}^{2+}/\mathrm{M})$ values for the $3d$ series (in V, NCERT Table 4.2): Ti -1.63, V -1.18, Cr -0.90, Mn -1.18, Fe -0.44, Co -0.28, Ni -0.25, Cu $+0.34$, Zn -0.76.

Step 2. Comment trend by trend.

- From Ti to V, the value becomes less negative: the $+2$ state becomes less stable.
- Cr is an exception: E° becomes less negative because removing the $3d^5 4s^1$ configuration (loss of s and one d) costs more energy than expected.
- Mn shows a more negative E° again: the resulting Mn^{2+} (d^5) is extra-stable.
- Fe, Co, Ni show progressively less negative E°: the $+2$ state becomes harder to obtain but Fe(II), Co(II), Ni(II) are still stable in aqueous solution.
- Cu shows a positive E° because of the very high $\Delta_i H_1 + \Delta_i H_2$ (resulting from the stable $3d^{10}$ in Cu^+) and a smaller hydration enthalpy of Cu^{2+}. Hence Cu cannot liberate H_2 from acid.
- Zn shows -0.76 V because Zn^{2+} is very stable (d^{10}): the $+2$ state is the only

state Zn shows.

Step 3. Configuration view of stability of M^{2+}: Mn^{2+} (d^5) and Zn^{2+} (d^{10}) are most stable; Cu^{2+} (d^9) is also reasonably stable thanks to large hydration energy; Cr^{2+} (d^4) is least stable in solution (a strong reducing agent).



> **Final Answer:** $E^\circ(M^{2+}/M)$ generally becomes less negative across Ti to Cu, indicating decreasing stability of M^{2+}, with two notable irregularities at Mn (extra-stable d^5) and at Cu (positive E°, large $\Delta_i H$ outweighs hydration). Zn shows -0.76 V again because of d^{10} stability.

EXPERT'S SOLUTION *: Ishaan Rao, M.Sc Chemistry, IIT Kanpur*

Strategic angle. Plot $E^\circ(M^{2+}/M)$ across the row, then explain the two dips (Mn, Zn) and the one positive value (Cu) by configuration.

Energy partition view. $E^\circ(M^{2+}/M)$ depends on three terms: $\Delta_{\text{atom}}H$ (atomisation enthalpy), $\Delta_i H_1 + \Delta_i H_2$ (first two ionisation enthalpies), and $\Delta_{\text{hyd}}H(M^{2+})$ (hydration enthalpy). For a more negative E° we want low atomisation, low ionisation cost, and large negative hydration. Mn wins (low $\Delta_{\text{atom}}H = 281$ kJ/mol; reasonable $\Sigma\Delta_i H$; very negative $\Delta_{\text{hyd}}H$ thanks to d^5 stability). Cu loses (reasonable atomisation but $\Sigma\Delta_i H_{1+2}$ is high because of breaking $3d^{10}$, and hydration cannot compensate).

Step 1. Quote the data: nine values from Ti to Zn, in V. Sketch them mentally on a single curve.

Step 2. Identify the dips: Mn at -1.18 V and Zn at -0.76 V are more negative than their immediate neighbours, because their M^{2+} ions (d^5, d^{10}) are extra stable. The Mn dip is the more striking — Mn metal in water reduces H^+ faster than Cr or Fe.

Step 3. Identify the peak: Cu at $+0.34$ V (only positive value) is a consequence of Cu^+ being very stable ($3d^{10}$) and the large $\Delta_i H$ for the second ionisation, which more than offsets the hydration energy gain of Cu^{2+}. This is why copper does not dissolve in dilute non-oxidising acids (HCl, dilute H_2SO_4). Copper requires oxidising acids (HNO_3, conc. H_2SO_4) to oxidise the metal.

Step 4. Apply: the displacement series follows from these E° values. Zn (more negative) displaces Cu^{2+} from $CuSO_4$: $Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$, with $E^\circ_{\text{cell}} = +0.34 - (-0.76) = +1.10$ V. This is the Daniell cell.

Numerical cross-check. The actual ordering by E° (most negative to most positive, i.e. most reactive to least reactive toward H^+): Ti -1.63, Mn -1.18, V -1.18, Cr -0.90, Zn -0.76, Fe -0.44, Co -0.28, Ni -0.25, Cu $+0.34$. The non-monotonic shape is the signature of configuration-driven stability.

Concept linkage. The same energy-partition analysis explains why Ag^+/Ag has $E^\circ = +0.80$ V (Ag^+ is $4d^{10}$, very stable, expensive to form Ag^{2+}) and why Au^+/Au is even more positive. The closed d^{10} shell creates an extra ionisation "cliff" that even hydration cannot fully discount.

Why this matters. Knowing the order of E° values tells us at a glance which metals will displace which others, and explains why Mn metal is highly reactive while Cu metal is essentially inert in HCl. Industrial electrowinning of copper from $CuSO_4$ solutions and zinc-air batteries are direct applications of the E° ladder.

> **Final Answer:** $E^\circ(M^{2+}/M)$ becomes less negative left-to-right, with notable extrema: Mn (d^5) very negative, Cu positive (cannot be oxidised by dilute HCl), Zn (d^{10}) negative again.

✗ Cu does NOT liberate H_2 from HCl

A frequent error: writing $Cu + 2\,HCl \longrightarrow CuCl_2 + H_2$. This is wrong. $E^\circ(Cu^{2+}/Cu) = +0.34$ V, more positive than $E^\circ(H^+/H_2) = 0.00$ V, so the reverse reaction is spontaneous. Copper does react with oxidising acids (HNO_3, hot conc H_2SO_4) but not by simple displacement of H^+.

Q 4.20 Compare the chemistry of actinoids with that of the lanthanoids with special reference to: (i) electronic configuration, (ii) atomic and ionic sizes and (iii) oxidation state, (iv) chemical reactivity.

SOLUTION

Concept used. Lanthanoids (Ce to Lu, Z = 58 to 71) fill the $4f$ sub-shell; actinoids (Th to Lr, Z = 90 to 103) fill the $5f$ sub-shell. Their similarities (both belong to the f-block) and differences ($5f$ orbitals lie deeper but are more spatially extended than $4f$) follow from this.

Step 1. **(i) Electronic configuration.**

- Lanthanoid: $[Xe]\,4f^{1-14}\,5d^{0-1}\,6s^2$. Examples: Ce $[Xe]4f^1 5d^1 6s^2$, Sm $[Xe]4f^6 6s^2$, Gd $[Xe]4f^7 5d^1 6s^2$.

- Actinoid: $[\mathrm{Rn}]\,5f^{1-14}\,6d^{0-1}\,7s^2$. Examples: Th $[\mathrm{Rn}]6d^27s^2$ (no $5f$!), U $[\mathrm{Rn}]5f^36d^17s^2$, Am $[\mathrm{Rn}]5f^77s^2$.

The configurations of actinoids are less regular because the $5f$, $6d$ and $7s$ orbitals lie close in energy.

Step 2. **(ii) Atomic and ionic sizes.** Both series show a contraction: **lanthanoid contraction** (cumulative ∼14–18 pm) and **actinoid contraction** (∼15–20 pm). Actinoid contraction is greater per step because the $5f$ electrons shield outer electrons even more poorly than $4f$ electrons (the $5f$ orbitals are more diffuse).

Step 3. **(iii) Oxidation states.** Lanthanoids show mainly $+3$; only Ce $(+4)$, Eu, Yb $(+2)$, Tb $(+4)$, Sm $(+2)$ are exceptions. Actinoids show a much wider range: $+3$ to $+7$ is found among Np, Pu, Am, U. In particular, UF_6 (U $+6$), ${NpO_2}^{2+}$ $(+5)$, ${PuO_2}^{2+}$ $(+6)$ and even $+7$ for Np exist. The wider variability is due to the smaller energy gap between $5f$, $6d$ and $7s$ orbitals in actinoids: more electrons can take part in bonding.

Step 4. **(iv) Chemical reactivity.** Lanthanoids are highly reactive electropositive metals (similar reactivity to Ca); they tarnish in air, react with water and dilute acids to give H_2. Actinoids are also highly reactive but the early actinoids (Th, U, Pa) are more reactive and the late actinoids (Cm onwards) less well-studied. Many actinoids are radioactive, which makes their experimental chemistry complicated. The early actinoids react more like transition metals (variable O.S., complex formation, partial covalent bonding), while the late actinoids resemble lanthanoids more (mostly $+3$).

Lanthanoids	Actinoids
$[\mathrm{Xe}]4f^{1-14}5d^{0-1}6s^2$	$[\mathrm{Rn}]5f^{1-14}6d^{0-1}7s^2$
Contraction ∼14–18 pm	Contraction ∼15–20 pm (larger)
Mostly $+3$	$+3$ to $+7$
Reactive (like Ca)	Reactive; radioactive

Final Answer: Lanthanoids: $4f$ filling, regular configurations, mostly $+3$, smaller contraction. Actinoids: $5f$ filling, irregular configurations, oxidation states $+3$ to $+7$, larger contraction; many are radioactive.

EXPERT'S SOLUTION *: Meera Banerjee, Ph.D Organic Chemistry, IISc Bangalore*

Structural observation. The single key difference is that $5f$ orbitals are more spatially extended than $4f$, which makes them chemically more active. So actinoids show a wider range of oxidation states and stronger complex-forming ability.

Orbital extension and energy gap. For lanthanoids: the $4f$–$5d$ energy gap is $\sim$5–7 eV (large), so $4f$ electrons stay in the core. For actinoids: the $5f$–$6d$ gap is only $\sim$1–2 eV (small), so $5f$ electrons are in the chemical valence shell. This gap difference is the structural root of the wider actinoid oxidation-state range.

Step 1. Configuration: Ln: $[\mathrm{Xe}]4f^n\ldots$; An: $[\mathrm{Rn}]5f^n\ldots$. Actinoid configurations are less regular because the energy gap between $5f$, $6d$, $7s$ is small. Examples of irregularity: Th ($[\mathrm{Rn}]6d^2 7s^2$, no $5f$), Pa ($[\mathrm{Rn}]5f^2 6d^1 7s^2$), Cm ($[\mathrm{Rn}]5f^7 6d^1 7s^2$ — extra $6d$ for $5f^7$ half-filled stability, just like Gd in lanthanoids).

Step 2. Sizes: both shrink across the series; actinoid contraction is somewhat greater per element, because $5f$ shields the nucleus less effectively (more diffuse orbitals). Total contraction: lanthanoid 14–18 pm, actinoid 15–20 pm.

Step 3. Oxidation states: Ln mostly $+3$ (range $+2$ to $+4$); An $+3$ to $+7$ (much wider). Examples: UF_6 (U $+6$), ${UO_2}^{2+}$ (uranyl, U $+6$), ${NpO_2}^{+}$ (Np $+5$), ${PuO_2}^{2+}$ (Pu $+6$), ${NpO_5}^{3-}$ or ${PuO_5}^{3-}$ ($+7$). The oxoanions ${UO_2}^{2+}$ and ${NpO_2}^{2+}$ have a characteristic linear O=M=O geometry.

Step 4. Reactivity: both are electropositive and reactive; actinoids are additionally radioactive. Early actinoids (Th, U) resemble transition metals (variable O.S., complex formation with π-acceptor ligands like CO in early actinoid carbonyls); later actinoids (Cm onwards) resemble lanthanoids more.

Numerical anchor. Atomic radii: La 187 pm vs Ac 188 pm (start nearly equal); Lu 173 pm vs Lr $\sim$166 pm (Lr smaller due to greater actinoid contraction). Compare maximum oxidation states: Lu (group 3) +3; Lr (group 3) +3; but U (Z = 92) reaches +6 in UF_6 and ${UO_2}^{2+}$, while Nd (Z = 60, same column-position) reaches only +3 in $NdCl_3$. The accessibility of higher oxidation states is the actinoid hallmark.

Concept linkage. The PUREX (Plutonium-URanium-EXtraction) process used in nuclear fuel reprocessing depends entirely on the ability to switch Pu between +4 and +3 oxidation states (and U between +6 and +4) to selectively partition them between aqueous and organic phases. No analogous process exists for lanthanoids because their +3 chemistry is so uniform — separation must use ion-exchange or solvent-extraction with subtle selectivity rather than redox switching.

Why this matters. The nuclear-fuel chemistry of U, Pu, Np sits entirely on the wide oxidation-state range of actinoids and their ability to form oxoanions (${UO_2}^{2+}$, ${PuO_2}^{2+}$). Lanthanoid chemistry is, by contrast, much more uniform. The same reason makes Eu(II) doping in phosphors (single $+2$ state) easy and clean, while Pu(IV) chemistry requires careful redox handling.

Final Answer: Lanthanoid: $4f$ filling, mostly +3; actinoid: $5f$ filling, +3 to +7, larger contraction, all radioactive.

♥ Why nuclear fuel reprocessing works

The five-step PUREX process uses tributyl phosphate (TBP) extraction in kerosene to selectively pull $UO_2(NO_3)_2 \cdot {}_2$ TBP (U^{6+} neutral complex) and $Pu(NO_3)_4 \cdot {}_2$ TBP (Pu^{4+} neutral complex) from spent-fuel nitric acid solutions, leaving the fission products behind. Then U and Pu are separated by reducing Pu(IV) to Pu(III) — the trivalent ion is not extracted by TBP. The whole process is impossible without actinoid redox flexibility.

Q 4.21 **How would you account for the following:**

(i) Of the d^4 species, Cr^{2+} is strongly reducing while manganese(III) is strongly oxidising.

(ii) Cobalt(II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.

(iii) The d^1 configuration is very unstable in ions.

SOLUTION

Concept used. A species with a d^n configuration prefers to move (by gaining or losing one electron) to a more stable d-configuration, especially toward d^0, d^3, d^5 or d^{10}. "Reducing" means the species loses an electron easily; "oxidising" means it gains one easily.

Step 1. **(i) Cr^{2+} vs Mn^{3+}, both d^4.**

- Cr^{2+}: d^4. Loses 1 e^- to become Cr^{3+} (d^3, half-filled t_{2g}, very stable). So Cr^{2+} is easily oxidised, i.e. a strong *reducing agent*.

$$E^\circ(\mathrm{Cr^{3+}/Cr^{2+}}) = -0.41\,\mathrm{V}.$$

The negative value means the reverse process (oxidation of Cr^{2+}) is favoured.

- Mn^{3+}: d^4. Gains 1 e^- to become Mn^{2+} (d^5, half-filled, extra stable). So Mn^{3+} is easily reduced, i.e. a strong *oxidising agent*.

$$E^\circ(\mathrm{Mn^{3+}/Mn^{2+}}) = +1.57\,\mathrm{V}.$$

Both species are d^4, but one is one step away from d^3 (Cr) and the other from d^5 (Mn).

Step 2. **(ii) Cobalt(II) in water vs in complexes.** $[Co(H_2O)_6]^{2+}$ (pink) has Co(II) in a weak ligand field; it is stable in aqueous solution because the oxidation

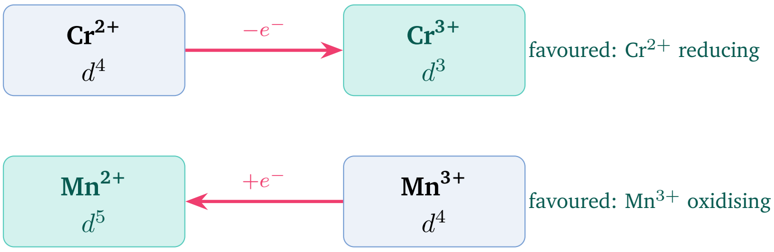
$Co^{2+} \longrightarrow Co^{3+}$ would require breaking the d^7 arrangement and the resulting Co^{3+} (d^6) is unstable in water ($E°(Co^{3+}/Co^{2+}) = +1.97$ V, strongly oxidising in aqueous medium). In the presence of strong-field ligands like NH_3, CN^-, en, the situation flips. The Co(III) complex $[Co(NH_3)_6]^{3+}$ is a low-spin d^6 (t_{2g}^6, all paired) with very large **crystal field stabilisation energy** (CFSE = $-2.4\Delta_o$). The huge CFSE makes Co(III) much more stable than Co(II) when bound to strong-field ligands. So Co^{2+} is easily oxidised to $[Co(NH_3)_6]^{3+}$ (often by aerial O_2). Compare the same couple's $E°$ values:

$$E°([Co(H_2O)_6]^{3+}/[Co(H_2O)_6]^{2+}) \approx +1.97\,V,$$

$$E°([Co(NH_3)_6]^{3+}/[Co(NH_3)_6]^{2+}) \approx +0.11\,V.$$

The drop from $+1.97$ to $+0.11$ V tells the whole story.

Step 3. **(iii) Why d^1 is unstable.** A d^1 ion is one electron away from both d^0 (empty, stable) and d^2 (a step toward d^3). In practice, ions like Ti^{3+} (d^1) readily lose the single d-electron and become d^0 Ti^{4+}. V^{4+} (VO^{2+}) also tends to disproportionate or be oxidised. So d^1 is a transient configuration in aqueous chemistry: in air or in mild oxidants, it is converted to the more stable d^0.



Final Answer: (i) Both are d^4; Cr^{2+} loses e^- to give stable d^3 Cr^{3+}, hence reducing. Mn^{3+} gains e^- to give stable d^5 Mn^{2+}, hence oxidising. (ii) Co(II) is stable in water but a strong-field ligand stabilises Co(III) by very large CFSE, so it is easily oxidised. (iii) d^1 ions readily lose the single electron to reach the more stable d^0 configuration.

EXPERT'S SOLUTION *: Kavya Gupta, M.Sc Physical Chemistry, IIT Madras*

Strategic angle. Three short electronic-structure arguments, one per part. "Move to d^0, d^3, d^5 or d^{10} where possible" is the recurring rule.

Electronic-config reasoning. Two ions can share the same d^n count but lie next to different "magic" configurations, making them behave oppositely. Cr^{2+} (d^4) is one e^- *above* stable d^3; lose one e^- and gain stability — Cr^{2+} acts as a reducing agent. Mn^{3+} (d^4) is one e^- *below* stable d^5; gain one e^- and gain stability — Mn^{3+} acts as an oxidising agent. Same configuration, opposite role.

Step 1. Same d^4, different neighbours. For Cr: the thermodynamically favoured step is $d^4 \rightarrow d^3$, so Cr^{2+} is reducing. For Mn: the thermodynamically favoured step is $d^4 \rightarrow d^5$, so Mn^{3+} is oxidising. The numerical E° values (-0.41 vs $+1.57$) confirm this. Difference of 1.98 V ($= 191$ kJ/mol/e$^-$) measures the gap between "moving toward d^3" and "moving toward d^5".

Step 2. Crystal-field role. Strong-field ligands such as NH_3, CN^-, en, generate a large Δ_o and make low-spin d^6 Co(III) (t_{2g}^6, CFSE $= -2.4\Delta_o$) very stable. So $[Co(NH_3)_6]^{2+}$ is easily oxidised to $[Co(NH_3)_6]^{3+}$, often by atmospheric O_2. Numerical comparison: $E^\circ([Co(H_2O)_6]^{3+}/[Co(H_2O)_6]^{2+}) = +1.97$ V (aqueous, hard to maintain Co(III)); $E^\circ([Co(NH_3)_6]^{3+}/[Co(NH_3)_6]^{2+}) = +0.11$ V (Co(III) is now the stable form). A swing of 1.86 V due purely to changing ligand!

Step 3. d^1 instability: one step away from the stable d^0. Ti^{3+} (d^1, purple) oxidises to Ti^{4+} (d^0, colourless) on standing in air; VO^{2+} (d^1, blue) oxidises to $VO_2{}^+$ (d^0, yellow). The trend is general: d^1 ions are reducing agents because oxidation reaches the stable d^0 shell.

Step 4. Numerical check on part (i): ΔG° for $Cr^{2+} \longrightarrow Cr^{3+} + e^-$ is $-nFE^\circ_{\text{ox}} = +nFE^\circ_{\text{red}} = +1 \cdot 96.5 \cdot (-0.41) = -40$ kJ/mol (favourable). For $Mn^{3+} + e^- \longrightarrow Mn^{2+}$: $\Delta G^\circ = -1 \cdot 96.5 \cdot 1.57 = -151$ kJ/mol (strongly favourable). The Mn step is roughly 4 times more downhill than the Cr step.

Concept linkage. The strong-field stabilisation of $[Co(NH_3)_6]^{3+}$ has a parallel in $[Fe(CN)_6]^{4-}$: Fe(II) is normally easily oxidised, but with strong-field CN^- the low-spin d^6 configuration is so stable that ferrocyanide is practically inert. Same crystal-field mechanism.

Why this matters. The same crystal-field argument used in (ii) explains why so many cobalt(III)-amine complexes (such as $[Co(NH_3)_6]Cl_3$) are kinetically and thermodynamically stable, whereas the hydrate $[Co(H_2O)_6]^{3+}$ is not. JEE-level question: "Why is $[Co(NH_3)_6]^{3+}$ inert while $[Co(H_2O)_6]^{3+}$ is labile?" — same crystal-field stabilisation reasoning.

Final Answer: (i) $d^4 \rightarrow d^3$ vs $d^4 \rightarrow d^5$ explains reducing vs oxidising. (ii) Strong-field ligands stabilise Co(III) by large CFSE. (iii) d^1 ions easily lose the lone electron to reach d^0.

☞ **CFSE values for d^n in O_h field**

d^0: 0 (no electrons); d^3: $-1.2\Delta_o$ (half-filled t_{2g}); d^6 low-spin: $-2.4\Delta_o$ (maximum); d^{10}: 0 (full shell). The maximum CFSE at d^6 low-spin is why Co(III)-amine complexes are so stable.

☞ Same d^n, different ion: ask “which way is downhill?”

When two ions share a configuration, draw a small ladder: d^{n-1} (below) – d^n (your ion) – d^{n+1} (above). The favoured direction is whichever lands on d^0, d^3, d^5 or d^{10}. Same idea works for V^{4+}/V^{5+} ($d^1 \to d^0$, reducing) and Co^{3+}/Co^{2+} ($d^6 \to d^7$, oxidising in water).

Q 4.22 What is meant by “disproportionation”? Give two examples of disproportionation reaction in aqueous solution.

SOLUTION

Concept used. Disproportionation is a redox reaction in which the same element in a given oxidation state is simultaneously oxidised *and* reduced, ending up in two different oxidation states (one higher and one lower than the original). Two essential features: (i) only one element changes oxidation state, and (ii) some of its atoms are oxidised while others are reduced.

Step 1. General template: $nX^a \to pX^b + qX^c$ with $b > a > c$ and electrons balanced.

Step 2. **Example 1: copper(I).** Cu^+ disproportionates in aqueous solution:

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

Cu(I) → Cu(II) + Cu(0). Driving force: E° for Cu^+/Cu ($+0.52$ V) and for Cu^{2+}/Cu^+ ($+0.16$ V) are such that the net reaction has positive E°_{cell}. Equivalently, hydration energy of Cu^{2+} more than compensates for the second ionisation.

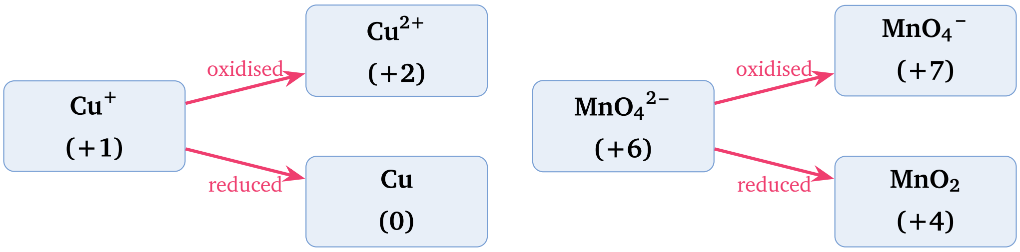
Step 3. **Example 2: manganate $MnO_4{}^{2-}$.** In acidic solution Mn(VI) disproportionates:

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

Mn(VI) → Mn(VII) + Mn(IV). This is exactly the step used in the industrial preparation of $KMnO_4$.

Step 4. Other examples worth knowing:

- $3\,ClO^- \longrightarrow 2\,Cl^- + ClO_3{}^-$ (Cl(I) → Cl(-I) + Cl(V)).
- $2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$ (O(-I) → O(-II) + O(0)).
- $P_4 + 3\,NaOH + 3\,H_2O \longrightarrow PH_3 + 3\,NaH_2PO_2$ (P(0) → P(-III) + P(+I)).



> **Final Answer:** Disproportionation: one element in a single oxidation state ends up in two states (one higher, one lower). Examples: $2\,Cu^{+} \longrightarrow Cu^{2+} + Cu$; $3\,MnO_4{}^{2-} + 4\,H^{+} \longrightarrow 2\,MnO_4{}^{-} + MnO_2 + 2\,H_2O$.

EXPERT'S SOLUTION *: Dev Bhat, B.Tech Chemical Engineering, IIT Bombay*

Quick reading. Take a species in oxidation state a; disproportionation gives products in states above and below a.

Thermodynamics in two potentials. Disproportionation $2\,X^{a+} \longrightarrow X^{b+} + X^{c+}$ (with $b > a > c$) is spontaneous when $E^\circ(X^{b+}/X^{a+}) < E^\circ(X^{a+}/X^{c+})$. For Cu^+: $E^\circ(Cu^{2+}/Cu^{+}) = +0.16$ V and $E^\circ(Cu^{+}/Cu) = +0.52$ V; the second is bigger, so disproportionation $2\,Cu^{+} \longrightarrow Cu^{2+} + Cu$ has $E^\circ_{cell} = 0.52 - 0.16 = +0.36$ V, hence spontaneous ($\Delta G < 0$).

Step 1. Define "self-oxidation-and-reduction": same element, single starting state, two end states. The element is both the oxidant and the reductant; only its oxidation states differ in the products.

Step 2. Cu(I) example: solid Cu plus blue Cu^{2+} from clear Cu^{+}. Driving force is the large hydration enthalpy of Cu^{2+} plus the favourable lattice energy / metallic bonding of Cu(0). $\Delta_{hyd}H$ values: Cu^{2+} -2099 kJ/mol, Cu^{+} -582 kJ/mol — a $\sim$1500 kJ/mol asymmetry that the second ionisation ($\Delta_i H_2 = 1958$ kJ/mol) cannot quite overcome, leaving the disproportionation favourable.

Step 3. Mn(VI) example: in acid $MnO_4{}^{2-}$ splits into $MnO_4{}^{-}$ and MnO_2. This is the principle behind preparing $KMnO_4$ from K_2MnO_4. $3\,MnO_4{}^{2-} + 4\,H^{+} \longrightarrow 2\,MnO_4{}^{-} + MnO_2 + 2\,H_2O$. Stoichiometry check: 3 Mn^{6+} ($+18$ total) $\rightarrow$ 2 Mn^{7+} ($+14$) + 1 Mn^{4+} ($+4$); total $+18$ on both sides. Charge: $3(-2) + 4(+1) = -2$ on LHS; $2(-1) + 0 + 0 = -2$ on RHS. Balanced.

Step 4. Other classic disproportionations: $3\,ClO^{-} \longrightarrow 2\,Cl^{-} + ClO_3{}^{-}$ ($Cl^{+1} \rightarrow Cl^{-1}$ + Cl^{+5}); $2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$ ($O^{-1} \rightarrow O^{-2}$ + O^{0}). The pattern is identical: one species splits to two oxidation states.

Step 5. Reverse process, comproportionation: $Cu^{2+} + Cu \longrightarrow 2\,Cu^{+}$ in non-aqueous solvents or molten media where hydration of Cu^{2+} is absent. So Cu(I)/Cu(II)/Cu(0) interconvert depending on the medium.

Numerical anchor. For $2\,Cu^{+} \longrightarrow Cu^{2+} + Cu$: $\Delta G^\circ = -nFE^\circ_{cell} = -2 \cdot 96485 \cdot 0.36 = -69.5$ kJ/mol — well-favourable, but not enormous, which is why Cu^{+} can be stabilised in non-aqueous solvents (acetonitrile, where the hydration asymmetry is absent) and in solid lattices (CuCl, Cu_2O).

Concept linkage. The pH-dependence of permanganate disproportionation: $3\,MnO_4{}^{2-} + 4\,H^{+} \longrightarrow 2\,MnO_4{}^{-} + MnO_2 + 2\,H_2O$ — needs acid; in alkaline solution

${MnO_4}^{2-}$ is stable. So the prep of $KMnO_4$ from K_2MnO_4 requires careful pH control. The same species, two media, two different outcomes — Le Chatelier in action.
Why this matters. Disproportionation explains why Cu(I) salts are rare in aqueous solution (yet stable in solids: CuCl, Cu_2O, Cu_2S) and why $KMnO_4$ has to be purified through a careful acid-precipitation cycle. Industrially, the disproportionation of Cl_2 in cold dilute NaOH gives household bleach ($Cl_2 + 2\,NaOH \longrightarrow NaCl + NaClO + H_2O$), and in hot conc. NaOH gives $NaClO_3$ ($3\,Cl_2 + 6\,NaOH \longrightarrow 5\,NaCl + NaClO_3 + 3\,H_2O$).

> **Final Answer:** Disproportionation: same element, same starting O.S., two product O.S. (one higher, one lower). Examples: Cu^+ and ${MnO_4}^{2-}$.

☞ **Three disproportionations to memorise**

$2\,Cu^+ \longrightarrow Cu^{2+} + Cu$ ($Cu^{+1} \to Cu^{+2} + Cu^0$); $3\,{MnO_4}^{2-} + 4\,H^+ \longrightarrow 2\,{MnO_4}^- + MnO_2 + 2\,H_2O$ ($Mn^{+6} \to Mn^{+7} + Mn^{+4}$); $Cl_2 + H_2O \longrightarrow HCl + HOCl$ ($Cl^0 \to Cl^{-1} + Cl^{+1}$). Two transition-metal cases, one p-block.

Q 4.23 Which metal in the first series of transition metals exhibits $+1$ oxidation state most frequently and why?

SOLUTION

Concept used. For a $3d$ metal to show $+1$ as a major oxidation state in compounds, the resulting cation should be electronically stable. The ion Cu^+ has the fully filled $3d^{10}$ configuration, which is energetically very favourable.

Step 1. Compute the cation configuration on losing one electron from each $3d$ element.

- Sc^+: $3d^1 4s^1$ (unstable, $+3$ preferred).
- Ti^+: $3d^2 4s^1$ (unstable).
- ...
- Cu^+: $3d^{10}$ (fully filled, very stable).
- Zn^+: $3d^{10} 4s^1$ (unstable; Zn forms only $+2$).

Step 2. Identify the winner: Cu^+ is the only $3d$ cation with a fully filled d^{10} shell from the $+1$ oxidation state. It is found in many solid copper(I) compounds: Cu_2O (cuprous oxide), CuCl (cuprous chloride), Cu_2S, and the complexes $[Cu(NH_3)_2]^+$, $[Cu(CN)_2]^-$.

Step 3. Note the caveat about aqueous solution. Cu^+ is unstable in water: it disproportionates $2\,Cu^+ \longrightarrow Cu^{2+} + Cu$. So Cu^+ dominates only in solid salts, in non-aqueous solvents and inside complexes. Despite this, Cu is the answer because no other $3d$ metal gives a stable $+1$ ion at all.

> **Final Answer: Copper (Cu)** shows the $+1$ state most often, because Cu^+ has the fully filled $3d^{10}$ configuration, which is energetically very stable. Examples: Cu_2O, CuCl, $[Cu(NH_3)_2]^+$.

EXPERT'S SOLUTION *: Ishita Kapoor, M.Sc Chemistry, IIT Kanpur*

Strategic angle. The $+1$ state needs a stable cation configuration. Across $3d$, only Cu^+ (d^{10}) qualifies, so Cu is the unique answer.

Periodic-trend angle. The $+1$ oxidation state requires the metal to lose only its ns electron(s). For Cu ($3d^{10}4s^1$), losing the single $4s$ electron gives the closed-shell $3d^{10}$ Cu^+. No other $3d$ element offers this — they all need to lose $4s^2$ as a pair (e.g. Sc would give Sc^+ as $3d^14s^1$, still open-shell and reactive). Cu's $4s^1$ singleton is what makes the $+1$ state energetically isolated and accessible.

Step 1. Confirm: $Cu^+ = [Ar]3d^{10}$, fully filled and therefore very stable. Diamagnetic ($\mu = 0$, no unpaired electrons). Colourless (no $d-d$ transition possible).

Step 2. List solid copper(I) compounds: Cu_2O (cuprous oxide, red, used in solar-cell research), CuCl (white), CuI (white, used in iodometric titrations), Cu_2S (chalcocite ore), $[Cu(NH_3)_2]^+$ and $[Cu(CN)_2]^-$ as complex examples. Note that the Cu(I) salt is almost always less soluble than the corresponding Cu(II) salt — this difference is what saves Cu(I) from disproportionation in solid form.

Step 3. Caveat: in water Cu^+ disproportionates to Cu^{2+} and Cu, because the hydration enthalpy of Cu^{2+} (-2099 kJ/mol) is much larger than that of Cu^+ (-582 kJ/mol) and far outweighs the second ionisation cost ($\Delta_i H_2 = 1958$ kJ/mol).

Step 4. Stabilisation strategies: (a) use insoluble salts (CuCl is only sparingly soluble, so Cu^+ stays put); (b) complex with π-acceptor ligands (CN^-, PR_3); (c) use non-aqueous solvents (acetonitrile co-ordinates Cu^+ preferentially over Cu^{2+}).

Step 5. Periodic comparison: in groups 11 of $4d$ and $5d$, Ag^+ and Au^+ are also d^{10} and even more stable than Cu^+ (Ag chemistry is dominated by Ag(I); Au chemistry by Au(I) and Au(III)). Down the group, d^{10} stability rises.

Numerical cross-check. $E^\circ(Cu^{2+}/Cu^+) = +0.16$ V; $E^\circ(Cu^+/Cu) = +0.52$ V. Since the second is larger, Cu^+ disproportionates in water: E°_{cell} for $2\,Cu^+ \longrightarrow Cu^{2+} + Cu$ is $+0.36$ V, $\Delta G = -69.5$ kJ/mol. Hence aqueous Cu^+ is unstable but solid CuCl, where the lattice energy compensates, is stable.

Concept linkage. Cu(I) chemistry is the bridge between the d-block (where Cu(II) dominates in water) and the late d-block d^{10} ions (Zn^{2+}, Cd^{2+}, Hg_2^{2+}). It is the "half-way" state that requires special conditions to survive.

Why this matters. Recognising d^{10} stability is the $3d$-block analogue of the inert-pair effect in the p-block: a full sub-shell is hard to disturb. Industrially, CuCl catalyses the Sandmeyer reaction (diazonium → aryl halide), and Cu_2O is the basis of the Tollens reagent test for aldehydes (Cu^+ oxidising to Cu^{2+} via aldehyde-mediated Fehling's solution).

> **Final Answer:** Cu, because Cu^+ has $3d^{10}$ (fully filled and very stable). Solid Cu(I) compounds include Cu_2O and CuCl.

♥ The white precipitate test

The classic test for halide ions in solution uses Cu^+ (in $[Cu(NH_3)_2]^+$ form) precipitating with Cl^-, Br^-, I^- as CuCl (white), CuBr (off-white), CuI (yellow). The Cu^+ state is preserved through this whole sequence because each halide salt is sufficiently insoluble to anchor the oxidation state.

Q 4.24 Calculate the number of unpaired electrons in the following gaseous ions: Mn^{3+}, Cr^{3+}, V^{3+} and Ti^{3+}. Which one of these is the most stable in aqueous solution?

SOLUTION

Concept used. To count unpaired electrons in a gaseous $3d$ ion, write its electron configuration and place the electrons in the five degenerate $3d$ orbitals following **Hund's rule**: first fill each orbital with one electron of parallel spin, then pair them up. The number left unpaired gives n. The spin-only magnetic moment is then

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

Step 1. **Ti^{3+} (Z = 22).** Neutral Ti: $[Ar]3d^24s^2$. Ti^{3+}: remove 3 electrons (two $4s$, one $3d$): $[Ar]\,3d^1$. So $n = 1$, and

$$\mu = \sqrt{1\cdot 3} = \sqrt{3} = 1.73\ \text{BM}.$$

Step 2. **V^{3+} (Z = 23).** Neutral V: $[Ar]3d^34s^2$. V^{3+}: $[Ar]\,3d^2$. So $n = 2$, and

$$\mu = \sqrt{2\cdot 4} = \sqrt{8} = 2.83\ \text{BM}.$$

Step 3. **Cr^{3+} (Z = 24).** Neutral Cr: $[Ar]3d^54s^1$. Cr^{3+}: $[Ar]\,3d^3$. So $n = 3$, and

$$\mu = \sqrt{3\cdot 5} = \sqrt{15} = 3.87\ \text{BM}.$$

Step 4. **Mn^{3+} (Z = 25).** Neutral Mn: $[Ar]3d^54s^2$. Mn^{3+}: $[Ar]\,3d^4$. So $n = 4$, and

$$\mu = \sqrt{4\cdot 6} = \sqrt{24} = 4.90\ \text{BM}.$$

Step 5. Most stable in aqueous solution: **Cr^{3+}** (d^3). The half-filled t_{2g}^3 set in an octahedral water environment gives a large CFSE of $-1.2\,\Delta_o$ and no Jahn-Teller distortion. The E° data also support Cr^{3+} as the most stable: $E^\circ(\mathrm{Cr^{3+}/Cr^{2+}}) = -0.41$ V (so Cr^{3+} is hard to reduce) while $E^\circ(\mathrm{Mn^{3+}/Mn^{2+}}) = +1.57$ V (so Mn^{3+} is easily reduced).

Ion	d^n	n	μ (BM)
Ti^{3+}	d^1	1	1.73
V^{3+}	d^2	2	2.83
Cr^{3+}	d^3	3	3.87
Mn^{3+}	d^4	4	4.90

> **Final Answer:** Unpaired electrons: Ti^{3+}: 1, V^{3+}: 2, Cr^{3+}: 3, Mn^{3+}: 4. Most stable in water: Cr^{3+} (d^3, half-filled t_{2g}, large CFSE).

EXPERT'S SOLUTION : *Aanya Chatterjee, Ph.D Organic Chemistry, IISc Bangalore*

Picture-first. Draw five $3d$ boxes; fill electrons by Hund's rule; count unpaired.
Numerical workflow. Each M^{3+} ion's $3d$ count = Z − 18 − 3 = Z − 21 (since we remove all $4s^2$ plus one d on going to +3). Ti(22): d^1. V(23): d^2. Cr(24): d^3. Mn(25): d^4. The arithmetic is mechanical; the physics is the spin-only μ formula.

Step 1. Ti^{3+}: 1 box occupied $\Rightarrow$ 1 unpaired $\Rightarrow \mu = \sqrt{1 \cdot 3} = \sqrt{3} = 1.73$ BM. Solution colour: violet (absorbs ~500 nm).

Step 2. V^{3+}: 2 boxes occupied (one electron each) $\Rightarrow$ 2 unpaired $\Rightarrow$ $\mu = \sqrt{2 \cdot 4} = \sqrt{8} = 2.83$ BM. Colour: green.

Step 3. Cr^{3+}: 3 boxes occupied $\Rightarrow$ 3 unpaired $\Rightarrow \mu = \sqrt{3 \cdot 5} = \sqrt{15} = 3.87$ BM. Colour: violet (chrome alum).

Step 4. Mn^{3+}: 4 boxes used (one box is filling first, but in high-spin all four start as singly occupied) $\Rightarrow$ 4 unpaired $\Rightarrow \mu = \sqrt{4 \cdot 6} = \sqrt{24} = 4.90$ BM. Colour: cherry-red (unstable in water).

Step 5. For stability in water: choose the half-filled t_{2g}^3 configuration, which is Cr^{3+}. It is stable both electronically (half-filled t_{2g}, CFSE = $-1.2\Delta_o$) and kinetically ($[Cr(H_2O)_6]^{3+}$ is famously inert, water-exchange half-life ~10 hours at 25 °C). Compare to other ions of the same row: $[\mathrm{Mn(H_2O)_6}]^{2+}$ exchanges water in ~10 ns — a 10^{12}-fold faster!

Step 6. Cross-check with electrode potentials: $E^\circ(\mathrm{Cr^{3+}/Cr^{2+}}) = -0.41$ V (Cr^{3+} stable); $E^\circ(\mathrm{Mn^{3+}/Mn^{2+}}) = +1.57$ V (Mn^{3+} unstable, easily reduced); $E^\circ(\mathrm{V^{3+}/V^{2+}}) = -0.26$ V (V^{3+} moderately stable); $E^\circ(\mathrm{Ti^{3+}/Ti^{2+}}) = -0.37$ V (Ti^{3+} moderately stable, but its d^1 oxidises easily to d^0 Ti^{4+} in air).

Numerical anchor. The four μ values 1.73, 2.83, 3.87, 4.90 BM are the Bohr-magneton signature of $n = 1, 2, 3, 4$ unpaired electrons. The progression $\mu \propto \sqrt{n(n+2)}$ is non-linear: each additional electron adds less than the previous one (diminishing-return). The next value, $n = 5$, gives 5.92 BM.

Concept linkage. The half-filled-t_{2g} inertness of Cr^{3+} is analogous to the half-filled-shell stability we have seen for Mn^{2+} (d^5). In both cases the cation enjoys maximum exchange-energy stabilisation. The difference: Mn^{2+} has the half-filled set in free atom (no ligand field needed); Cr^{3+} needs the octahedral ligand field to split the five d orbitals into the three-orbital t_{2g} set.

Why this matters. The t_{2g}^3 inertness of $[\mathrm{Cr(H_2O)_6}]^{3+}$ is one of the most-cited examples of CFSE in inorganic chemistry. Its half-life for water exchange is hours, not nanoseconds — making Cr(III) complexes the favourite “kinetically inert” systems for studying mechanism. Same logic explains why $[Cr(NH_3)_6]^{3+}$ can be made and isolated as a discrete complex while $[\mathrm{Mn(NH_3)_6}]^{2+}$ falls apart quickly.

> **Final Answer:** 1, 2, 3, 4 unpaired electrons for Ti^{3+}, V^{3+}, Cr^{3+}, Mn^{3+} respectively; Cr^{3+} is most stable in aqueous solution.

✗ Mn^{3+} has 4 unpaired electrons, not 3

A frequent error is to write Mn^{3+} as $3d^5$ (mistaking it for Mn^{2+}). Correct: Mn(Z=25) is $3d^5 4s^2$, so removing 3 electrons (two $4s$, one $3d$) gives $3d^4$ for Mn^{3+}. Four unpaired electrons, $\mu = 4.90$ BM. The $3d^5$ ion is Mn^{2+}.

☞ Spin-only μ memory table

$n = 0$: $\mu = 0$; $n = 1$: 1.73; $n = 2$: 2.83; $n = 3$: 3.87; $n = 4$: 4.90; $n = 5$: 5.92 BM. Five values memorised gives you every spin-only answer in this chapter.

Q 4.25 Give examples and suggest reasons for the following features of the transition metal chemistry:

(i) The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.

(ii) A transition metal exhibits highest oxidation state in oxides and fluorides.

(iii) The highest oxidation state is exhibited in oxoanions of a metal.

SOLUTION

Concept used. The oxide of a metal is basic when the metal is in a low oxidation state and the bond M–O is largely ionic; it is acidic when the metal is in a high oxidation state and the bond M–O is largely covalent. O^{2-} and F^- are strong oxidising ligands and can stabilise the highest oxidation states of a metal.

Step 1. **(i) Basic to acidic with increasing O.S.** Manganese illustrates the trend perfectly:

- MnO (Mn $+2$): basic, dissolves in acid only.
- Mn_2O_3 (Mn $+3$): basic, weakly amphoteric.
- MnO_2 (Mn $+4$): amphoteric.
- Mn_2O_7 (Mn $+7$): strongly acidic, gives $HMnO_4$ (permanganic acid) with water.

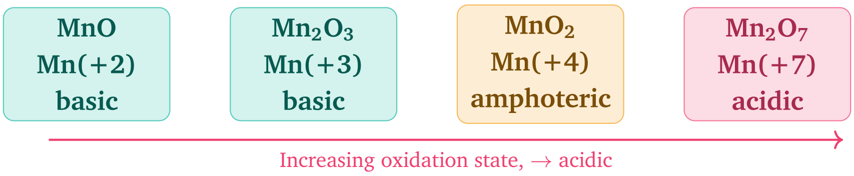
Reason: at low O.S. the metal cation is large with low charge and the M–O bond is essentially ionic (M^{2+}–O^{2-}), so the oxide acts as a base (releases O^{2-} which then takes a proton). At high O.S. the cation is small and highly charged; the M–O bond is covalent and the oxide behaves as an acid (releases H^+ through hydroxide groups).

Step 2. **(ii) Highest O.S. shown in oxides/fluorides.** Examples:

- Mn: highest O.S. $+7$ in Mn_2O_7 and $MnO_4{}^-$.
- Cr: highest O.S. $+6$ in CrO_3, CrF_6.
- Ru: highest O.S. $+8$ in RuO_4; Os: $+8$ in OsO_4, OsF_8.
- V: $+5$ in V_2O_5, VF_5.

Reason: O^{2-} and F^- are small, highly electronegative and capable of forming multiple bonds with the metal centre (especially O^{2-} can form $p\pi$-$d\pi$ double bonds). They thus accept many electrons from the metal, pushing it into a high oxidation state. Other ligands (Cl^-, Br^-, I^-) are larger and less electronegative; they cannot stabilise such high states (e.g. $MnCl_4$ is unknown, but MnF_4 and $MnO_4{}^-$ exist; $MnCl_7$ or $Mn_2(SO_4)_7$ are unknown).

Step 3. **(iii) Highest O.S. shown in oxoanions.** Examples: $MnO_4{}^-$ (Mn $+7$), $CrO_4{}^{2-}$ (Cr $+6$), $Cr_2O_7{}^{2-}$ (Cr $+6$), $VO_4{}^{3-}$ (V $+5$), $FeO_4{}^{2-}$ (Fe $+6$ in ferrate). Reason: in oxoanions the metal is surrounded by several O^{2-} ligands. Each oxide donates electron density (including $p\pi$ via filled p-orbitals into vacant d of the metal), and the strongly oxidising environment forces the metal to its highest accessible state.



Final Answer: (i) At low O.S. the M–O bond is ionic, oxide is basic; at high O.S. it is covalent, oxide is acidic (Mn series MnO → Mn_2O_7). (ii) Highest O.S. is shown in fluorides and oxides because F^- and O^{2-} are small, highly electronegative and (for O) can π-bond to the metal, stabilising the high state. (iii) Highest O.S. is shown in oxoanions ($MnO_4{}^-$, $CrO_4{}^{2-}$, $VO_4{}^{3-}$) for the same reasons: multiple O^{2-} donate enough electron density to make the very high cation feasible.

EXPERT'S SOLUTION *: Rahul Verma, B.Tech Chemical Engineering, IIT Bombay*

Structural observation. Three parts, one common thread: high-electronegativity, small, π-donating ligands such as O^{2-} and F^- pull a metal up to its highest oxidation state, and at those high states the oxide behaves like an acid.

Acid-base spectrum reasoning. The M–O bond character runs from ionic (low oxidation state, cation released easily, basic) to covalent (high oxidation state, lone pair tightly held, acidic). Fajan's rules quantify this: small, highly charged cations polarise the surrounding anion's electron cloud, producing covalent M–O bonds. So Mn^{2+} in MnO (ionic) gives basic oxide; Mn^{7+} in Mn_2O_7 (covalent, "acid anhydride") gives acidic oxide.

Step 1. Cite Mn series: MnO (basic), Mn_2O_3 (basic, weakly amphoteric), MnO_2 (amphoteric), Mn_2O_7 (acidic, → $HMnO_4$ with water). The transition from basic to acidic occurs at ∼+4 to +5. Reactions: $\mathrm{MnO} + 2\,\mathrm{HCl} \longrightarrow \mathrm{MnCl_2} + \mathrm{H_2O}$ (basic behaviour); $\mathrm{Mn_2O_7} + \mathrm{H_2O} \longrightarrow 2\,\mathrm{HMnO_4}$ (acidic behaviour).

Step 2. Quote highest O.S. examples: $MnO_4{}^-$ (+7), CrO_3 (+6), OsO_4 (+8). All are oxides or fluorides. Additional examples: V_2O_5 (+5), $ReO_4{}^-$ (+7), RuO_4 (+8), $TcO_4{}^-$ (+7).

Step 3. Reason: O^{2-} can form $p\pi$-$d\pi$ multiple bonds to the metal; F^- is the most electronegative single-bond ligand. Together they stabilise very high O.S. Quantitatively, χ(O) = 3.44 and χ(F) = 3.98 are the two highest non-metallic electronegativities; the difference χ(metal) $-\chi$(O) is large enough to produce highly polar M–O bonds, with significant ionic and covalent contributions.

Step 4. Oxoanion examples ((iii)): $MnO_4{}^-$ (Mn $+7$, 4 oxygens), $CrO_4{}^{2-}$, $Cr_2O_7{}^{2-}$ (Cr $+6$), $VO_4{}^{3-}$ (V $+5$), $FeO_4{}^{2-}$ (Fe $+6$ in ferrate, a powerful oxidant). In each, multiple O^{2-} donate enough electron density via π-bonds that the metal can survive in its highest oxidation state.

Step 5. Counter-example: $MnCl_7$ or Mn_2Br_7 do not exist. Heavy halogens cannot stabilise the +7 state because they are less electronegative and cannot form effective π-bonds. Their loose electron density makes the M–X bond too covalent (electron-rich) and not polar enough to sustain a very high metal oxidation state.

Numerical anchor. Comparing pK_a values of metal oxides shows the trend. MnO: p$K_a(\mathrm{Mn(OH)_2})$ of $-\log K_b \sim 12.7$, weakly basic. $HMnO_4$: p$K_a \approx -2.25$ (strong acid). The pK_a scale spans roughly 15 units across the manganese oxide series — a million-billion-fold acidity swing driven by a single thing: oxidation state.
Concept linkage. The acidic-to-basic trend is mirrored down in the p-block: Na_2O basic, Al_2O_3 amphoteric, SO_3 acidic. There the trend is left-to-right (changing element); here it is within one element (changing oxidation state). Same logic in two guises.
Why this matters. Predicting whether a high-state metal compound is realistic: if the ligand is small and electronegative (O, F), the high state is accessible; if the ligand is large and polarisable (Br, I, S), only low states are typical. JEE/NEET classic: "Why does Mn not form MnI_7?" — same answer.

> **Final Answer:** Low O.S. → ionic M–O → basic; high O.S. → covalent M–O → acidic. Highest O.S. attained with O^{2-} (multiple bonding) and F^- (high electronegativity), hence oxides/fluorides and oxoanions.

☞ Three Mn oxides and one acid

MnO (basic, Mn^{+2}), MnO_2 (amphoteric, Mn^{+4}), Mn_2O_7 (acidic, Mn^{+7}, the anhydride of permanganic acid $HMnO_4$). The boundary between basic and acidic occurs around oxidation state +4 or +5 for most transition metals.

♥ Ferrates, manganates and the chemistry of green oxoanions

Ferrate ${FeO_4}^{2-}$ (Fe +6, deep purple) and manganate ${MnO_4}^{2-}$ (Mn +6, green) are unusual high-oxidation oxoanions of the late $3d$ row. Both are unstable in acid (they oxidise water). Both are produced industrially in research as "green" oxidants for wastewater treatment because their reduction product (Fe_2O_3 or MnO_2) is harmless. The chemistry of the highest oxidation states of transition metals has both academic and environmental relevance.

Q 4.26 Indicate the steps in the preparation of:

(i) $K_2Cr_2O_7$ from chromite ore.

(ii) $KMnO_4$ from pyrolusite ore.

SOLUTION

Concept used. Both preparations follow the same general template: (a) oxidising fusion of the ore with an alkali in air or with an oxidising agent; (b) aqueous workup and acid/base manipulation; (c) cation exchange to crystallise the potassium salt. The oxidising fusion converts the metal in its low ore-state to a high-valent oxoanion.

Step 1. **(i) $K_2Cr_2O_7$ from chromite $FeCr_2O_4$.**

- Step 1, oxidising fusion:

$$4\,\mathrm{FeCr_2O_4} + 8\,\mathrm{Na_2CO_3} + 7\,\mathrm{O_2} \longrightarrow 8\,\mathrm{Na_2CrO_4} + 2\,\mathrm{Fe_2O_3} + 8\,\mathrm{CO_2}.$$

  Cr in chromite goes from $+3$ to $+6$; Fe stays $+3$ and is filtered out as Fe_2O_3 residue.
- Step 2, water leach and filter: the yellow Na_2CrO_4 dissolves; insoluble Fe_2O_3 is filtered.
- Step 3, acidify with H_2SO_4 (chromate → dichromate):

$$2\,\mathrm{Na_2CrO_4} + \mathrm{H_2SO_4} \longrightarrow \mathrm{Na_2Cr_2O_7} + \mathrm{Na_2SO_4} + \mathrm{H_2O}.$$

  Colour changes from yellow to orange.
- Step 4, cation exchange with KCl:

$$\mathrm{Na_2Cr_2O_7} + 2\,\mathrm{KCl} \longrightarrow \mathrm{K_2Cr_2O_7}\,(\mathrm{s}) + 2\,\mathrm{NaCl}.$$

  On cooling, the much less soluble orange $K_2Cr_2O_7$ crystallises out.

Step 2. (ii) $KMnO_4$ from pyrolusite MnO_2.

- Step 1, alkaline oxidative fusion (Mn $+4 \rightarrow$ Mn $+6$):

$$2\,\mathrm{MnO_2} + 4\,\mathrm{KOH} + \mathrm{O_2} \longrightarrow 2\,\mathrm{K_2MnO_4} + 2\,\mathrm{H_2O}.$$

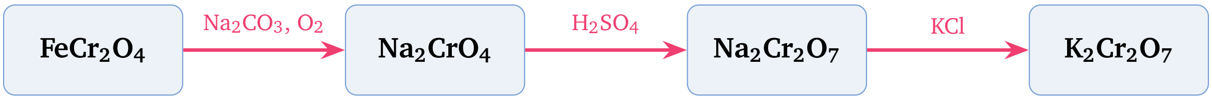
  (Sometimes KNO_3 is used as the oxidant in place of air.) Dark green K_2MnO_4 is produced.
- Step 2a, electrolytic oxidation of ${MnO_4}^{2-}$ ($+6$) to ${MnO_4}^{-}$ ($+7$):

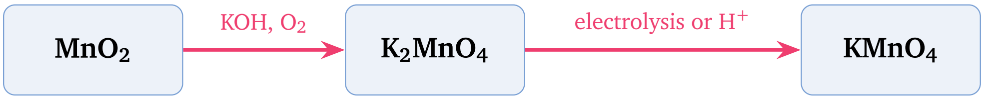
$$\mathrm{MnO_4}^{2-} \longrightarrow \mathrm{MnO_4}^{-} + \mathrm{e}^{-}.$$

- Step 2b, alternatively, acid-disproportionation:

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

- Step 3, evaporate and crystallise dark-purple $KMnO_4$.





Final Answer: (i) Chromite → Na_2CrO_4 (via Na_2CO_3, O_2) → $Na_2Cr_2O_7$ (via H_2SO_4) → $K_2Cr_2O_7$ (via KCl). (ii) MnO_2 → K_2MnO_4 (via KOH, O_2) → $KMnO_4$ (via electrolysis or H^+).

EXPERT'S SOLUTION : *Sneha Mehta, M.Sc Chemistry, IIT Kanpur*

Strategic angle. Each preparation has three or four named steps; learn them as one flow chart per metal.

Comparison of two preps. The two preparations follow the same template: oxidising fusion of the ore → aqueous extraction → further oxidation → crystallisation. The first metal (Cr) needs alkaline carbonate fusion to handle the chromite ($FeCr_2O_4$) and an acidification step to convert chromate to dichromate. The second (Mn) needs alkaline hydroxide fusion of MnO_2 and a second electrochemical or acid step to reach +7. Both involve a total oxidation-state change of +3 in chromium, +3 in manganese (starting from the ore's value).

Step 1. $K_2Cr_2O_7$: chromite (Cr^{3+}) + soda + air → Na_2CrO_4 (Cr^{6+}); acidify with H_2SO_4 to dichromate; crystallise with KCl. The final orange product is the well-known oxidising agent. Equation:
$4\,FeCr_2O_4 + 8\,Na_2CO_3 + 7\,O_2 \longrightarrow 8\,Na_2CrO_4 + 2\,Fe_2O_3 + 8\,CO_2$. $\Delta H \approx -1700$ kJ/mol — strongly exothermic, no external heating needed once the fusion starts.

Step 2. $KMnO_4$: pyrolusite (MnO_2, Mn^{4+}) + KOH + air → K_2MnO_4 (Mn^{6+}); then +6 → +7 by electrolysis (anodic oxidation in alkaline solution) or acidification (disproportionation). Purple crystals on cooling. Equations:
$2\,MnO_2 + 4\,KOH + O_2 \longrightarrow 2\,K_2MnO_4 + 2\,H_2O$;
$3\,K_2MnO_4 + 4\,HCl \longrightarrow 2\,KMnO_4 + MnO_2 + 4\,KCl + 2\,H_2O$ (acid method); or anodic oxidation: $MnO_4{}^{2-} \longrightarrow MnO_4{}^{-} + e^{-}$ (at the anode).

Step 3. Side products: in the chromite process, Fe_2O_3 residue is a saleable iron oxide. In the pyrolusite process, the electrolytic step produces H_2 at the cathode (recoverable as fuel gas).

Step 4. Common pitfall: the second step in $KMnO_4$ preparation (K_2MnO_4 → $KMnO_4$) needs careful pH control. Acidify too much and $KMnO_4$ disproportionates further to MnO_2. The lab-scale equation is run at pH ~3–4 or by electrolytic oxidation in alkaline medium.

Numerical anchor. The Cr balance: 4 $FeCr_2O_4$ contains 8 Cr^{3+}. Each Cr loses 3 electrons going to Cr^{6+}, so total electrons lost $= 24$. Plus 4 Fe^{2+} losing 1 electron each = 4. Total electrons lost = 28. The 7 O_2 ($= 14$ O atoms, each gaining 2 e^{-}) absorbs exactly 28 electrons. Stoichiometry balances.

Concept linkage. Both preparations involve transformation of a metal ion from a low oxidation state in the ore to a high oxidation state in the product. The fundamental method (oxidising alkaline fusion in air) is the same for many metallurgical preparations including chromium, manganese, vanadium and tungsten.

Why this matters. Both compounds are industrially important oxidising agents and the basis of standard volumetric analyses. $K_2Cr_2O_7$ is used in leather tanning and wood preservation; $KMnO_4$ in water purification, organic synthesis (Baeyer's test, oxidative cleavage of alkenes), and as a disinfectant ("Condy's crystals").

Final Answer: $K_2Cr_2O_7$: 3-step from chromite. $KMnO_4$: 2-step from pyrolusite.

☞ **Memory pattern**

Both preparations: ore + alkali + air → oxoanion (sodium- or potassium-containing), then further chemistry. Cr needs acidification + cation exchange; Mn needs further oxidation. The verb "oxidising fusion" carries the central idea — heat the ore in molten alkali with air to bump the metal to its high oxidation state.

Q 4.27 **What are alloys? Name an important alloy which contains some of the lanthanoid metals. Mention its uses.**

SOLUTION

Concept used. An alloy is a homogeneous mixture of two or more metals (or of a metal with a non-metal such as carbon) in which the host metal's lattice is preserved but some of its sites are occupied by atoms of the alloying element. Alloys often have better properties than any of the component metals (greater hardness, corrosion resistance, tensile strength).

Step 1. Define alloy. Examples: brass (Cu + Zn), bronze (Cu + Sn), steel (Fe + C), stainless steel (Fe + Cr + Ni + C).

Step 2. State the named lanthanoid alloy: Mischmetal. Composition (approximate): about 50% Ce, 25% La, with smaller amounts of Nd, Pr, and other lanthanoids, plus about 5% Fe and traces of S, C, Ca.

Step 3. Uses of mischmetal:

- **Lighter flints.** Mischmetal is pyrophoric: when scraped, it sheds tiny self-igniting sparks. The flint of cigarette lighters is mostly mischmetal alloyed with iron ("ferrocerium").
- **Bullets and shells.** Used in tracer bullets and incendiary devices because of the spark trail it produces.
- **Steelmaking.** Added in small quantities to steel as a deoxidiser and desulfuriser: the lanthanoids react preferentially with O and S to form stable inclusions, improving steel quality.
- **Magnesium alloys.** Mischmetal is added to Mg alloys to improve high-temperature creep resistance.

Final Answer: An alloy is a homogeneous mixture of two or more metals (or metal + non-metal) preserving a metallic lattice. **Mischmetal** (∼50% Ce, 25% La, balance Nd/Pr/Sm/Fe) is the most important lanthanoid alloy. Uses: lighter flints (pyrophoric), tracer bullets, deoxidiser/desulfuriser in steelmaking, Mg-alloy hardener.

EXPERT'S SOLUTION *: Priya Singh, M.Sc Physical Chemistry, IIT Madras*

Quick reading. Definition + Mischmetal + four uses; that is the complete answer.

Pyrophoric chemistry. A pyrophoric metal ignites spontaneously in air at room temperature. Mischmetal qualifies because its constituent lanthanoids have low first-ionisation enthalpies (~ 530–600 kJ/mol, compared with ~ 720 kJ/mol for Mn or 760 for Fe). The activation energy for oxidation is therefore small. When scraped, freshly exposed metal reacts exothermically with O_2 (~ -1800 kJ/mol per mole of Ce_2O_3), producing a shower of sparks at $\sim 3000\,°C$ — hot enough to ignite butane vapour.

Step 1. Define alloy in one line: a metallic solid solution where the host crystal lattice is preserved but partly occupied by atoms of the alloying element(s).

Step 2. Mischmetal ∼50% Ce + 25% La + rest other lanthanoids (Nd, Pr, Sm) and $\sim 5\%$ Fe. The Latin "misch" literally means "mixed" — the alloy is so-called because it preserves the mineralogical ratios of the rare-earth ore monazite or bastnaesite, without going to the trouble of separating individual lanthanoids.

Step 3. Uses: (i) pyrophoric flints in lighters and gas-grill igniters (Ce + Fe = "ferrocerium"); (ii) tracer ammunition and incendiary devices (spark trail visible in flight); (iii) steel-making as a deoxidiser and desulfuriser (lanthanoids react preferentially with O and S); (iv) Mg-alloy hardener for high-temperature creep resistance (Mg-RE alloys used in aerospace).

Step 4. Other lanthanoid alloys: $Nd_2Fe_{14}B$ (the strongest permanent magnet known, used in wind-turbine generators and hard-disk drives); $SmCo_5$ (high-temperature magnets); $LaNi_5$ (rechargeable hydride for NiMH batteries).

Numerical anchor. Density of mischmetal ~ 6.8 g/cm^3; m.p. $\sim 700\,°C$. Compare with pure Ce: 6.77 g/cm^3, m.p. 798 °C — alloying lowers the m.p. (classic solid-solution behaviour) and slightly tweaks density.

Concept linkage. The same low-ionisation-enthalpy reason that makes lanthanoid alloys pyrophoric also explains why lanthanoid metals are powerful reducing agents in their elemental form (used in lanthanide chemistry to reduce stubborn transition-metal complexes).

Why this matters. The unique pyrophoricity of mischmetal arises from the low ionisation energies of lanthanoids: scraping exposes fresh metal that oxidises violently in air, releasing enough heat to ignite the spark. The same physics powers every flint-based lighter in the world. Today, neodymium magnets, Nd-doped lasers and Eu-based phosphors make rare-earth alloys central to modern electronics.

> **Final Answer:** Mischmetal: ∼50% Ce + 25% La + minor lanthanoids/Fe. Used in lighter flints, tracer bullets, steel-making and Mg-alloys.

♥ Rare earths are not rare

"Rare-earth" is a misnomer dating from the 19th century. Ce is in fact the 25th most abundant element in Earth's crust — more abundant than copper. The "rarity" refers to the difficulty of separating the very similar lanthanoid ions, not their absolute abundance. Modern industries rely on rare-earth alloys for permanent magnets (electric vehicles), lasers (medical and industrial), and phosphors (LED lighting). China currently holds $\sim 70\%$ of the world's rare-earth refining capacity.

Q 4.28 What are inner transition elements? Decide which of the following atomic numbers are the atomic numbers of the inner transition elements: 29, 59, 74, 95, 102, 104.

SOLUTION

Concept used. **Inner transition elements** are the f-block elements: lanthanoids (Z = 57 to 71, also called rare earths) and actinoids (Z = 89 to 103). Their differentiating electron enters the deeply buried $4f$ (lanthanoids) or $5f$ (actinoids) sub-shell.

Step 1. State the inclusive ranges:

- Lanthanoids: Z = 57 (La) to 71 (Lu).
- Actinoids: Z = 89 (Ac) to 103 (Lr).

Step 2. Test each given atomic number:

- Z = 29: copper. d-block element (group 11). Not inner transition.
- Z = 59: praseodymium (Pr). Lies in $57–71 \Rightarrow$ **lanthanoid, inner transition**.
- Z = 74: tungsten (W). d-block element (group 6). Not inner transition.
- Z = 95: americium (Am). Lies in $89–103 \Rightarrow$ **actinoid, inner transition**.
- Z = 102: nobelium (No). Lies in $89–103 \Rightarrow$ **actinoid, inner transition**.
- Z = 104: rutherfordium (Rf). d-block (group 4 of the $6d$ series, a transactinide). Not inner transition.

Final Answer: Inner transition elements (the f-block) are the lanthanoids (Z $= 57$ to 71) and actinoids (Z $= 89$ to 103). From the list, Z $= 59, 95, 102$ are inner transition; the others (Z $= 29, 74, 104$) are not.

EXPERT'S SOLUTION *: Arjun Nair, B.Tech Chemical Engineering, IIT Bombay*

Quick reading. Memorise the two windows: 57–71 and 89–103. Anything inside is an inner transition element; anything outside is not.
Position rationale. The f-block sits below the main table because there are 14 elements per row (the f-sub-shell holds 14 electrons, $2 \times (2 \cdot 3 + 1) = 14$). They share group labels with the main table because their differentiating electron enters the buried $(n-2)f$ orbital, so chemically they all behave like group-3 metals. Placing them inside the main table would make it absurdly wide; pulling them out keeps the periodic table compact.

Step 1. Z = 29 (Cu): no — $3d$ transition metal (group 11).

Step 2. Z = 59 (Pr): yes, lanthanoid (Z in 57–71, $4f$ filling). Configuration: $[\mathrm{Xe}]4f^3 6s^2$.

Step 3. Z = 74 (W): no, $5d$ transition metal (group 6 of $5d$ series). Configuration: $[\mathrm{Xe}]4f^{14}5d^4 6s^2$.

Step 4. Z = 95 (Am): yes, actinoid (Z in 89–103, $5f$ filling). Configuration: $[\mathrm{Rn}]5f^7 7s^2$ — note the half-filled $5f^7$.

Step 5. Z = 102 (No): yes, actinoid. Configuration: $[\mathrm{Rn}]5f^{14}7s^2$ — the fully filled $5f^{14}$ marker right before lawrencium closes the row.

Step 6. Z = 104 (Rf, rutherfordium): no, $6d$ transactinide (group 4 of $6d$ series). Configuration: $[\mathrm{Rn}]5f^{14}6d^2 7s^2$, the post-actinoid analogue of Hf or Zr.

Numerical cross-check. Sum check: out of six given atomic numbers (29, 59, 74, 95, 102, 104), three (59, 95, 102) fall inside the two f-block windows; three (29, 74, 104) fall outside. So 3 inner-transition elements and 3 non-inner-transition.
Concept linkage. The same "window" test gives all 30 f-block elements: 15 lanthanoids (57–71) and 15 actinoids (89–103). The f-block thus comprises 30 of the periodic table's 118 elements ($\sim 25\%$ of the table).
Why this matters. The f-block sits below the main table because there are 14 elements per row and they share their group labels with the main table. Asking "inner transition or not" is really asking "does the differentiating electron sit in an f orbital?" — a simple yes/no question once the windows are memorised.

Final Answer: Z = 59 (Pr), 95 (Am), 102 (No) are inner transition.

☞ **Lanthanoid and actinoid windows**

Lanthanoids: 57 (La) – 71 (Lu), 15 elements, $4f$ block. Actinoids: 89 (Ac) – 103 (Lr), 15 elements, $5f$ block. (Some books exclude La and Ac from f-block proper since they have $4f^0$ and $5f^0$ ground states; NCERT, however, includes them as the first members.)

Q 4.29 The chemistry of the actinoid elements is not so smooth as that of the lanthanoids. Justify this statement by giving some examples from the oxidation state of these elements.

SOLUTION

Concept used. The lanthanoids show a remarkably uniform chemistry dominated by the $+3$ oxidation state because the $4f$ orbitals are deeply buried and barely participate in bonding. In contrast, the actinoids' $5f$ orbitals are spatially more extended and lie close in energy to $6d$ and $7s$, so multiple oxidation states arise easily.

Step 1. Lanthanoid pattern (smooth). All 15 lanthanoids show $+3$ as their dominant oxidation state. Only a few exceptions ($+4$ in Ce, $+2$ in Eu and Yb) and these are configuration-driven (reach $4f^0$ or $4f^7$ or $4f^{14}$). The chemistry of Ln^{3+} salts is so similar across the row that they are hard to separate.

Step 2. Actinoid pattern (irregular). Almost every actinoid from Th to Am shows several oxidation states:

- Th: $+3$, $+4$. ThO_2, ThF_4.
- U: $+3$, $+4$, $+5$, $+6$. UF_6, ${UO_2}^{2+}$, ${UO_2}^{+}$, UCl_3.
- Np: $+3$, $+4$, $+5$, $+6$, $+7$. ${NpO_2}^{+}$ (+5), ${NpO_2}^{2+}$ (+6).
- Pu: $+3$, $+4$, $+5$, $+6$, $+7$. PuF_4, PuO_2, ${PuO_2}^{2+}$, ${PuO_5}^{3-}$ (+7).
- Am: $+3$ to $+6$.

Beyond Am, the $+3$ state again dominates (because configuration is more lanthanoid-like for late actinoids with $5f^n$ buried more like $4f^n$).

Step 3. Reason. The $5f$, $6d$ and $7s$ energy levels in actinoids are very close, so removing 4, 5 or even 6 electrons from the metal is energetically accessible. In lanthanoids, by contrast, the gap between $4f$ and $5d/6s$ is too large for $4f$ electrons to be lost easily; only 3 electrons ($6s^2$, $5d^1$ or one $4f$) participate in bonding.

Final Answer: Lanthanoids: nearly uniform $+3$ state because $4f$ orbitals are buried. Actinoids: wide range of oxidation states ($+3$ to $+7$) because $5f$ orbitals are more spatially extended and lie close to $6d$ and $7s$ in energy. Examples: U shows +3, +4, +5, +6; Np and Pu show +3 to +7.

EXPERT'S SOLUTION : *Aarav Joshi, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle. Contrast configurations: lanthanoid $4f$ electrons are core-like, actinoid $5f$ electrons are valence-like.

Orbital extension reasoning. The radial maximum of a $4f$ orbital lies at ~ 0.4 Å from the nucleus, well inside the $5s$ and $5p$ shells. The radial maximum of $5f$ lies at ~ 0.9 Å, in the same range as $6d$ and $7s$. So $5f$ electrons can overlap with ligand orbitals while $4f$ cannot. This single fact explains the difference in oxidation-state range.

Step 1. Lanthanoids: $+3$ ubiquitous; only a few deviations. Specifically: $+2$ for Eu, Yb (and weakly Sm, Tm); $+4$ for Ce, Tb (and weakly Pr, Nd). Each deviation is configuration- driven (reach f^0, f^7, f^{14}).

Step 2. Actinoids: $+3$ to $+7$ widely seen; mention U, Np, Pu as prototypes.

- U: $+3, +4, +5, +6$ all stable in suitable conditions. $UO_2{}^{2+}$ (uranyl, +6) is the dominant solution form.
- Np: $+3, +4, +5, +6, +7$. Notable for stabilising the elusive +7 state in $NpO_5{}^{3-}$.
- Pu: $+3, +4, +5, +6, +7$. Famous for the colour-coded solution chemistry: Pu(III) blue, Pu(IV) brown, Pu(V) pink, Pu(VI) orange. The PUREX process exploits the redox cycle Pu(IV)/Pu(III) to separate Pu from U.
- Th: only $+4$ stable, with no $5f$ in ground state ($6d^2 7s^2$). Th behaves more like Zr/Hf than like a lanthanoid.

Step 3. Reason: $5f$ orbitals are more extended in space and overlap $6d/7s$ in energy, so more electrons are chemically active. Quantitatively: $E(5f)$ - $E(6d)$ is only ~1–2 eV for early actinoids, compared with ~5–7 eV for $4f$ vs $5d$ in early lanthanoids. The smaller gap explains the wider O.S. range.

Step 4. Numerical evidence: the cumulative $\Delta_i H$ for going from U^{3+} to U^{6+} is ~ 5500 kJ/mol — large but feasible because of low-energy $5f/6d$ orbitals. The corresponding values for Sm going to $+6$ would be far higher and the +6 state is consequently not observed.

Concept linkage. Lanthanoid behaviour is summarised as "unitary $+3$ chemistry"; actinoid behaviour as "transition-metal- like wide $+3$ to $+7$ chemistry". The transition between the two patterns happens at the middle of the actinoid series: early actinoids (Th, Pa, U, Np, Pu) act like transition metals; late actinoids (Cm onwards) act like lanthanoids.

Why this matters. The nuclear-fuel cycle's redox chemistry (extraction of U from ore as $UO_2{}^{2+}$, reduction to U^{4+} during purification) depends entirely on the actinoid wide-range oxidation chemistry. The Mn(VI)/Mn(VII) couple in $KMnO_4$ chemistry ($3d$) is mirrored by the U(IV)/U(VI) couple in nuclear chemistry ($5f$) — both rely on accessible higher oxidation states. The PUREX process is worth understanding deeply because it underpins both weapons-grade Pu separation and civilian-fuel recycling.

Final Answer: Lanthanoid chemistry is uniform (+3); actinoid chemistry is varied (+3 to +7) because $5f$ orbitals are more accessible.

☞ Two-bucket comparison

"Lanthanoid: $4f$ buried in core → +3 dominates. Actinoid: $5f$ in valence shell → +3 to +7 visible." One sentence per series captures the essence. Add one named example per series: Ce^{4+} for lanthanoid deviation; $UO_2{}^{2+}$ for actinoid wide range.

Q 4.30 **Which is the last element in the series of the actinoids? Write the electronic configuration of this element. Comment on the possible oxidation state of this element.**

SOLUTION

Concept used. The actinoid series runs from Ac (Z = 89) to Lr (Z = 103). The last element is lawrencium, Lr.

Step 1. **Identity:** Lawrencium (Lr), Z = 103, atomic mass approximately ~ 262. Element 103, named after E. O. Lawrence.

Step 2. **Electronic configuration:**

$$\text{Lr}: \ [\text{Rn}]\, 5f^{14}\, 6d^1\, 7s^2.$$

The $5f$ sub-shell is fully filled with 14 electrons; the last (differentiating) electron entered the $6d$, which makes Lr formally a transition-metal-like end of the actinoid series. (Some sources prefer $[\text{Rn}]5f^{14}7s^27p^1$ on the basis of relativistic calculations, but the IUPAC and NCERT convention uses the $6d^1$ form.)

Step 3. **Oxidation state:** Like the last lanthanoid Lu (which is $[\text{Xe}]4f^{14}5d^16s^2$ and shows only +3), Lr is expected to show predominantly the +3 oxidation state. On losing 3 electrons ($7s^2 + 6d^1$) it reaches $[\text{Rn}]5f^{14}$, a fully filled $5f$ shell. There is no easy way to access +2 or +4 because the next ionisation would have to break the closed $5f^{14}$ shell. So Lr's chemistry is essentially Lr(III).

Final Answer: Last actinoid: **Lawrencium (Lr, Z = 103).** Configuration $[\text{Rn}]\, 5f^{14}\, 6d^1\, 7s^2$. The only common and expected oxidation state is +3, giving the closed-shell $[\text{Rn}]\, 5f^{14}$ Lr^{3+} ion.

EXPERT'S SOLUTION : *Vivaan Singh, M.Sc Chemistry, IIT Kanpur*

Quick reading. Z = 103, Lr, $[\mathrm{Rn}]5f^{14}6d^{1}7s^{2}$, oxidation state $+3$.

Closing-the-row analogy. The lanthanoid row closes at Lu (Z=71, $[\mathrm{Xe}]4f^{14}5d^{1}6s^{2}$) with only the $+3$ state. The actinoid row closes at Lr (Z=103) with the same closed-shell f^{14} pattern and a single $d^{1}s^{2}$ valence shell. Both elements lose three electrons to a closed-shell core; both show $+3$ chemistry exclusively.

Step 1. Identify Lr at the end of the actinoid row. Lawrencium, named after Ernest O. Lawrence, was first synthesised in 1961 at Berkeley. All known isotopes are radioactive; the longest-lived is ^{266}Lr (half-life $\sim$11 hours).

Step 2. Configuration: 14 $5f$ electrons, plus $6d^{1}7s^{2}$ (three valence electrons available). Total electrons: $86 + 14 + 1 + 2 = 103$. Note: some relativistic calculations suggest $[\mathrm{Rn}]5f^{14}7s^{2}7p^{1}$ for Lr because the $7p_{1/2}$ orbital is lowered by relativistic effects below the $6d$. The NCERT/IUPAC textbook convention uses the $6d^{1}$ form, which we follow here.

Step 3. Lose all three valence electrons to give closed $[\mathrm{Rn}]5f^{14}$ as Lr^{3+}. Hence $+3$ is the only expected stable state. The closed $5f^{14}$ shell is so stable that further ionisation (to $+4$) would mean breaking it, requiring much more energy.

Step 4. Magnetic/colour check: $\mathrm{Lr}^{3+} = 5f^{14}$. All paired, $\mu = 0$ BM (diamagnetic). No f-f transitions possible (no vacancies), so Lr^{3+} compounds would be colourless. (In practice, Lr is so short-lived that compound characterisation is limited.)

Numerical anchor. Mass-103 element with 103 electrons; in Lr^{3+}, 100 electrons. Configuration check: $86 + 14 = 100$ (matches). First ionisation enthalpy of Lr is calculated to be $\sim$478 kJ/mol, low compared with $\sim$524 kJ/mol for Lu — consistent with the loosely bound $7p$ or $6d$ electron.

Concept linkage. "Periodic" analogy between the last lanthanoid (Lu) and the last actinoid (Lr): both have closed inner f-shells plus a $d^{1}s^{2}$ outer shell, and both show only +3 chemistry. The actinoid row mimics the lanthanoid row at its endpoints but diverges in the middle (where actinoids show variable O.S.).

Why this matters. The closing of the actinoid row at lawrencium mirrors the closing of the lanthanoid row at lutetium: both reach the configurations $f^{14}d^{1}s^{2}$ and both show only the $+3$ oxidation state in compounds. The post-Lr elements (rutherfordium Z=104 onwards) start a new transition row, the $6d$ series, where "transactinide" chemistry is studied with atom-at-a- time techniques.

> **Final Answer:** Lr (Z = 103), $[\mathrm{Rn}]5f^{14}6d^{1}7s^{2}$, $+3$ oxidation state.

☞ The four "closing" configurations

Each block closes with a closed-shell-plus-one-valence-electron pattern: s-block at ns^{2}; p-block at

ns^2np^6 (noble gas); d-block at $(n-1)d^{10}ns^2$; f-block at $(n-2)f^{14}(n-1)d^1ns^2$. Lu and Lr are the f-block end markers.

Q 4.31 **Use Hund's rule to derive the electronic configuration of Ce^{3+} ion, and calculate its magnetic moment on the basis of "spin-only" formula.**

SOLUTION

Concept used. **Hund's rule of maximum multiplicity** states that when electrons occupy degenerate orbitals (orbitals of the same energy), they enter singly with parallel spins until each of the degenerate orbitals has one electron; pairing begins only after that. The **spin-only** formula for the magnetic moment of an ion is

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

where n is the number of unpaired electrons and BM is the Bohr magneton.

Step 1. Start with the neutral atom Ce (Z = 58): $[\text{Xe}]\,4f^1\,5d^1\,6s^2$. The Xe core supplies the inner 54 electrons; the remaining four are valence.

Step 2. To form Ce^{3+}, remove three electrons starting from the highest-n shell. So remove the two $6s$ electrons first, then the one $5d$ electron:

$$\begin{aligned}\text{Ce} &: [\text{Xe}]\,4f^1\,5d^1\,6s^2,\\ \text{Ce}^{+} &: [\text{Xe}]\,4f^1\,5d^1\,6s^1,\\ \text{Ce}^{2+} &: [\text{Xe}]\,4f^1\,5d^1,\\ \text{Ce}^{3+} &: [\text{Xe}]\,4f^1.\end{aligned}$$

Step 3. By Hund's rule, the single $4f$ electron occupies one of the seven $4f$ orbitals on its own. So there is exactly $n = 1$ unpaired electron in Ce^{3+}.

Step 4. Apply the spin-only formula:

$$\mu = \sqrt{n(n+2)} = \sqrt{1\cdot(1+2)} = \sqrt{3}.$$

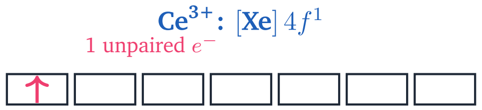
Evaluate the square root:

$$\sqrt{3} = 1.732.$$

Therefore

$$\mu \approx 1.73\ \text{BM}.$$

Step 5. Caveat for lanthanoids: the spin-only formula often underestimates the observed moment of f-block ions because the orbital angular momentum is not quenched. For Ce^{3+} the experimental value is about 2.4 BM (using the Landé formula); the question, however, asks for the spin-only value.



Seven $4f$ orbitals

Final Answer: Ce^{3+}: [Xe] $4f^1$; $n = 1$; spin-only $\mu = \sqrt{3} = 1.73$ BM.

EXPERT'S SOLUTION *: Pranav Desai, M.Sc Chemistry, IIT Kanpur*

Strategic angle. Identify the cation, count unpaired electrons, plug into the formula. The answer is one line.

Why spin-only fails for lanthanoids. Lanthanoid $4f$ electrons retain significant orbital angular momentum because the $4f$ orbitals are spatially compact (small radial extent) and relatively unperturbed by the surroundings (the crystal field on $4f$ is small, $\Delta \sim 100$ cm^{-1}, much less than the spin-orbit coupling). So the orbital moment is *not quenched* for lanthanoids — unlike $3d$ ions where the orbital moment is quenched and spin-only μ works. The proper formula is the Landé expression: $\mu = g_J\sqrt{J(J+1)}$ BM, where J is the total angular momentum quantum number.

Step 1. Neutral Ce has 58 electrons: [Xe]$4f^1 5d^1 6s^2$. Three electrons leave on $+3$ ionisation, starting from the outermost shell. So lose $6s^2$ first, then $5d^1$. Result: Ce^{3+} = [Xe]$4f^1$.

Step 2. By Hund's rule the single $4f$ electron is unpaired. So $n = 1$.

Step 3. Apply spin-only formula:

$$\mu = \sqrt{n(n+2)} = \sqrt{1 \cdot 3} = \sqrt{3} = 1.732\,\text{BM} \approx 1.73\,\text{BM}.$$

Step 4. Compare to experimental value: $\mu_{\text{obs}}(\text{Ce}^{3+}) \approx 2.4$ BM. Discrepancy is due to orbital contribution: the $4f^1$ electron has $\ell = 3$, $s = 1/2$, so by Landé: $L = 3$, $S = 1/2$, $J = L - S = 5/2$ (since shell is less than half full, $J = |L - S|$). Then $g_J = 6/7$, $\mu = (6/7)\sqrt{(5/2)(7/2)} = (6/7) \times 2.96 \approx 2.54$ BM, matching observation. The textbook calculation gives spin-only $\sqrt{3} = 1.73$ BM as asked.

Numerical anchor. Useful Landé values to know: Pr^{3+} (f^2) spin-only 2.83 BM, Landé 3.62 BM (obs 3.5); Nd^{3+} (f^3) spin-only 3.87, Landé 3.68 (obs 3.5); Sm^{3+} (f^5) spin-only 5.92, Landé 0.84 (obs 1.5). Note how Landé and spin-only diverge dramatically for some f-ions.

Concept linkage. The spin-only formula's accuracy is a property of orbital-moment quenching. For $3d$ ions in an octahedral field, the ligand field strongly splits the d orbitals, quenching L. For $4f$ ions, the field is too weak to do so. This is a key distinction between d-block and f-block magnetism.

Why this matters. For most $3d$ ions the spin-only formula gives a good estimate. For lanthanoid ions, orbital contribution is significant; but the NCERT exercise asks for the spin-only number, which is what we calculated. JEE/NEET style: "Why does the measured magnetic moment of Sm^{3+} differ greatly from the spin-only value?" — orbital contribution is the answer.

> **Final Answer:** Ce^{3+} is $4f^1$ with one unpaired electron; spin-only $\mu = \sqrt{3} \approx 1.73$ BM.

✗ Apply spin-only to lanthanoids only when asked

For $3d$ ions, spin-only $\mu = \sqrt{n(n+2)}$ matches experiment to within $\sim 5\%$. For $4f$ ions, the spin-only value can be off by 50–100%. If a question asks for "magnetic moment of Ce^{3+}" without qualifying, you should mention both the spin-only value (1.73 BM) and the experimental (2.4 BM, due to orbital contribution). If the question explicitly says "spin-only", stick to $\sqrt{n(n+2)}$.

Q 4.32 **Name the members of the lanthanoid series which exhibit $+4$ oxidation states and those which exhibit $+2$ oxidation states. Try to correlate this type of behaviour with the electronic configurations of these elements.**

SOLUTION

Concept used. Lanthanoids predominantly show the $+3$ oxidation state. Deviations to $+4$ or $+2$ occur when the resulting Ln^{4+} or Ln^{2+} ion has an extra-stable f-shell configuration: $4f^0$, $4f^7$ or $4f^{14}$.

Step 1. $+4$ **oxidation states.** The four lanthanoids that show $+4$ in well-characterised compounds are Ce, Pr, Tb, Nd (and to a lesser extent Dy). Check each:

- Ce ($4f^1 5d^1 6s^2$) $\rightarrow$ Ce^{4+}: $4f^0$, noble-gas [Xe] core. Very stable.
- Pr ($4f^3 6s^2$) $\rightarrow$ Pr^{4+}: $4f^1$. Less stable, exists in some solid oxides.
- Nd ($4f^4 6s^2$) $\rightarrow$ Nd^{4+}: $4f^2$. Even less stable.
- Tb ($4f^9 6s^2$) $\rightarrow$ Tb^{4+}: $4f^7$, half-filled, extra-stable.
- Dy ($4f^{10} 6s^2$) $\rightarrow$ Dy^{4+}: $4f^8$. Rarely observed.

The two most stable $+4$ states are clearly Ce ($4f^0$) and Tb ($4f^7$).

Step 2. $+2$ **oxidation states.** Show in Eu, Yb, Sm and Tm.

- Sm ($4f^6 6s^2$) $\rightarrow$ Sm^{2+}: $4f^6$. Mildly stable, reducing.
- Eu ($4f^7 6s^2$) $\rightarrow$ Eu^{2+}: $4f^7$, half-filled, extra-stable.
- Tm ($4f^{13} 6s^2$) $\rightarrow$ Tm^{2+}: $4f^{13}$. Less stable.

- Yb $(4f^{14}6s^2) \rightarrow$ Yb^{2+}: $4f^{14}$, fully filled, very stable.

The two most stable $+2$ states are Eu $(4f^7)$ and Yb $(4f^{14})$.

Step 3. **Correlation.** In every case the deviation from $+3$ is driven by the configuration of the resulting ion landing on or near an f^0, f^7 or f^{14} stable configuration. Configuration is the controlling factor; compounds of Ln^{2+} (or Ln^{4+}) far from these configurations are unstable or unknown.

Element	Ion	Config.	Reason
Ce	**Ce^{4+}**	$4f^0$	**Empty f**
Pr	Pr^{4+}	$4f^1$	Near f^0
Nd	Nd^{4+}	$4f^2$	(weak)
Tb	**Tb^{4+}**	$4f^7$	**Half-filled**
Sm	Sm^{2+}	$4f^6$	Near f^7
Eu	**Eu^{2+}**	$4f^7$	**Half-filled**
Tm	Tm^{2+}	$4f^{13}$	Near f^{14}
Yb	**Yb^{2+}**	$4f^{14}$	**Fully filled**

Final Answer: $+4$ shown by Ce, Pr, Nd, Tb, (Dy); most stable for Ce $(4f^0)$ and Tb $(4f^7)$. $+2$ shown by Sm, Eu, Tm, Yb; most stable for Eu $(4f^7)$ and Yb $(4f^{14})$. All deviations from $+3$ are driven by the resulting ion landing on or near f^0, f^7 or f^{14}.

EXPERT'S SOLUTION *: Tara Nair, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle. Match each non-standard oxidation state to the stable f-configuration it produces.

Symmetry argument. Three configurations are unusually stable: $4f^0$ (empty shell, noble-gas core), $4f^7$ (half-filled, maximum exchange energy), $4f^{14}$ (fully filled). Around each of these, adjacent lanthanoids can be pulled to non-standard oxidation states because the ion "wants" to reach them. So the deviations cluster near positions 0, 7, 14 — i.e. near La, Gd, Lu (which themselves are always $+3$ because their neutral configuration plus charge $+3$ already lands them at $4f^0, 4f^7, 4f^{14}$).

Step 1. $+4$ states (going to f^0 or f^7): Ce^{4+} (f^0), Tb^{4+} (f^7). Less stable: Pr, Nd, Dy. Ce is by far the most prominent — $(NH_4)_2[Ce(NO_3)_6]$ is ceric ammonium nitrate (CAN), the textbook one-electron oxidant in organic chemistry.
$E°(\mathrm{Ce}^{4+}/\mathrm{Ce}^{3+}) = +1.61$ V (in HClO_4): strong but clean oxidant.
$E°(\mathrm{Tb}^{4+}/\mathrm{Tb}^{3+}) \approx +3.1$ V: enormous, so Tb(IV) only exists in solid oxides like TbO_2.

Step 2. $+2$ states (going to f^7 or f^{14}): Eu^{2+} (f^7), Yb^{2+} (f^{14}). Less stable: Sm, Tm.
$E°(\mathrm{Eu}^{3+}/\mathrm{Eu}^{2+}) = -0.43$ V: only mildly reducing, so Eu(II) salts are isolable.
$E°(\mathrm{Yb}^{3+}/\mathrm{Yb}^{2+}) = -1.05$ V: more reducing but still accessible.
$E°(\mathrm{Sm}^{3+}/\mathrm{Sm}^{2+}) = -1.55$ V: strongly reducing. Used in SmI_2 (Kagan's reagent) for organic synthesis.

Step 3. Rule: lanthanoids prefer $+3$; deviations occur when the new ion has an exceptionally stable f-shell. The pattern across the series: deviations occur in the neighbourhood of the "magic" positions (f^0, f^7, f^{14}).

Step 4. Configuration check for Yb^{2+} ($4f^{14}$): all electrons paired; $\mu = 0$ BM (diamagnetic). For Eu^{2+} ($4f^7$): 7 unpaired electrons; spin-only $\mu = \sqrt{63} = 7.94$ BM, observed ~ 7.9 BM (great agreement because L is quenched for half-filled f^7).

Numerical anchor. Across the lanthanoid series, the deviation count is 4 (Eu, Yb $+2$; Ce, Tb $+4$, well-established) out of 15 elements — i.e. $\sim 27\%$ show non-+3 chemistry. The other 11 lanthanoids stay strictly $+3$ in all isolated compounds.
Concept linkage. The exception/rule logic is the same as for the $3d$ row's stability of d^0, d^5, d^{10} oxidation states. In the lanthanoids it's f^0, f^7, f^{14}; in the d-block d^0, d^5, d^{10}. Closed-shell-driven deviation is universal across blocks.
Why this matters. Ce^{4+} is a standard analytical oxidant (ceric sulphate titrations) precisely because Ce(III)/Ce(IV) is reversible and clean. Eu^{2+} salts are blue-fluorescent and used in modern lighting and X-ray screens. Both deviations are exploited industrially: rare-earth phosphor science is built on Eu(II) and Eu(III) emission; redox chemistry uses Ce(IV)/Ce(III).

> **Final Answer:** $+4$: Ce, Pr, Nd, Tb (Dy). $+2$: Sm, Eu, Tm, Yb. Drivers: f^0, f^7, f^{14} stability.

♥ Modern phosphors

The white LEDs in modern lights and TV screens contain Ce^{3+}-doped $Y_3Al_5O_{12}$ ("YAG") or Eu^{2+}-doped $(Sr, Ba, Ca)Si_2O_2N_2$ phosphors that emit yellow or green light when excited by a blue LED. Ce(III) and Eu(II) emission — the very deviations from +3 chemistry studied here — are the source of efficient yellow-green emission in display technology. The chemistry of f-block exceptions is therefore central to billions of dollars of LED industry.

Q 4.33 Compare the chemistry of the actinoids with that of lanthanoids with reference to: (i) electronic configuration, (ii) oxidation states and (iii) chemical reactivity.

SOLUTION

Concept used. The lanthanoids ($4f$ filling) and actinoids ($5f$ filling) show parallel but not identical trends. The key distinction is that $5f$ orbitals are spatially more extended than $4f$ orbitals and have lower binding energy, so they are far more chemically accessible.

Step 1. (i) Electronic configuration.

- Lanthanoids: general $[\mathrm{Xe}]\,4f^{1-14}\,5d^{0-1}\,6s^2$. Configurations are fairly regular: each successive element adds one $4f$ electron, with a $5d$ contribution at La, Ce, Gd, Lu.
- Actinoids: general $[\mathrm{Rn}]\,5f^{0-14}\,6d^{0-2}\,7s^2$. Less regular: Th has $6d^27s^2$ (no $5f$), Pa, U, Np have a mixed $5f^n6d^17s^2$, while later actinoids (Cm onwards) start to settle into $5f^n7s^2$ form.

Step 2. (ii) Oxidation states.

- Lanthanoids show mainly $+3$, with sporadic $+2$ (Eu, Yb, Sm, Tm) and $+4$ (Ce, Pr, Nd, Tb).
- Actinoids show a much wider range: $+3$, $+4$, $+5$, $+6$ and $+7$. For instance Np shows $+3$ to $+7$ ($NpO_5{}^{3-}$ is the $+7$ species).

Step 3. (iii) Chemical reactivity.

- Lanthanoids: very reactive, behave like Ca-type metals; tarnish in air to form oxides; react with water to release H_2.
- Actinoids: also highly reactive; react with boiling water to give oxide and H_2; with non-oxidising acids give An^{3+} and H_2. Many actinoids show variable redox chemistry in solution (e.g., $UO_2{}^{2+}/UO_2{}^{+}$ couple, $E^\circ = 0.06$ V) and form numerous oxo-, halide-, organometallic complexes. Additionally, all actinoids are radioactive.

Overall: actinoid chemistry is more complex because of wider O.S., more covalent character ($5f$ orbitals can take part in covalent bonding to a greater extent) and radioactivity.

Final Answer: (i) Both are f-block; lanthanoids fill $4f$, actinoids fill $5f$; lanthanoid configurations are regular, actinoid ones irregular. (ii) Lanthanoids mainly $+3$; actinoids $+3$ to $+7$. (iii) Both reactive and electropositive; actinoids additionally radioactive and form a richer complex chemistry because $5f$ orbitals are more extended.

EXPERT'S SOLUTION *: Aditya Kapoor, M.Tech Chemical Engineering, IIT Delhi*

Quick reading. The headline difference is the extension of the $5f$ orbitals into the bonding region, which gives actinoids a wider oxidation-state range, more covalent character and (unrelatedly but importantly) radioactivity.
Numerical comparison. Cumulative contractions across the two series: lanthanoid ∼14–18 pm (atomic), ∼17 pm (ionic); actinoid ∼15–20 pm. Maximum oxidation state observed: lanthanoid +4 (Ce, Tb); actinoid +7 (Np, Pu). Both contractions are real and important; the actinoid wider O.S. range is the more chemically consequential difference.

Step 1. Configurations: $4f^{1-14}5d^{0-1}6s^2$ vs $5f^{0-14}6d^{0-2}7s^2$. Actinoid configs are less regular. Specific irregularities to remember: Th ($6d^27s^2$, no $5f$); Pa ($5f^26d^17s^2$); U ($5f^36d^17s^2$); Np ($5f^46d^17s^2$); Cm ($5f^76d^17s^2$, with the extra $6d$ for half-filled $5f^7$ stability — Gd-analog).

Step 2. Oxidation states: lanthanoids mostly $+3$; actinoids $+3$ to $+7$. Pu and Np uniquely show all states from $+3$ to $+7$. $NpO_5{}^{3-}$ and $PuO_5{}^{3-}$ for $+7$; $UO_2{}^{2+}$ and $PuO_2{}^{2+}$ for $+6$; $NpO_2{}^{+}$, $UO_2{}^{+}$ for $+5$; $Pu(NO_3)_4$, ThF_4 for $+4$; $PuCl_3$ for $+3$.

Step 3. Reactivity: both highly reactive electropositive metals; actinoids also radioactive. The complex chemistry of actinoids (e.g. $UO_2(NO_3)_2$, Pu(IV) oxidation/reduction in the PUREX process) far exceeds that of lanthanoids. Actinoids attack water, halogens, oxygen, sulfur, nitrogen at moderate heat; concentrated nitric or hydrochloric acid dissolves them readily.

Step 4. Radioactivity: every actinoid isotope is unstable (all decay by α, β, or fission). Half-lives range from seconds (Lr) to billions of years (Th-232, U-238). No lanthanoid is radioactive (except ^{147}Pm, an artificial radio-isotope; natural Pm does not exist on Earth).

Step 5. Concept link to bonding character: $5f$ electrons can contribute to chemical bonds in early actinoids — this gives actinoid complexes a more covalent character (e.g. $UO_2{}^{2+}$ has a triple-bond character in the linear O=U=O moiety, with significant $5f \rightarrow$ ligand backbonding). Lanthanoid complexes are almost purely ionic.

Numerical cross-check. E° for lanthanoid Ln^{3+}/Ln couples range from -1.99 V (Eu) to

-2.52 V (Lu) — all negative, all reducing. Actinoid An^{3+}/An couples range from -1.83 V (U) to -2.13 V (Es) — also strongly reducing. Both series are electropositive but actinoids show a wider range due to varied electronic structure.

Concept linkage. Just as the chemistry of $3d$ (Sc-Zn) is more varied than the chemistry of $4d$ and $5d$ in some respects (more colour, easier $+2$ states), the chemistry of $5f$ (early actinoids) is more varied than that of $4f$. Across both pairs, the heavier (deeper-orbital) series shows more diversity through shell-overlap effects.

Why this matters. The PUREX process used to recycle nuclear fuel rides on switching Pu between $+4$ and $+3$ to separate it from U. Such redox manipulation is impossible for lanthanoids because of their fixed $+3$ chemistry. Modern actinoid research (Th-fuel reactors, recycling of spent fuel, transmutation of long-lived waste) is built on the same wide redox range of actinoids.

> **Final Answer:** Lanthanoids: regular $4f$ filling, $+3$-dominant chemistry. Actinoids: irregular $5f$ filling, $+3$ to $+7$ chemistry, radioactive.

☞ Three-pillar answer for the comparison

"(i) Lanthanoid: $4f^{1-14}5d^{0-1}6s^2$ regular; actinoid: $5f^{0-14}6d^{0-2}7s^2$ irregular. (ii) Lanthanoid: mostly $+3$; actinoid: $+3$ to $+7$. (iii) Both reactive electropositive metals; actinoids additionally radioactive." Three sentences, every key term present.

Q 4.34 Write the electronic configurations of the elements with the atomic numbers 61, 91, 101, and 109.

SOLUTION

Concept used. Identify each element from its atomic number, then write the configuration by filling sub-shells in the order given by the Aufbau diagonal rule, with the famous exceptions for d- and f-block elements.

Step 1. **Z = 61: Promethium (Pm).** A lanthanoid (between Nd and Sm).

$$\mathrm{Pm} : [\mathrm{Xe}]\, 4f^5\, 6s^2.$$

Check: 54 (Xe core) + 5 ($4f$) + 2 ($6s$) = 61. Correct.

Step 2. **Z = 91: Protactinium (Pa).** An actinoid (between Th and U).

$$\mathrm{Pa} : [\mathrm{Rn}]\, 5f^2\, 6d^1\, 7s^2.$$

Check: 86 (Rn core) + 2 + 1 + 2 = 91. Correct.

Step 3. **Z = 101: Mendelevium (Md).** An actinoid (between Fm and No).

$$\mathrm{Md} : [\mathrm{Rn}]\, 5f^{13}\, 7s^2.$$

Check: 86 + 13 + 2 = 101. Correct. (No $6d$ electron.)

Step 4. **Z = 109: Meitnerium (Mt).** A transactinide (group 9, $6d$ series).

$$\mathrm{Mt} : [\mathrm{Rn}]\, 5f^{14}\, 6d^7\, 7s^2.$$

Check: 86 + 14 + 7 + 2 = 109. Correct.

Z	Element	Configuration
61	Pm	$[\mathrm{Xe}]\, 4f^5\, 6s^2$
91	Pa	$[\mathrm{Rn}]\, 5f^2\, 6d^1\, 7s^2$
101	Md	$[\mathrm{Rn}]\, 5f^{13}\, 7s^2$
109	Mt	$[\mathrm{Rn}]\, 5f^{14}\, 6d^7\, 7s^2$

Final Answer: Z=61 Pm: $[\mathrm{Xe}]4f^5 6s^2$. Z=91 Pa: $[\mathrm{Rn}]5f^2 6d^1 7s^2$. Z=101 Md: $[\mathrm{Rn}]5f^{13} 7s^2$. Z=109 Mt: $[\mathrm{Rn}]5f^{14} 6d^7 7s^2$.

EXPERT'S SOLUTION *: Karan Mehta, M.Sc Chemistry, IIT Kanpur*

Quick reading. Identify each by element then add electrons on top of the noble-gas core.

Block identification. Z values map to blocks: 57–71 lanthanoid ($4f$); 89–103 actinoid ($5f$); 104–118 transactinide ($6d$ + $7p$). So a quick three-rule sort: 61 is lanthanoid, 91 and 101 are actinoid, 109 is transactinide ($6d$ series).

Step 1. Z = 61: Pm (promethium), $[\mathrm{Xe}]4f^5 6s^2$ (lanthanoid, fits $4f$ series). Total electrons: $54 + 5 + 2 = 61$. Verify: Pm is artificial, no stable isotope on Earth; longest-lived ^{145}Pm has half-life 17.7 years. Used in luminous paints for instrument dials and as a β-source.

Step 2. Z = 91: Pa (protactinium), $[\mathrm{Rn}]5f^2 6d^1 7s^2$ (early actinoid, retains a $6d$ electron). Total electrons: $86 + 2 + 1 + 2 = 91$. Verify: Pa is the daughter of ^{235}U decay; named "proto-actinium" (parent of actinium). One of the rarest naturally-occurring elements.

Step 3. Z = 101: Md (mendelevium), $[\mathrm{Rn}]5f^{13} 7s^2$ (late actinoid, $6d$ empty). Total electrons: $86 + 13 + 2 = 101$. Verify: Md is synthetic; named after Dmitri Mendeleev. Configuration has no $6d$ — the $5f$ shell is nearly full so electrons prefer $5f$ over $6d$. Common oxidation state: $+3$, but Md(II) ($5f^{14}$, fully filled) is unusually stable.

Step 4. Z = 109: Mt (meitnerium), $[\mathrm{Rn}]5f^{14}6d^7 7s^2$ (transactinide, group 9 of the $6d$ series). Total electrons: $86 + 14 + 7 + 2 = 109$. Verify: synthesised in 1982 at GSI Darmstadt; named after Lise Meitner. Group 9 means it sits below Ir/Rh/Co — but its chemistry is barely studied because of the very short half-lives (longest ^{278}Mt: 7 seconds).

Numerical cross-check. For each, confirm total e^- matches Z: Pm: 54 + 5 + 2 = 61. Pa: 86 + 2 + 1 + 2 = 91. Md: 86 + 13 + 2 = 101. Mt: 86 + 14 + 7 + 2 = 109.
Concept linkage. Three of the four elements (Pm, Md, Mt) are synthetic and short-lived; only Pa is found naturally (and even then in tiny amounts). The configurations illustrate the pattern: early actinoid (Pa) retains $6d$ for variable oxidation states; late actinoid (Md) loses $6d$ for stable $+3$ behaviour; transactinide (Mt) is a $6d$ transition metal proper.
Why this matters. The presence or absence of a $6d$ electron in the early actinoids is a small but important detail: it explains why Pa and U show easily accessible $+5$ and $+6$ oxidation states. Configurations of synthesised elements are predicted by Aufbau but verified by atom-at-a-time chemistry at heavy-ion accelerators (GSI Darmstadt, LBNL Berkeley, JINR Dubna).

> **Final Answer:** Configurations: Pm $4f^5 6s^2$; Pa $5f^2 6d^1 7s^2$; Md $5f^{13} 7s^2$; Mt $5f^{14} 6d^7 7s^2$ (each on top of the appropriate noble-gas core).

☞ **Block windows by Z**

s-block: Z = 1, 3, 4, 11, 12, 19, 20, 37, 38, 55, 56, 87, 88; p-block: 5–10, 13–18, 31–36, 49–54, 81–86, 113–118; d-block: 21–30, 39–48, 72–80, 104–112; f-block: 57–71, 89–103. Pick Z, find block, count electrons.

Q 4.35 Compare the general characteristics of the first series of the transition metals with those of the second and third series metals in the respective vertical columns. Give special emphasis on the following points:
(i) electronic configurations, (ii) oxidation states, (iii) ionisation enthalpies and (iv) atomic sizes.

SOLUTION

Concept used. Going down a group within the d-block we move from $3d$ to $4d$ to $5d$ series. Several global trends emerge: configurations become less regular because of s-d promotion; heavier elements tend to show *higher* oxidation states; ionisation enthalpies of $5d$ are unusually high because of **lanthanoid contraction**; and atomic sizes of $4d$ and $5d$ within the same group are almost identical for the same reason.

Step 1. **(i) Electronic configurations.**

- $3d$ series: $3d^{1-10}4s^{1-2}$.
- $4d$ series: less regular; e.g. Pd has $4d^{10}5s^0$, Ru is $4d^7 5s^1$, Ag is $4d^{10}5s^1$, Rh is $4d^8 5s^1$, Mo is $4d^5 5s^1$.
- $5d$ series: includes lanthanoid contraction. Configurations of W, Re, Os, Ir, Pt, Au show $5d^x 6s^{1-2}$ with several exceptions; e.g. Au is $5d^{10}6s^1$.

Step 2. **(ii) Oxidation states.** Higher oxidation states are more common (and more stable) in $4d$ and $5d$ series than in $3d$.

- Group 6: Cr (max $+6$) but for Mo and W $+6$ is stable (MoO_3, WO_3).
- Group 7: Mn (max $+7$); Tc and Re also reach $+7$ (TcO_4^-, ReO_4^-) but $+7$ is *more* stable for Re than for Mn.
- Group 8: Fe (max $+6$, rare); Ru and Os reach $+8$ (RuO_4, OsO_4), unique to heavier transition metals.

Step 3. **(iii) Ionisation enthalpies.**

- $4d$ ionisation enthalpies are smaller than $3d$ in the same group (because of larger size).
- $5d$ ionisation enthalpies are typically *higher* than $4d$, because of (a) lanthanoid contraction (no real size gain) and (b) poor shielding of $5d$ by intervening $4f$.

Step 4. **(iv) Atomic sizes.**

- $3d < 4d$: as expected from adding a shell.
- $4d \approx 5d$: lanthanoid contraction wipes out the expected size increase. Atomic radius of Zr (160 pm) is almost equal to that of Hf (159 pm); Nb $\approx$ Ta; Mo $\approx$ W.

Property	$3d$ (first)	$4d/5d$ (heavier)
Configurations	Mostly regular	Many exceptions
Max O.S.	Smaller (up to $+7$)	Larger (up to $+8$)
Ionisation $\Delta_i H$	Lower	$5d$ higher than $4d$
Atomic radius	Smallest	$4d \approx 5d$ (contraction)

> **Final Answer:** Heavier transition series have less regular configurations, show higher and more stable oxidation states, larger atomic radii than $3d$ but with $4d \approx 5d$ (lanthanoid contraction), and unusually high $5d$ ionisation enthalpies.

EXPERT'S SOLUTION *: Sanya Iyer, B.Tech Engineering Physics, IIT Bombay*

Strategic angle. The contrasts to highlight are: more exceptions in heavier configurations; higher max O.S. for $4d/5d$; $4d \approx 5d$ in size and high $5d$ ionisation enthalpies caused by lanthanoid contraction.

Lanthanoid contraction is the master variable. Almost every contrast between $3d$ and $4d/5d$ is downstream of lanthanoid contraction. It makes $5d$ atoms about the same size as $4d$, leading to similar chemistry within group; it raises Z_{eff} on the $5d$ shell, raising ionisation enthalpies; it stabilises higher oxidation states for $4d/5d$ because the metal cation is more compact.

Step 1. Configurations: $4d^n 5s^{1 \text{ or } 2}$ with many exceptions (Mo $4d^5 5s^1$, Ru $4d^7 5s^1$, Rh $4d^8 5s^1$, Pd $4d^{10} 5s^0$, Ag $4d^{10} 5s^1$); $5d^n 6s^2$ generally, with Pt ($5d^9 6s^1$) and Au ($5d^{10} 6s^1$). Reason for exceptions: smaller energy gap between $(n-1)d$ and ns, plus half-/fully-filled d-shell stability.

Step 2. Higher max O.S.: OsO_4 ($+8$), RuO_4 ($+8$), ReO_4^- ($+7$ more stable than MnO_4^-), WO_3 ($+6$, more stable than CrO_3). Higher states are thermodynamically more accessible for heavier metals. Numerical evidence: the highest oxidation state across the $3d$ row peaks at Mn ($+7$) and then falls; across $4d$ it peaks at Ru ($+8$); across $5d$ at Os ($+8$). Heavier metals sustain higher states because they have more d-orbital radius and less repulsion in the high state.

Step 3. Ionisation enthalpies: $5d > 4d > 3d$ for many groups, with $5d$ being unexpectedly high because of lanthanoid contraction increasing Z_{eff}. Sample values (group 4, $\Delta_i H_1$ in kJ/mol): Ti 661, Zr 660, Hf 654 — nearly flat for Zr/Hf because the contraction has wiped out the expected size growth. Group 11: Cu 745, Ag 731, Au 890 — Au is unusual because of strong relativistic effects in $6s$.

Step 4. Atomic sizes: Zr (160 pm) ≈ Hf (159 pm); Mo (140 pm) ≈ W (141 pm), within a few pm. The $4d$ and $5d$ series are pinned together by lanthanoid contraction. Densities: Mo 10.2, W 19.3 g/cm^3 — twofold ratio for equal atomic radius, because W has twice the atomic mass in roughly the same volume. Hence W's reputation for density.

Step 5. Coordination number trend: $3d$ usually 4 or 6; $4d/5d$ often higher (7, 8, 9, sometimes 12). $[Mo(CN)_8]^{4-}$ and $[W(CN)_8]^{4-}$ are dodecahedral 8-coordinate complexes that have no $3d$ analog.

Numerical anchor. Across the four most-tested groups:

- Group 4: r(Ti, Zr, Hf) = 132, 160, 159 pm. Note 4d → 5d gain $= -1$ pm (contraction effect).
- Group 6: max O.S. Cr (+6), Mo (+6), W (+6); the +6 state gets more stable down the group.
- Group 8: max O.S. Fe (+6 rare), Ru (+8), Os (+8) — Ru and Os unique in reaching +8.
- Group 11: $E°$(M+/M) Cu $+0.34$, Ag $+0.80$, Au $+1.69$ V — increasingly noble down the group.

Concept linkage. The chemistry of Zr/Hf, Nb/Ta and Mo/W similarities is the practical manifestation of lanthanoid contraction. The chemistry of Ru/Os max-O.S. similarity (RuO_4, OsO_4 both volatile, both +8) is the manifestation of heavier-metal high-state stability.

Why this matters. The chemistry of Zr/Hf, Nb/Ta and Mo/W pairs is so similar that it took decades to separate them. The pairs also share important industrial uses: Zr/Hf in nuclear engineering, Nb/Ta in capacitors and superconductors. Au and Pt are the noble metals of jewellery, catalysis (Pt in catalytic converters), and medicine (cisplatin).

> **Final Answer:** Heavier series: less regular configurations, higher and more stable oxidation states, $4d \approx 5d$ in size due to lanthanoid contraction, and higher $5d$ ionisation enthalpies than $3d/4d$.

♥ Why Zr/Hf separation matters for reactors

Zirconium is "neutron-transparent" (absorption cross-section $\sigma \approx 0.18$ b) — ideal for nuclear-fuel cladding tubes that must not slow down the chain reaction. Hafnium is the opposite, an excellent neutron absorber ($\sigma \approx 100$ b) — ideal for control rods. They are chemically near-identical (lanthanoid contraction!) and naturally occur together. Modern nuclear engineering depends on separating them, typically by solvent extraction at $\sim 0.1\%$ residual Hf level.

Q 4.36 **Write down the number of $3d$ electrons in each of the following ions: Ti^{2+}, V^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+}. Indicate how would you expect the five $3d$ orbitals to be occupied for these hydrated ions (octahedral).**

SOLUTION

Concept used. For a hydrated ion $[M(H_2O)_6]^{n+}$, the ligand field is *weak* (water is a weak-field ligand in the spectrochemical series). Therefore the d-electrons occupy the t_{2g} and e_g orbitals in the **high-spin** manner: each of the five d-orbitals first receives one electron with parallel spin (Hund's rule), pairing begins only after all five are singly occupied.

Step 1. Write the cation configuration and count $3d$ electrons.

Step 2. For each, place electrons in the split t_{2g} (lower, 3 orbitals) and e_g (upper, 2 orbitals) following Hund's rule, high-spin in water.

Ion	$3d^n$	t_{2g}	e_g	Unpaired
Ti^{2+}	d^2	↑↑		2
V^{2+}	d^3	↑↑↑		3
Cr^{3+}	d^3	↑↑↑		3
Mn^{2+}	d^5	↑↑↑	↑↑	5
Fe^{2+}	d^6	↑↓↑↑	↑↑	4
Fe^{3+}	d^5	↑↑↑	↑↑	5
Co^{2+}	d^7	↑↓↑↓↑	↑↑	3
Ni^{2+}	d^8	↑↓↑↓↑↓	↑↑	2
Cu^{2+}	d^9	↑↓↑↓↑↓	↑↓↑	1

Final Answer: $3d$ electron counts (and unpaired electrons in high-spin water environment): Ti^{2+} d^2 (2); V^{2+} d^3 (3); Cr^{3+} d^3 (3); Mn^{2+} d^5 (5); Fe^{2+} d^6 (4); Fe^{3+} d^5 (5); Co^{2+} d^7 (3); Ni^{2+} d^8 (2); Cu^{2+} d^9 (1).

EXPERT'S SOLUTION *: Aanya Verma, M.Sc Physical Chemistry, IIT Madras*

Picture-first. Five d-orbitals split by a water (weak) ligand field into a lower 3-orbital t_{2g} set and an upper 2-orbital e_g set. Apply Hund's rule, fill singly first.
Procedure summary. Steps: (i) find d^n for the ion; (ii) fill t_{2g} singly to a max of 3 e^-; (iii) fill e_g singly to a max of 2 e^- (now 5 electrons, all unpaired); (iv) pair electrons in t_{2g} first (HS-water; LS would jump straight to t_{2g} filling). After all 5 orbitals are singly occupied, the 6th electron pairs in t_{2g}, and so on.

Step 1. For each ion read off d^n from neutral atom configuration minus the charge (electrons leave $4s$ first). Ti^{2+}: d^2. V^{2+}: d^3. Cr^{3+}: d^3. Mn^{2+}: d^5. Fe^{2+}: d^6. Fe^{3+}: d^5. Co^{2+}: d^7. Ni^{2+}: d^8. Cu^{2+}: d^9.

Step 2. Place n electrons in the $(t_{2g})^x(e_g)^y$ pattern, with $x \le 6$, $y \le 4$, Hund's rule. Ti^{2+}: $t_{2g}^2e_g^0$, 2 unpaired. V^{2+}: $t_{2g}^3e_g^0$, 3 unpaired. Cr^{3+}: $t_{2g}^3e_g^0$, 3 unpaired. Mn^{2+}: $t_{2g}^3e_g^2$, 5 unpaired. Fe^{2+}: $t_{2g}^4e_g^2$, 4 unpaired. Fe^{3+}: $t_{2g}^3e_g^2$, 5 unpaired. Co^{2+}: $t_{2g}^5e_g^2$, 3 unpaired. Ni^{2+}: $t_{2g}^6e_g^2$, 2 unpaired. Cu^{2+}: $t_{2g}^6e_g^3$, 1 unpaired.

Step 3. Unpaired count formula: n if $n \le 5$, else $10 - n$ (high-spin octahedral). Confirm with the table above.

Step 4. Magnetic moment table (spin-only): Ti^{2+} 2.83; V^{2+} 3.87; Cr^{3+} 3.87; Mn^{2+} 5.92; Fe^{2+} 4.90; Fe^{3+} 5.92; Co^{2+} 3.87; Ni^{2+} 2.83; Cu^{2+} 1.73 BM.

Numerical anchor. Note that V^{2+}, Cr^{3+}, Co^{2+} all give spin-only $\mu = 3.87$ BM despite having different d^n counts (3, 3, and 7 respectively). The reason is the symmetry of the spin-only formula around half-filled d^5.
Concept linkage. Without information about ligand field strength, octahedral $3d$ ions almost always default to high-spin in water. With strong-field ligands (CN^-, NH_3, en), low-spin configurations become possible: e.g. $[Fe(CN)_6]^{4-}$ is $t_{2g}^6e_g^0$, 0 unpaired, diamagnetic — same Fe(II), different ligand, opposite magnetism.
Why this matters. The number of unpaired electrons is what the magnetic moment measures via $\mu = \sqrt{n(n+2)}$ BM. So this table is the foundation for every magnetic-property question about hydrated $3d$ ions. NEET-level question: "Compute the magnetic moment of $[Co(H_2O)_6]^{2+}$" — answer 3.87 BM from this table.

> **Final Answer:** d^n counts: 2, 3, 3, 5, 6, 5, 7, 8, 9; unpaired electrons: 2, 3, 3, 5, 4, 5, 3, 2, 1 (high-spin in water).

☞ **Symmetry of unpaired-count**

Going around the d^n ladder: d^0: 0 unpaired; d^1: 1; d^2: 2; d^3: 3; d^4: 4; d^5: 5 (maximum); d^6: 4; d^7: 3; d^8: 2; d^9: 1; d^{10}: 0. The pattern is 0–1–2–3–4–5–4–3–2–1–0, symmetric about d^5 (high-spin).

Q 4.37 **Comment on the statement that elements of the first transition series possess many properties different from those of heavier transition elements.**

SOLUTION

Concept used. Going from $3d$ to $4d$ and $5d$, several properties change qualitatively because of: larger ion sizes, deeper-penetrating $5d$ orbitals, lanthanoid contraction (which makes $5d$ smaller than expected) and more covalent metal-ligand bonds.

Step 1. **Atomic sizes.** $3d$ atoms are the smallest; $4d$ are larger; $5d$ are about the same size as $4d$ (lanthanoid contraction).

Step 2. **Oxidation states.** $3d$ metals show many states with the lower state often the most stable in water (e.g. Fe^{2+} comparable in stability to Fe^{3+}). $4d$ and $5d$ metals tend to show higher and more stable oxidation states (e.g. OsO_4 +8; ReO_4^- +7 more stable than MnO_4^-).

Step 3. **Coordination.** $3d$ metals usually adopt coordination number 6 (octahedral). $4d$ and $5d$ metals more frequently adopt higher coordination numbers (7, 8) and form more covalent compounds.

Step 4. **Magnetic properties.** $3d$ metal ions are often magnetically described well by the spin-only formula ($\mu = \sqrt{n(n+2)}$ BM). For $4d$ and $5d$ the orbital angular momentum makes a bigger contribution, so the spin-only formula is less accurate.

Step 5. **Metallic and lattice properties.** $4d$ and $5d$ metals have higher melting points (W has the highest m.p. of any metal, 3422 °C), greater hardness and often higher density (because of lanthanoid contraction + heavier nuclei).

Step 6. **Ionisation enthalpies.** $4d$ values are lower than $3d$, but $5d$ values are higher than $4d$ because of the lanthanoid contraction effect.

Step 7. **Coloured compounds.** $3d$ compounds tend to be more coloured (smaller Δ_o for weak-field water, falling in the visible). $4d$ and $5d$ have larger Δ_o, often pushing the $d-d$ transitions into the UV.

> **Final Answer:** The first series differs from heavier series in: smaller atoms, lower stable oxidation states, more reliable spin-only magnetism, lower melting points and densities, and a wider colour range. The heavier series have larger maximum oxidation states, higher m.p./density, more covalent bonding, and (because of lanthanoid contraction) $4d$ and $5d$ are similar in size and many properties.

EXPERT'S SOLUTION : *Yash Bhat, M.Sc Chemistry, IIT Kanpur*

Strategic angle. List five contrasts and put a one-line reason for each.
Root-cause logic. Most of the contrasts have one of three root causes: (a) lanthanoid contraction making $5d$ smaller than expected; (b) larger spatial extent of $4d/5d$ orbitals (compared to $3d$); (c) stronger ligand-field interactions in $4d/5d$ because of deeper-penetrating orbitals. Once you trace each contrast to one of these three, the answer practically writes itself.

Step 1. Size: $3d$ smallest; $4d$ and $5d$ similar (lanthanoid contraction). r(3d, group 6, Cr) = 128 pm; r(4d, Mo) = 140 pm; r(5d, W) = 141 pm. Cause (a): lanthanoid contraction pins 5d to 4d.

Step 2. Oxidation states: heavier series favour higher and more stable states; OsO_4 and ReO_4^- have no $3d$ analogue in stability. Maximum O.S. across $3d$: Mn +7 (only as oxidant in $KMnO_4$); $4d$: Ru +8 (stable in RuO_4 solid); $5d$: Os +8 (very stable OsO_4). Cause (b): larger orbital radius makes high-O.S. cations easier to form because electron-electron repulsion is smaller.

Step 3. Magnetism: spin-only formula works for $3d$; not for $4d/5d$ because of larger spin-orbit coupling. For $3d$, $\zeta \sim$ 300–600 cm^{-1}; for $4d$, $\zeta \sim$ 1000–2000 cm^{-1}; for $5d$, $\zeta \sim$ 3000–6000 cm^{-1}. Increasing ζ couples spin and orbital moments, breaking spin-only's assumption. Cause (b): heavier nuclei have larger spin-orbit coupling.

Step 4. Coordination: $3d$ prefers 4 or 6 coordinate; $4d$ and $5d$ often go to 7, 8 (e.g. $[Mo(CN)_8]^{4-}$, $[W(CN)_8]^{4-}$). Cause (a) + (b): larger atoms can host more ligands.

Step 5. Physical: heavier series higher m.p., density, ionisation enthalpies. W has the highest m.p. of any metal, 3422 °C. Os density 22.6 g/cm^3 is highest stable element. $\Delta_i H_1$(Au) = 890 kJ/mol, very high due to relativistic effects on $6s$ orbital. Cause (a): high Z_{eff} from contraction; cause (c): tighter d-orbital overlap in metallic lattice.

Step 6. Coloured compounds: $3d$ compounds tend to be more deeply coloured (smaller Δ_o in the visible). $4d$ and $5d$ complexes often colourless or yellow because Δ_o is large enough to push transitions into UV. Numerical: Δ_o in $[Co(NH_3)_6]^{3+}$ $\sim$23 000 cm^{-1}; in $[Rh(NH_3)_6]^{3+}$ $\sim$34 000 cm^{-1} (UV-absorbing, so the complex is colourless).

Numerical cross-check. Spin-only μ for $5d$ Os(IV) (d^4): predicted 4.90 BM; observed ~ 1.6 BM. The huge discrepancy is due to spin-orbit coupling — orbital moment partially opposes spin moment. This is one reason that μ for $5d$ complexes is rarely the simple Hund value.

Concept linkage. The same five contrasts run through every exam question on transition-metal periodicity. "Why is W refractory?" (metallic bonding + contraction). "Why does OsO_4 exist but FeO_4 barely?" (heavier max O.S.). "Why do $[Mo(CN)_8]^{4-}$ and $[Cr(CN)_6]^{3-}$ have different coordination numbers?" (4d larger than 3d).

Why this matters. The qualitative differences feed directly into industrial chemistry: refractory $5d$ metals (W, Re) are used in high-temperature alloys (jet-engine turbine blades); high-coordination $4d/5d$ complexes are key in homogeneous catalysis (Wilkinson's catalyst $Rh(PPh_3)_3Cl$ for hydrogenation; Pt complexes in cisplatin for chemotherapy).

> **Final Answer:** First series: smaller atoms, lower max O.S., simpler magnetism, lower m.p. Heavier series: larger atoms, higher and more stable O.S., complex magnetism, higher density and m.p.

☞ **Six-point comparison checklist**

For any $3d$-vs-$4d/5d$ contrast question, run through six points: (1) radius, (2) max O.S., (3) magnetism, (4) coordination number, (5) m.p./density, (6) colour intensity. Mention one number per point and you have a complete answer.

Q 4.38 What can be inferred from the magnetic moment values of the following complex species?

$K_4[Mn(CN)_6]$: 2.2 BM

$[Fe(H_2O)_6]^{2+}$: 5.3 BM

$K_2[MnCl_4]$: 5.9 BM

SOLUTION

Concept used. For a transition-metal complex, the observed magnetic moment (in BM) is compared with the spin-only value

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

A close match indicates the number of unpaired electrons and reveals whether the complex is *high-spin* (weak-field ligands, maximum unpaired) or *low-spin* (strong-field ligands, electrons paired into t_{2g}).

Step 1. $K_4[Mn(CN)_6]$, $\mu = 2.2$ BM.

- Mn is in $+2$ (since CN^- is -1 and the four K^+ balance four units of negative charge from the complex; complex anion is $[Mn(CN)_6]^{4-}$; with 6 CN^- contributing -6, Mn must be $+2$).
- Mn^{2+}: $3d^5$ (5 electrons).
- CN^- is a strong-field ligand $\Rightarrow$ low-spin. In a low-spin d^5 octahedral, the t_{2g} orbitals hold all 5 electrons: $t_{2g}^5\, e_g^0$. Pair up to give 1 unpaired electron.
- Spin-only $\mu = \sqrt{1\cdot 3} = \sqrt{3} = 1.73$ BM. Observed 2.2 BM is slightly larger because of a small orbital contribution, consistent with 1 unpaired electron.

Step 2. $[Fe(H_2O)_6]^{2+}$, $\mu = 5.3$ BM.

- Fe in $+2$, $3d^6$.
- H_2O is a weak-field ligand $\Rightarrow$ high-spin. In a high-spin d^6 octahedral the configuration is $t_{2g}^4\, e_g^2$ with 4 unpaired electrons.
- Spin-only $\mu = \sqrt{4\cdot 6} = \sqrt{24} = 4.90$ BM. Observed 5.3 BM is slightly higher because of a modest orbital contribution and is consistent with 4 unpaired electrons.

Step 3. $K_2[MnCl_4]$, $\mu = 5.9$ BM.

- Mn in $+2$ (Mn charge + $4(Cl^-) = -2$; with two K^+ balancing, Mn = $+2$).

- Mn^{2+}: $3d^5$. Five electrons.
- Cl^- is a weak-field ligand $\Rightarrow$ high-spin. Five electrons singly occupy the five d orbitals: 5 unpaired.
- Spin-only $\mu = \sqrt{5 \cdot 7} = \sqrt{35} = 5.92$ BM. Observed 5.9 BM matches almost perfectly.

Complex	d^n, spin	n unpaired	μ (BM) calc / obs
$K_4[Mn(CN)_6]$	d^5, low-spin	1	1.73 / 2.2
$[Fe(H_2O)_6]^{2+}$	d^6, high-spin	4	4.90 / 5.3
$K_2[MnCl_4]$	d^5, high-spin	5	5.92 / 5.9

Final Answer: From the moments: (i) $K_4[Mn(CN)_6]$ 2.2 BM $\rightarrow$ low-spin d^5 with 1 unpaired electron (CN^- strong-field). (ii) $[Fe(H_2O)_6]^{2+}$ 5.3 BM $\rightarrow$ high-spin d^6 with 4 unpaired (H_2O weak-field). (iii) $K_2[MnCl_4]$ 5.9 BM $\rightarrow$ high-spin d^5 with 5 unpaired (Cl^- weak-field).

EXPERT'S SOLUTION : *Sneha Joshi, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle. Pair each observed moment with a spin-only-calculated moment, choose the unpaired-electron count that matches, then read off the spin state.

Workflow. (1) Determine the metal's oxidation state from the complex's overall charge minus ligand charges. (2) Find d^n from the cation. (3) Calculate spin-only μ for both possible spin states (HS and LS for d^4 through d^7 in O_h). (4) Match observed μ to one of these. (5) Cross-check with ligand-field strength (spectrochemical series).

Step 1. $K_4[Mn(CN)_6]$: Mn(II) d^5. Possible n values: 5 (high-spin, $\mu = 5.92$ BM) or 1 (low-spin, $\mu = 1.73$). Observed 2.2 BM is close to 1.73, so low-spin with 1 unpaired. CN^- is a strong-field ligand, confirming. Octahedral splitting check: Δ_o(CN^- with Mn(II)) ~ 35000 cm^{-1}; pairing energy $P \sim 25000$ cm^{-1}. Since $\Delta_o > P$, low-spin is favoured.

Step 2. $[Fe(H_2O)_6]^{2+}$: Fe(II) d^6. Possible n values: 4 (high-spin) or 0 (low-spin). Observed 5.3 BM is close to 4.90, so 4 unpaired, high-spin. H_2O is weak-field. Δ_o(H_2O on Fe(II)) ~ 10000 cm^{-1}; pairing energy ~ 17600 cm^{-1}. $\Delta_o < P$ enforces high-spin.

Step 3. $K_2[MnCl_4]$: Mn(II) d^5 but tetrahedral. In tetrahedral $\Delta_t = (4/9)\Delta_o$, so for any ligand $\Delta_t < P$ and tetrahedral complexes are essentially always high-spin. With d^5 this gives 5 unpaired electrons, $\mu = \sqrt{35} = 5.92$ BM. Observed 5.9 matches almost perfectly.

Step 4. Compare the three numbers: $\mu_{\text{Mn(CN)6}}/\mu_{\text{MnCl4}} = 2.2/5.9 = 0.37$. Same metal ($Mn^{2+}$), $\sim$3-fold change in μ from switching ligand. This is what crystal-field theory predicts.

Step 5. Note the role of geometry. In octahedral $[Mn(H_2O)_6]^{2+}$ with weak-field water, μ would also be 5.92 BM (high-spin d^5). So octahedral-CN^- vs octahedral-H_2O changes spin state; octahedral-H_2O vs tetrahedral-Cl^- gives same spin state.

Numerical cross-check. For $[Mn(CN)_6]^{4-}$, the orbital contribution slightly raises observed μ above spin-only 1.73 BM to 2.2 BM. The orbital contribution formula for low-spin t_{2g}^5: $\mu = \sqrt{\mu_S^2 + \alpha L^2}$ where α depends on geometry and ligand. For t_{2g}^5, there is one t_{2g} vacancy, so some orbital moment survives — hence the lift from 1.73 to 2.2 BM.

Concept linkage. The same logic applies to $[Co(NH_3)_6]^{3+}$ (low-spin d^6, $\mu = 0$, diamagnetic), $[Fe(CN)_6]^{4-}$ (low-spin d^6, $\mu = 0$), $[FeF_6]^{3-}$ (high-spin d^5, $\mu = 5.92$). Strong-field ligands force low-spin in d^4–d^7 octahedral cases; weak-field ligands enforce high-spin.

Why this matters. Magnetic-moment measurements are the most direct route to deducing geometry, oxidation state and spin state of a transition-metal complex. This question shows the standard workflow. Bioinorganic chemists use magnetic susceptibility to identify the Fe(II)/Fe(III) and high-spin/low-spin state of haemoglobin's iron in different states (oxy-, deoxy-, met-).

> **Final Answer:** Low-spin Mn(II) in $[Mn(CN)_6]^{4-}$ (1 unpaired); high-spin Fe(II) in $[Fe(H_2O)_6]^{2+}$ (4 unpaired); high-spin Mn(II) in $[MnCl_4]^{2-}$ (5 unpaired).

✗ Tetrahedral complexes are always high-spin in school level

A frequent error: predicting low-spin tetrahedral $[MnCl_4]^{2-}$ because Cl^- "sounds intermediate". Wrong on two counts: (i) Cl^- is a weak-field ligand (left of H_2O in the spectrochemical series), and (ii) tetrahedral Δ_t is only $4/9$ of octahedral Δ_o for the same ligand, far less than the pairing energy. So all tetrahedral $3d$ complexes are high-spin at school level.

☞ Spectrochemical series, weak-to-strong

$I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 <$ en $< CN^- \approx$ CO. Anything to the right of H_2O can induce low-spin in d^4–d^7 octahedral complexes; left of H_2O cannot. Halides and H_2O are weak-field; NH_3, en, CN^-, CO are strong-field.

Key Takeaways

- Transition metals (groups 3 to 12) have the general configuration $(n-1)d^{1-10}\,ns^{0-2}$; their close d/s orbital energies give variable oxidation states, paramagnetism, coloured ions, catalytic activity and a rich complex chemistry.
- Stability of oxidation states is governed by the configuration of the resulting cation: d^0, d^3, d^5 and d^{10} are extra stable; deviations from $+3$ in lanthanoids occur only when the new ion lands on f^0, f^7 or f^{14}.
- Spin-only magnetic moment is given by $\mu = \sqrt{n(n+2)}$ BM with n = number of unpaired electrons; it works very well for $3d$ ions and approximately for f-block ions.
- Standard reduction potentials decide redox stability: a very negative $E^\circ(\mathrm{M^{2+}/M})$ means the metal is easily oxidised (Mn, Cr); a strongly positive $E^\circ(\mathrm{M^{3+}/M^{2+}})$ means M^{3+} is unstable (Mn). Cu has a positive $E^\circ(\mathrm{M^{2+}/M})$ and so does not displace H_2 from acid.
- Lanthanoid contraction (about 1 pm per element across La to Lu) causes $4d$ and $5d$ atoms to be of nearly equal size, explains the high densities of $5d$ metals and makes separation of Zr/Hf, Nb/Ta, Mo/W difficult.
- Actinoids ($5f$ filling) show a wider range of oxidation states ($+3$ to $+7$) than lanthanoids ($+3$ dominant) because $5f$ orbitals are spatially more extended and lie close in energy to $6d$ and $7s$.
- $K_2Cr_2O_7$ (chromite + soda + air; acidify; KCl) and $KMnO_4$ (pyrolusite + KOH + air; electrolyse) are the two flagship oxidising agents; dichromate prefers acid and chromate prefers alkaline media via $\mathrm{Cr_2O_7{}^{2-} + 2\,OH^- \rightleftharpoons 2\,CrO_4{}^{2-} + H_2O}$.
- Hydrated $3d$ ions are almost always *high-spin* (H_2O is a weak-field ligand); strong-field ligands such as CN^- produce low-spin complexes (e.g. $K_4[Mn(CN)_6]$ has only 1 unpaired electron).

End of Chapter 4 Exercises