NCERT Exemplar Solutions

Solved NCERT Exemplar Problems for Class 12th Chemistry, Chapter 4

Chapter 4: The d- and f-Block Elements

About this Chapter

The **d- and f-Block Elements** chapter unites the *transition metals* (groups 3–12, d orbitals partly filled in their atoms or common ions) and the inner-transition **lanthanoids** and **actinoids** ($4f$ and $5f$ series). This Exemplar set drills the recurring themes: electronic configurations and oxidation-state diversity, colour and magnetic behaviour from unpaired d/f electrons, **lanthanoid contraction**, the chemistry of $KMnO_4$ and $K_2Cr_2O_7$, interstitial compounds, catalytic behaviour and the assertion-reason fact bank that the JEE/NEET papers love.

Topics covered: Transition d-block • Electronic configurations • Oxidation states • Colour & magnetic moment • $KMnO_4$ & $K_2Cr_2O_7$ • Lanthanoid contraction • Actinoids • Interstitial compounds • Catalysis

Quick Formula Sheet

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

Transition-metal config: $[\text{Ar}]\,3d^x4s^y$, ions lose $4s$ first

Lanthanoid contraction: $r(\text{La}^{3+})$=1.06 Å → $r(\text{Lu}^{3+})$=0.85 Å

$KMnO_4$ in acid: $\text{MnO}_4{}^- + 8\,\text{H}^+ + 5\,\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\,\text{H}_2\text{O}$

Dichromate-chromate equilibrium: $\text{Cr}_2\text{O}_7{}^{2-} + 2\,\text{OH}^- \rightleftharpoons 2\,\text{CrO}_4{}^{2-} + \text{H}_2\text{O}$

I. Multiple Choice Questions (Type-I)

Q 4.1 **Electronic configuration of a transition element X in $+3$ oxidation state is $[\text{Ar}]\,3d^5$. What is its atomic number?**

(i) 25

(ii) 26

(iii) 27

(iv) 24

SOLUTION

Correct option: (ii) 26.

Concept used. A neutral transition atom X has electronic configuration $[\text{Ar}]\,3d^x4s^y$. When it forms X^{n+}, electrons are removed first from the outer $4s$ orbital, then from the inner $3d$ orbital. So

$$\text{electrons in } X^{3+} \;=\; Z-3,$$

where Z is the atomic number of X. Argon (Ar) has 18 electrons, so the $[\text{Ar}]\,3d^5$ ion holds $18+5=23$ electrons.

Step 1. Count the electrons in X^{3+}:

$$n(X^{3+}) = 18\,(\text{from Ar core}) + 5\,(\text{from } 3d^5) = 23.$$

Step 2. Restore the three lost electrons to obtain the neutral atom:

$$Z = n(X) = n(X^{3+}) + 3 = 23 + 3 = 26.$$

Step 3. Identify the element: $Z = 26$ is iron (Fe). The neutral atom is $[\text{Ar}]\,3d^64s^2$ (lose $2\times 4s$ and $1\times 3d$ to land at $[\text{Ar}]\,3d^5$, the half-filled stable Fe^{3+}). Check: Fe^{3+} is indeed $[\text{Ar}]\,3d^5$. ✓

Final Answer: Atomic number of X is **26**, i.e. iron (Fe); option **(ii)**.

☞ **Ion building rule**

For first-row transition ions: write the neutral $[\text{Ar}]3d^x4s^y$ configuration, then remove electrons $4s$ *first*, $3d$ *second*.

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

Backward count angle. Start from the ion's electron tally and work back; this avoids confusing yourself with the neutral configuration.

Concept used. Total electron count of a cation equals $Z-q$ where q is the positive charge. For X^{3+} to be $[\text{Ar}]3d^5$, the ion has $18+5=23$ electrons, hence $Z=23+3$.

Step 1. Tally electrons in $[\text{Ar}]3d^5$: Ar contributes 18; $3d^5$ contributes 5; total $=23$.

Step 2. Cation charge is $+3$, so

$$Z = 23 + 3 = 26.$$

Step 3. Cross-check with the periodic table: $Z=26$ is Fe, whose common $+3$ oxidation state has the half-filled $3d^5$ configuration (which is itself extra stable by exchange-energy). That stability is precisely why Fe^{3+} shows up so often.

Why this matters. The same logic decodes any cation: e.g. "which ion is $[\text{Ar}]3d^6$ with $+2$ charge?" $\Rightarrow Z = 24+2 = 26$ (Fe^{2+}).

Final Answer: $Z = 26$, iron; option **(ii)**.

Q 4.2 **The electronic configuration of $\mathrm{Cu(II)}$ is $3d^9$ whereas that of $\mathrm{Cu(I)}$ is $3d^{10}$. Which of the following is correct?**

(i) $\mathrm{Cu(II)}$ **is more stable**

(ii) $\mathrm{Cu(II)}$ **is less stable**

(iii) $\mathrm{Cu(I)}$ **and** $\mathrm{Cu(II)}$ **are equally stable**

(iv) Stability of $\mathrm{Cu(I)}$ **and** $\mathrm{Cu(II)}$ **depends on nature of copper salts**

SOLUTION

Correct option: (i) $\mathrm{Cu(II)}$ is more stable.

Concept used. The stability of a metal ion *in aqueous solution* is decided not only by its gas-phase electron configuration but also by the **hydration enthalpy** $\Delta_{\text{hyd}}H$. A more highly charged, smaller cation is hydrated far more exothermically. For copper,

$$\Delta_{\text{hyd}}H(\mathrm{Cu^{2+}}) \approx -2100\,\text{kJ/mol}, \quad \Delta_{\text{hyd}}H(\mathrm{Cu^{+}}) \approx -582\,\text{kJ/mol}.$$

The difference of $\sim 1500\,\text{kJ/mol}$ swamps the second ionisation energy needed to make $\mathrm{Cu^{2+}}$ from $\mathrm{Cu^{+}}$.

Step 1. Write the disproportionation reaction in water:

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

This reaction is spontaneous:
$E^\circ_{\text{cell}} = E^\circ(\mathrm{Cu^{+}/Cu}) - E^\circ(\mathrm{Cu^{2+}/Cu^{+}}) = 0.52 - 0.16 = +0.36\,\text{V} > 0.$

Step 2. Apply the thermodynamic identity:

$$\Delta_r G^\circ = -nFE^\circ = -(1)(96485)(0.36) = -34.7\,\text{kJ/mol} < 0.$$

So $\mathrm{Cu^{+}}$ disproportionates in water, leaving $\mathrm{Cu^{2+}}$ as the stable species.

Step 3. Compare to the gas-phase argument: $3d^{10}$ (closed shell) looks more stable than $3d^9$, which would predict $\mathrm{Cu^{+}}$ favoured. But the high $\Delta_{\text{hyd}}H$ of $\mathrm{Cu^{2+}}$ flips the order in solution. Hence option (i) is correct.

Final Answer: In aqueous medium $\mathrm{Cu(II)}$ is more stable than $\mathrm{Cu(I)}$; option **(i)**.

✗ Common Pitfall

"Closed shell wins" is a gas-phase intuition. In water the $+2$ ion is favoured for copper because hydration enthalpy beats ionisation enthalpy. Don't read $3d^{10}$ as "automatically more stable in solution".

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

Thermochemical-cycle angle. The cleanest justification is a Born–Haber-style cycle around the disproportionation $2\,\mathrm{Cu}^{+} \longrightarrow \mathrm{Cu}^{2+} + \mathrm{Cu}$.

Concept used. The free energy of the disproportionation in aqueous solution can be decomposed into IE_2 (cost to make Cu^{2+} from Cu^{+}) and hydration plus lattice/atomisation terms; the hydration of Cu^{2+} dominates.

Step 1. Estimate the energy bookkeeping (per mole of Cu^{+} disproportionated):
$\mathrm{IE}_2(\mathrm{Cu}) \approx +1958\,$kJ/mol,
$\Delta_{\text{hyd}}H(\mathrm{Cu}^{2+}) - 2\Delta_{\text{hyd}}H(\mathrm{Cu}^{+}) \approx -2100 - 2(-582) = -936\,$kJ/mol, atomisation gain on plating out $\mathrm{Cu\,(s)} \approx -338\,$kJ/mol. Net $\approx 1958 - 936 - 338 = +684\,$kJ/mol for IE–hydration–atomisation alone.

Step 2. This rough count would predict Cu^{+} stable, but the full free-energy difference (electrochemistry, $E^{\circ}_{\text{cell}} = +0.36$ V $\Rightarrow \Delta G^{\circ} = -34.7$ kJ/mol) shows the reaction is actually spontaneous; refined hydration and entropic terms tip the balance toward Cu^{2+}.

Step 3. Conclusion: in water, Cu^{+} is unstable; in the gas phase or in poorly-coordinating media (e.g. inside $\mathrm{Cu_2Cl_2}$), Cu^{+} survives.

♥ Solid-vs-solution contrast

This is why $\mathrm{Cu_2O}$ and $\mathrm{Cu_2Cl_2}$ (solid, low coordination to water) are stable cuprous species, but dissolving them in water produces Cu^{2+} and metallic Cu. The reaction is famous as the disproportionation of Cu^{+}.

Final Answer: Cu(II) is more stable in aqueous medium; option **(i)**.

Q 4.3 **Metallic radii of some transition elements are given below. Which of these elements will have highest density?**

Element	Fe	Co	Ni	Cu
Metallic radii/pm	126	125	125	128

(i) Fe

(ii) Ni

(iii) Co

(iv) Cu

SOLUTION

Correct option: (iv) Cu.

Concept used. For a metal that crystallises in a close-packed lattice, density scales as

$$\rho = \frac{Z\,M}{N_A\,V_{\text{cell}}}, \qquad V_{\text{cell}} \propto r^3,$$

where Z is atoms per unit cell, M is atomic mass, r is metallic radius and V_{cell} is unit-cell volume. With the four elements packing in essentially the same lattice and Z, N_A the same, density is driven by the ratio M/r^3. A larger atomic mass and a smaller radius both push density up.

Step 1. Tabulate atomic masses (g/mol) and radii (pm): $\text{Fe} = 55.85,\ r = 126;$ $\text{Co} = 58.93,\ r = 125;$ $\text{Ni} = 58.69,\ r = 125;$ $\text{Cu} = 63.55,\ r = 128.$

Step 2. Compute the proxy M/r^3 (in g mol^{-1}/pm^3, absolute scale irrelevant since we only compare):

$$\text{Fe} : 55.85/126^3 = 2.79 \times 10^{-5}, \quad \text{Co} : 58.93/125^3 = 3.02 \times 10^{-5},$$

$$\text{Ni} : 58.69/125^3 = 3.01 \times 10^{-5}, \quad \text{Cu} : 63.55/128^3 = 3.03 \times 10^{-5}.$$

Step 3. The largest proxy is for Cu, consistent with the observed densities (g/cm^3): $\text{Fe} = 7.87$, $\text{Co} = 8.90$, $\text{Ni} = 8.91$, $\text{Cu} = 8.95$. Cu wins because its $\sim 8\%$ heavier mass outweighs its $\sim 2.4\%$ larger radius.

Final Answer: Copper has the highest density; option **(iv)**.

EXPERT'S SOLUTION *: Vivaan Patel, M.Tech Chemical Engineering, IIT Delhi*

Mass-vs-radius angle. Density is a tug of war between mass (numerator) and volume (denominator). Among the four, Cu's mass jumps $\sim 8\%$ over Ni; its radius grows only $\sim 2.4\%$. The cube on r amplifies the radius change, but the mass jump still wins.

Concept used. For atoms of comparable size and packing, density tracks M/r^3. A factor of $(1 + \delta_M)/(1 + \delta_r)^3 \approx 1 + \delta_M - 3\delta_r$ summarises a small change in mass and radius.

Step 1. Take Cu over Ni: $\delta_M = (63.55 - 58.69)/58.69 = 0.0828$ and $\delta_r = (128 - 125)/125 = 0.024.$

$$1 + 0.0828 - 3(0.024) = 1.011,$$

so density should rise by $\sim 1.1\%$ from Ni (8.91) to ~ 9.01. Observed $\rho(\text{Cu}) = 8.95$ g/cm^3 – close enough given that crystal structure also matters

(Cu is fcc, Ni is fcc, Co is hcp, Fe is bcc/α).

Step 2. Reject (i) Fe (largest radius, lightest of the heavy three). Reject (ii) Ni and (iii) Co – nearly identical to each other but Cu still beats both because of its extra mass.

> ☞ **Exam shortcut**
>
> For 3d-series "which has highest density" questions, the answer is almost always the heaviest of the late 3d metals (Cu, Ni, Co cluster near $8.9\,\text{g/cm}^3$; Cu just edges them out at 8.95).

> **Final Answer:** Cu has the highest density; option **(iv)**.

Q 4.4 **Generally transition elements form coloured salts due to the presence of unpaired electrons. Which of the following compounds will be coloured in solid state?**

(i) Ag_2SO_4
(ii) CuF_2
(iii) ZnF_2
(iv) Cu_2Cl_2

SOLUTION

Correct option: (ii) CuF_2.

Concept used. The colour of a transition-metal compound arises from d–d **electronic transitions**: visible-light photons promote an electron from a lower-energy d orbital (t_{2g} or e_g depending on geometry) to a higher one. This is only possible when the metal ion has *partly filled* d orbitals (one or more unpaired electrons, or at least a vacant d orbital to receive an electron). Closed-shell ions (d^0 or d^{10}) cannot show d–d transitions; they are usually colourless unless charge-transfer bands fall in the visible.

Step 1. Identify the metal-ion configuration in each option:

- Ag_2SO_4: Ag^+ is $[\text{Kr}]\,4d^{10}$ – closed shell. Colourless.
- CuF_2: Cu^{2+} is $[\text{Ar}]\,3d^9$ – one unpaired electron. Coloured (blue).
- ZnF_2: Zn^{2+} is $[\text{Ar}]\,3d^{10}$ – closed shell. Colourless.
- Cu_2Cl_2: Cu^+ is $[\text{Ar}]\,3d^{10}$ – closed shell. Colourless (white).

Step 2. Only CuF_2 has a partly-filled d shell.

Step 3. Hence (ii) is the only coloured solid in the list.

Final Answer: CuF_2 is coloured (blue); option **(ii)**.

☞ **Quick filter for "coloured?"**

Find the metal's d^n. If $n = 0$ or 10, colourless. Otherwise coloured (subject to ligand-field strength).

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

Closed-shell elimination angle. List d^n for every ion in the four salts; whichever is not d^0 or d^{10} wins.

Concept used. A d–d transition requires the receiving orbital to be (i) of d-character and (ii) accessible (i.e. either half-empty or empty). d^{10} has every d orbital full; d^0 has every d orbital empty so no source electron is available.

Step 1. $Ag^+ = 4d^{10}$ ✗, $Cu^+ = 3d^{10}$ ✗, $Zn^{2+} = 3d^{10}$ ✗.

Step 2. $Cu^{2+} = 3d^9$ ✓ (one hole in e_g in octahedral $[Cu(H_2O)_6]^{2+}$, transition $t_{2g} \to e_g$ absorbs red, complex looks blue).

Step 3. Thus the only coloured solid is CuF_2.

Final Answer: Only CuF_2 ($Cu^{2+} = 3d^9$) is coloured; option **(ii)**.

Q 4.5 **On addition of small amount of $KMnO_4$ to concentrated H_2SO_4, a green oily compound is obtained which is highly explosive in nature. Identify the compound from the following.**

(i) Mn_2O_7

(ii) MnO_2

(iii) $MnSO_4$

(iv) Mn_2O_3

SOLUTION

Correct option: (i) Mn_2O_7.

Concept used. Concentrated H_2SO_4 is a strong dehydrating agent. When it acts on $KMnO_4$ it strips water from the permanganate to give the **anhydride** of permanganic acid, which is Mn_2O_7 – a dark-green oily liquid that is thermodynamically very unstable and detonates above $55°C$.

Step 1. Write the dehydration:

$$2\,KMnO_4 + H_2SO_4\,(conc\cdot) \longrightarrow Mn_2O_7 + K_2SO_4 + H_2O\,\cdot$$

Manganese stays in the $+7$ oxidation state on both sides – this is acid–base chemistry, not redox.

Step 2. Check the colour and properties: Mn_2O_7 is described in textbooks as "dark green/red oil"; in thin films it appears deep green. It decomposes explosively:

$$2\,Mn_2O_7 \longrightarrow 4\,MnO_2 + 3\,O_2\uparrow.$$

Step 3. Eliminate distractors: MnO_2 is brown/black solid (not oily); $MnSO_4$ is pale pink crystalline salt; Mn_2O_3 is black-brown solid. Only Mn_2O_7 matches "green oily explosive".

Final Answer: The green oily explosive is Mn_2O_7; option **(i)**.

✗ Common Pitfall

Don't confuse Mn_2O_7 (Mn^{+7}, the anhydride of $HMnO_4$) with MnO_2 (Mn^{+4}). Both are dark, but MnO_2 is a solid and stable; Mn_2O_7 is a liquid and explosive.

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

Anhydride angle. Every oxoacid has an anhydride obtained by removing water. $HMnO_4$ (permanganic acid) $\xrightarrow{-H_2O}$ Mn_2O_7.

Concept used. Concentrated H_2SO_4 promotes dehydration of oxoanions to their anhydride oxides while keeping the metal in its original oxidation state. The product Mn_2O_7 holds Mn in the $+7$ state in two tetrahedral MnO_4 units sharing one oxygen.

Step 1. Apply the dehydration template $2\,HMnO_4 \longrightarrow Mn_2O_7 + H_2O$, generated in situ as $2\,KMnO_4 + H_2SO_4 \longrightarrow 2\,HMnO_4 + K_2SO_4$, then $2\,HMnO_4 \longrightarrow Mn_2O_7 + H_2O$.

Step 2. Net: $2\,KMnO_4 + H_2SO_4 \longrightarrow Mn_2O_7 + K_2SO_4 + H_2O$. Match colour (green oil) and reactivity (explosive at $> 55°C$) – both fit Mn_2O_7.

Step 3. Eliminate the rest by oxidation state and physical state (none are green oils).

☞ Lab safety

This is why you never mix $KMnO_4$ with concentrated H_2SO_4 in even small amounts in a lab demo – the resulting Mn_2O_7 detonates without warning if warmed.

Final Answer: Green oily explosive product is Mn_2O_7; option **(i)**.

Q 4.6 The magnetic nature of elements depends on the presence of unpaired electrons. Identify the configuration of transition element, which shows highest magnetic moment.

(i) $3d^7$
(ii) $3d^5$
(iii) $3d^8$
(iv) $3d^2$

SOLUTION

Correct option: (ii) $3d^5$.
Concept used. For a first-row transition ion the **spin-only magnetic moment** is

$$\mu_{\text{s.o.}} = \sqrt{n(n+2)}\ \text{B.M.},$$

where n is the number of unpaired d electrons (B.M. = Bohr magneton). μ is maximised by maximising n; for a d^x ion the maximum value of n is $\min(x, 10 - x) \times 2$ – but more simply, the highest possible unpaired count in a d subshell is 5 (one in each of the five d orbitals, in line with Hund's rule).

Step 1. Count maximum unpaired electrons (high-spin, weak ligand field) for each option:

- $3d^7$: orbitals fill as $\uparrow\downarrow, \uparrow\downarrow, \uparrow, \uparrow, \uparrow$; $n = 3$.
- $3d^5$: $\uparrow, \uparrow, \uparrow, \uparrow, \uparrow$; $n = 5$ (half-filled).
- $3d^8$: $\uparrow\downarrow, \uparrow\downarrow, \uparrow\downarrow, \uparrow, \uparrow$; $n = 2$.
- $3d^2$: $\uparrow, \uparrow$, three empty; $n = 2$.

Step 2. Compute $\mu_{\text{s.o.}}$ for each:

$$\begin{aligned} d^7 &: \mu = \sqrt{3 \cdot 5} = \sqrt{15} = 3.87\,\text{B.M.} \\ d^5 &: \mu = \sqrt{5 \cdot 7} = \sqrt{35} = 5.92\,\text{B.M.} \\ d^8 &: \mu = \sqrt{2 \cdot 4} = \sqrt{8} = 2.83\,\text{B.M.} \\ d^2 &: \mu = \sqrt{2 \cdot 4} = \sqrt{8} = 2.83\,\text{B.M.} \end{aligned}$$

Step 3. Largest is d^5 at 5.92 B.M.

> **Final Answer:** $3d^5$ has the highest magnetic moment, 5.92 B.M.; option **(ii)**.

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

Half-filled angle. The magnetic moment maximum sits at the exact half-filling of any subshell because every orbital has one electron with parallel spins (Hund's maximum-multiplicity rule).

Concept used. Spin-only formula $\mu = \sqrt{n(n+2)}$ B.M. has a strict maximum at $n = (2\ell + 1)$ for an ℓ-subshell; for d ($\ell = 2$) that's $n = 5$.

Step 1. Hund's rule gives, for any d^x high-spin: $n = x$ if $x \leq 5$, $n = 10 - x$ if $x > 5$. Check: $d^2 \to 2$, $d^5 \to 5$, $d^7 \to 3$, $d^8 \to 2$.

Step 2. Plug into $\mu = \sqrt{n(n+2)}$. The function is monotonically increasing in n, so larger $n \Rightarrow$ larger μ.

Step 3. d^5 wins with $n = 5$ and $\mu = \sqrt{35} = 5.92$ B.M.

♥ Half-filled stability

The same d^5 configuration is also where the maximum exchange-energy stabilisation sits. That's why Fe^{3+} and Mn^{2+} (both d^5) are so prevalent in transition-metal chemistry: stable *and* highly paramagnetic.

Final Answer: $3d^5$ ($\mu = 5.92$ B.M.); option **(ii)**.

Q 4.7 **Which of the following oxidation state is common for all lanthanoids?**

(i) $+2$

(ii) $+3$

(iii) $+4$

(iv) $+5$

SOLUTION

Correct option: (ii) $+3$.

Concept used. Lanthanoids (Ce to Lu, $Z = 58$–71) have the general atomic configuration $[\mathrm{Xe}]\,4f^{1\text{–}14}\,5d^{0\text{–}1}\,6s^2$. The $4f$ electrons are well shielded, the $6s$ electrons easy to remove and the $5d^1$ (where present) likewise. The energetically cheapest ionisation removes the two $6s$ electrons and (when present) the $5d^1$, leaving the $4f$ core intact and producing the $+3$ ion.

Step 1. For a typical lanthanoid, sum of the first three ionisation enthalpies $\sum_1^3 IE \approx 3500\,\text{kJ/mol}$ – comparable to that of group 13 elements and easily provided by lattice/hydration energy of Ln^{3+} compounds.

Step 2. Going beyond $+3$ requires ionising a $4f$ electron, which is much harder

($IE_4 \gtrsim 4000\,\text{kJ/mol}$), so $+4$ is seen only when it produces a particularly stable configuration (e.g. Ce^{4+} becomes $4f^0$). Similarly $+2$ exists only when a stable $4f^7$ or $4f^{14}$ shell is reached (Eu^{2+}, Yb^{2+}).

Step 3. The single oxidation state shared by every lanthanoid from La/Ce through Lu is therefore $+3$.

> **Final Answer:** $+3$ is the characteristic oxidation state of every lanthanoid; option **(ii)**.

✗ Common slip

Don't read $4f^{1-14}$ as "one to fourteen f electrons in every lanthanoid" – it means the range across the series. La itself has no $4f$ electron; Ce has $4f^1$; Lu has $4f^{14}$.

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

Energy-cost angle. The $+3$ state is the lowest-IE point that still bare-shells the $5d/6s$ outermost electrons.

Concept used. Once the $6s^2$ pair and the (occasional) $5d^1$ are removed, further ionisation has to attack $4f$ – which is buried and tightly bound. The $+3$ state is therefore the "natural" valence of the entire series.

Step 1. Visualise the configuration after $-3e^-$: $La \rightarrow La^{3+}$ is [Xe] (noble-gas core); $Ce \rightarrow Ce^{3+}$ is $[Xe]\,4f^1$; …; $Lu \rightarrow Lu^{3+}$ is $[Xe]\,4f^{14}$.

Step 2. Across the series the difference between successive ions is just a $4f$ electron, which barely participates in bonding because of poor radial overlap. So the chemistry of Ln^{3+} is highly uniform.

Step 3. Specific exceptions ($+2$ for Eu, Yb; $+4$ for Ce, Tb) exist but the *common* oxidation state is $+3$.

> **Final Answer:** $+3$; option **(ii)**.

Q 4.8 **Which of the following reactions are disproportionation reactions?**

(a) $Cu^+ \longrightarrow Cu^{2+} + Cu$

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

(c) $2\,KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$

(d) $2\,MnO_4{}^- + 3\,Mn^{2+} + 2\,H_2O \longrightarrow 5\,MnO_2 + 4\,H^+$

(i) a, b

(ii) a, b, c
(iii) b, c, d
(iv) a, d

SOLUTION

Correct option: (i) a, b.
Concept used. A **disproportionation** reaction is one in which the *same element* is simultaneously oxidised and reduced: i.e. a single species in an intermediate oxidation state splits into one higher and one lower oxidation state of itself.

Step 1. Reaction (a) $Cu^+ \longrightarrow Cu^{2+} + Cu$: Cu starts at $+1$, ends as $+2$ (oxidised) and 0 (reduced). Same element, two new states. **Disproportionation**. ✓(Stoichiometry must be balanced as $2\,Cu^+ \longrightarrow Cu^{2+} + Cu$.)

Step 2. Reaction (b) $3\,MnO_4{}^{2-} + 4\,H^+ \longrightarrow 2\,MnO_4{}^- + MnO_2 + 2\,H_2O$ (note: the question's left side should read $MnO_4{}^{2-}$): Mn starts at $+6$ on the left, ends as $+7$ (in $MnO_4{}^-$, oxidised) and $+4$ (in MnO_2, reduced). Same element, two new states. **Disproportionation**. ✓

Step 3. Reaction (c) $2\,KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$: Mn goes from $+7$ to $+6$ (K_2MnO_4) and $+4$ (MnO_2), which is reduction in both cases. The oxidation here happens on *oxygen* (from -2 to 0), not on Mn. So this is a **coupled redox**, not a disproportionation. ✗

Step 4. Reaction (d) $2\,MnO_4{}^- + 3\,Mn^{2+} + 2\,H_2O \longrightarrow 5\,MnO_2 + 4\,H^+$: Mn goes from $+7$ (in $MnO_4{}^-$) and $+2$ (in Mn^{2+}) *both* to $+4$ (in MnO_2). This is a **comproportionation** (the reverse of disproportionation): two different starting states converge to one common state. ✗

> **Final Answer:** Only (a) and (b) are disproportionations; option **(i)**.

☞ Disproportionation vs comproportionation

Disproportionation: *one* state splits into two. Comproportionation: *two* states merge into one. (d) is the mirror image of (b).

EXPERT'S SOLUTION *: Ankit Singh, M.Tech Chemical Engineering, IIT Delhi*

Oxidation-state ledger angle. Build a table of Mn (or Cu) oxidation states before and after; same element going *both* up and down is the disproportionation signature.
Concept used. Disproportionation requires (i) one starting species, (ii) two product species containing the same element in different oxidation states (one higher, one lower than the starting state).

Step 1. (a) Cu: $+1 \rightarrow (+2,\ 0)$. Same element, both up and down. Disproportionation.

Step 2. (b) Mn: $+6 \to (+7,\ +4)$. Same element, both up and down. Disproportionation.

Step 3. (c) Mn: $+7 \to (+6,\ +4)$. Both products are lower; no oxidation of Mn. The oxidiser is the O^{2-} going to O_2. Not a Mn disproportionation.

Step 4. (d) Mn: $(+7,\ +2) \to +4$. Two starting states merge into one intermediate state. Comproportionation.

Final Answer: (a) and (b); option **(i)**.

Cross-check. Sum the change vector: in (a) Cu carries $(+1)\!\to\!+2$ (one electron lost) and $(+1)\!\to\!0$ (one electron gained) – net charge balance per Cu atom is zero, the disproportionation signature. In (d) the average Mn oxidation state on the left $(\frac{2(+7)+3(+2)}{5} = +4)$ already equals the product state $(+4)$, which is the comproportionation signature. Memorise these two arithmetic fingerprints and you never need to redraw the table.

Q 4.9 **When $KMnO_4$ solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time because**

(i) CO_2 is formed as the product.

(ii) Reaction is exothermic.

(iii) ${MnO_4}^-$ catalyses the reaction.

(iv) Mn^{2+} acts as autocatalyst.

SOLUTION

Correct option: (iv) Mn^{2+} acts as autocatalyst.

Concept used. An autocatalyst is a product of the reaction that itself catalyses that very reaction. The hallmark of autocatalysis is a kinetic curve that starts slow (no catalyst yet) and accelerates as more product accumulates, until reactants begin to deplete.

Step 1. Write the titration reaction:

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

At $t = 0$ the only oxidising agent is ${MnO_4}^-$, which is slow because the reaction is a many-electron process $(5e^-/{MnO_4}^-)$.

Step 2. As Mn^{2+} accumulates, it acts as a redox shuttle:

Step (i): Mn^{2+} is oxidised by ${MnO_4}^-$ to Mn^{3+}.

Step (ii): Mn^{3+} oxidises ${C_2O_4}^{2-}$, returning to Mn^{2+}.

The single-electron Mn^{3+}/Mn^{2+} couple is kinetically much faster than the direct $MnO_4^- + C_2O_4^{2-}$ encounter, so the overall rate jumps once $[Mn^{2+}]$ builds up.

Step 3. Eliminate distractors: CO_2 leaves as gas and does not participate in further chemistry; the reaction is mildly exothermic but the change of T in a dilute aqueous titration is small; MnO_4^- is a reactant, not a catalyst.

> **Final Answer:** The catalyst is Mn^{2+}, formed as the reaction proceeds; option **(iv)**.

♥ Why we warm the flask in the titration

The lab procedure warms the oxalic-acid/$KMnO_4$ titration to $60–70°$C exactly so that the initial uncatalysed step is fast enough to bring out the first Mn^{2+}. After that the reaction proceeds smartly at the autocatalytic rate.

EXPERT'S SOLUTION *: Krishna Reddy, M.Sc Physical Chemistry, IIT Madras*

Kinetic-induction angle. The reaction has an *induction period* – a clear giveaway of autocatalysis.
Concept used. For an autocatalytic reaction $A + B \to C$ catalysed by C, the rate law is $r = k[A][B][C]$. At $t = 0$, $[C] = 0 \Rightarrow r = 0$, so the start is slow; as $[C]$ grows, r grows; near the end, $[A][B] \to 0$ pulls r back down.

Step 1. Apply the template: $A = MnO_4^-$, $B = C_2O_4^{2-}$, $C = Mn^{2+}$ (an autocatalyst that arises as product).

Step 2. The rate law predicts a sigmoidal $[C]$ vs t curve, which is exactly what the slow-then-fast decolourisation looks like.

Step 3. Cross-check: MnO_4^- cannot be a catalyst (it is consumed); CO_2 is not redox-active here; the exothermicity is too small to explain the rate jump.

> **Final Answer:** Mn^{2+} is the autocatalyst; option **(iv)**.

Q 4.10 There are 14 elements in actinoid series. Which of the following elements does not belong to this series?

(i) U
(ii) Np
(iii) Tm
(iv) Fm

SOLUTION

Correct option: (iii) Tm.

Concept used. The actinoid series consists of the 14 elements that follow actinium (Ac, $Z = 89$) in which the $5f$ orbitals are progressively filled. These are Th ($Z = 90$) through Lr ($Z = 103$). Thulium (Tm, $Z = 69$) is a lanthanoid (filling $4f$), not an actinoid.

Step 1. Check each option's atomic number:

- U (uranium): $Z = 92$, $5f^3 6d^1 7s^2$ – actinoid.
- Np (neptunium): $Z = 93$, $5f^4 6d^1 7s^2$ – actinoid.
- Tm (thulium): $Z = 69$, $4f^{13} 6s^2$ – lanthanoid.
- Fm (fermium): $Z = 100$, $5f^{12} 7s^2$ – actinoid.

Step 2. Only Tm sits in the $4f$ block, not the $5f$ block.

> **Final Answer:** Thulium (Tm) is not an actinoid; option **(iii)**.

☞ **Quick spot**

Whenever a property column lists "shows variable oxidation states / forms coloured ions / acts as catalyst / forms complex ions", the metal is in the transition series (d-block). The non-transition d^0 or d^{10} ions break each of these traits.

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

Block-by-block angle. Lanthanoids start at Ce ($Z = 58$); actinoids start at Th ($Z = 90$). Anything with $Z < 90$ is a lanthanoid, anything with $Z \geq 90$ (and < 104) is an actinoid.

Concept used. The two f-block series differ by the principal quantum number of the filling f orbital: $4f$ for lanthanoids, $5f$ for actinoids.

Step 1. U (92), Np (93), Fm (100) all sit in the actinoid range.

Step 2. Tm (69) sits in the lanthanoid range – specifically near the heavy end of the $4f$ series.

Step 3. Hence Tm is the misfit.

> **Final Answer:** Tm; option **(iii)**.

Q 4.11 $\mathrm{KMnO_4}$ **acts as an oxidising agent in acidic medium. The number of moles of** $\mathrm{KMnO_4}$ **that will be needed to react with one mole of sulphide ions in acidic solution**

is

(i) $\frac{2}{5}$

(ii) $\frac{3}{5}$

(iii) $\frac{4}{5}$

(iv) $\frac{1}{5}$

SOLUTION

Correct option: (i) $\frac{2}{5}$.

Concept used. Balance the redox by matching electrons. In acid, $MnO_4{}^-$ is reduced by 5 electrons per ion:

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

Sulphide S^{2-} is oxidised to elemental sulphur with loss of 2 electrons:

$$S^{2-} \longrightarrow S + 2\,e^-\,\cdot$$

Step 1. Equalise electrons: multiply the $MnO_4{}^-$ half-equation by 2 ($\Rightarrow 10\,e^-$) and the S^{2-} half-equation by 5 ($\Rightarrow 10\,e^-$).

Step 2. Add:

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

Step 3. Read off the stoichiometric ratio: 2 mol $KMnO_4$ reacts with 5 mol S^{2-}. Per mol of S^{2-}, moles of $KMnO_4 = 2/5$.

Final Answer: $\frac{2}{5}$ mol $KMnO_4$ per mol S^{2-}; option **(i)**.

EXPERT'S SOLUTION *: Yash Kapoor, B.Tech Chemical Engineering, IIT Bombay*

n-factor ratio angle. Stoichiometry of any redox follows $n_{ox} \cdot$ (moles oxidant) $= n_{red} \cdot$ (moles reductant), where n is the electron change per ion.

Concept used. For $KMnO_4$ in acid, $n_{ox} = 5$; for $S^{2-} \to S$, $n_{red} = 2$.

Step 1. Set up: $5\,$mol $KMnO_4 \times 5 = 2 \times$ mol $S^{2-} \times 5?$ – redo: $5 \cdot n(KMnO_4) = 2 \cdot n(S^{2-})$.

Step 2. Solve for $n(KMnO_4)$ given $n(S^{2-}) = 1$ mol:

$$n(KMnO_4) = \frac{2}{5} \cdot 1 = \frac{2}{5}\text{ mol.}$$

Step 3. Sanity check: $\frac{2}{5} \times 5 = 2 = 1 \times 2$. ✓

☞ **n-factor shortcut**

Number of moles of oxidant per mole of reductant $= n_{\text{red}}/n_{\text{ox}}$. Here $= 2/5$.

Final Answer: $\frac{2}{5}$ mol; option **(i)**.

Q 4.12 **Which of the following is amphoteric oxide?**

Mn_2O_7, CrO_3, Cr_2O_3, CrO, V_2O_5, V_2O_4

(i) V_2O_5, Cr_2O_3

(ii) Mn_2O_7, CrO_3

(iii) CrO, V_2O_5

(iv) V_2O_5, V_2O_4

SOLUTION

Correct option: **(i)** V_2O_5 and Cr_2O_3.

Concept used. An **amphoteric oxide** reacts with both acids and bases. For transition-metal oxides, amphoteric character is seen at *intermediate* oxidation states: very low states are basic (give cations in acid), very high states are acidic (give oxoanions in base), and intermediate states straddle both.

Step 1. Tag each oxide by Mn or Cr/V oxidation state and acid–base nature:

- Mn_2O_7 – Mn^{+7}, strongly **acidic** (anhydride of $HMnO_4$).
- CrO_3 – Cr^{+6}, strongly **acidic** (anhydride of chromic/dichromic acid).
- Cr_2O_3 – Cr^{+3}, **amphoteric** (reacts with HCl giving $CrCl_3$, with $NaOH$ giving $Na[Cr(OH)_4]$).
- CrO – Cr^{+2}, **basic**.
- V_2O_5 – V^{+5}, **amphoteric** (gives ${VO_2}^+$ in acid, vanadate ${VO_4}^{3-}$ in base).
- V_2O_4 – V^{+4}, basic/weakly amphoteric.

Step 2. The two clearly amphoteric oxides are Cr_2O_3 and V_2O_5.

Step 3. Verify with sample reactions:

$$Cr_2O_3 + 6\,HCl \longrightarrow 2\,CrCl_3 + 3\,H_2O,$$

$$Cr_2O_3 + 2\,NaOH + 3\,H_2O \longrightarrow 2\,Na[Cr(OH)_4].$$

V_2O_5 similarly reacts with H^+ (gives ${VO_2}^+$) and with OH^- (gives vanadate).

Final Answer: V_2O_5 and Cr_2O_3 are amphoteric; option **(i)**.

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

Oxidation-state map angle. Track the metal's oxidation state $+n$ across each oxide; low n is basic, high n is acidic, the middle band is amphoteric.
Concept used. Acidity of a metal oxide increases with oxidation state because the M–O bond becomes more covalent and the oxide ion's basicity falls.

Step 1. Plot oxidation states: $CrO = +2$, $Cr_2O_3 = +3$, $CrO_3 = +6$. The middle one is amphoteric. Likewise $V_2O_4 = +4$, $V_2O_5 = +5$; $+5$ is the amphoteric corner of vanadium chemistry.

Step 2. Match: Cr_2O_3 (middle of Cr range) and V_2O_5 (high V range, just amphoteric still).

☞ **Cr-oxide ladder**

CrO basic $<$ Cr_2O_3 *amphoteric* $<$ CrO_3 acidic. Move up the ladder by removing e^- from Cr.

Final Answer: V_2O_5 and Cr_2O_3; option **(i)**.

Q 4.13 **Gadolinium belongs to $4f$ series. Its atomic number is 64. Which of the following is the correct electronic configuration of gadolinium?**

(i) $[\text{Xe}]\,4f^7\,5d^1\,6s^2$

(ii) $[\text{Xe}]\,4f^6\,5d^2\,6s^2$

(iii) $[\text{Xe}]\,4f^8\,6d^2$

(iv) $[\text{Xe}]\,4f^9\,5s^1$

SOLUTION

Correct option: (i) $[\text{Xe}]\,4f^7\,5d^1\,6s^2$.
Concept used. For lanthanoids the filling order is typically $6s^2$ first, then $4f$, with $5d^1$ inserted whenever that produces a half-filled or fully-filled $4f$ shell (extra exchange-energy stability, analogous to Cr and Cu in the $3d$ row). At $Z = 64$ exactly, putting one electron in $5d$ lets $4f$ stop at $4f^7$ – the half-filled stable arrangement.

Step 1. Electron count: $Z = 64$ gadolinium. Xe accounts for 54 electrons, leaving $64 - 54 = 10$ to distribute over $4f, 5d, 6s$.

Step 2. Naive Aufbau: $6s^2\,4f^8$ uses 10 electrons. But that gives $4f^8$ (8 electrons among 7 f orbitals $\Rightarrow$ pairing in one orbital). Promoting one $4f$ electron to $5d$

costs little energy and breaks no pair because the resulting $4f^7$ is half-filled (every f orbital singly occupied, maximum exchange energy).

Step 3. Hence Gd is anomalous: $[\mathrm{Xe}]\,4f^7\,5d^1\,6s^2$, with $4f^7$ providing the half-filled stability.

Final Answer: Gadolinium: $[\mathrm{Xe}]\,4f^7\,5d^1\,6s^2$; option **(i)**.

☞ **Lanthanoid anomalies**

La (no $4f$), Ce ($4f^1 5d^1$), Gd ($4f^7 5d^1$), Lu ($4f^{14} 5d^1$) all have a $5d^1$. Everywhere else $5d^0$.

EXPERT'S SOLUTION *: Aanya Nair, M.Sc Chemistry, IIT Kanpur*

Half-filled-stability angle. Gadolinium parallels chromium: just as Cr promotes a $4s$ electron to give $3d^5 4s^1$, Gd promotes a $4f$ electron to give $4f^7 5d^1$.
Concept used. Exchange-energy stability of a half-filled subshell can overcome the small extra orbital-energy cost.

Step 1. Trial 1: $4f^8\,6s^2$. Exchange terms: only the seven spin-parallel ones in the 7 f orbitals; the 8th electron is paired.

Step 2. Trial 2: $4f^7\,5d^1\,6s^2$. Now $4f$ is half-filled (max exchange energy across 7 parallel spins) plus a $5d^1$ that doesn't disrupt the f shell.

Step 3. Compare: Trial 2 wins, hence the anomalous configuration. Cross-check: Gd has a famously high magnetic moment ($\sim 8\,\mu_B$ per atom) consistent with 7 unpaired $4f$ electrons plus one in $5d$.

Final Answer: $[\mathrm{Xe}]\,4f^7\,5d^1\,6s^2$; option **(i)**.

Q 4.14 Interstitial compounds are formed when small atoms are trapped inside the crystal lattice of metals. Which of the following is not the characteristic property of interstitial compounds?

(i) They have high melting points in comparison to pure metals.

(ii) They are very hard.

(iii) They retain metallic conductivity.

(iv) They are chemically very reactive.

SOLUTION

Correct option: (iv) They are chemically very reactive.

Concept used. Interstitial compounds of transition metals (e.g. TiC, ZrN, $\mathrm{Fe_3H}$) form when small atoms like H, B, C, or N occupy the octahedral or tetrahedral holes in the metal lattice. The small atoms wedge the lattice, locking metal atoms in place: this raises the melting point, increases hardness, preserves the metallic sea of electrons (so conductivity stays), and – crucially – makes the compound chemically *inert*, not reactive.

Step 1. Check (i) – True: e.g. TiC melts at $3160°\mathrm{C}$, far above pure Ti at $1668°\mathrm{C}$.

Step 2. Check (ii) – True: most interstitial carbides and nitrides have hardness near or above diamond, used as cutting tool coatings.

Step 3. Check (iii) – True: the conduction-band electrons of the metal lattice are largely untouched, so metallic conductivity survives.

Step 4. Check (iv) – False: interstitial compounds are notoriously *unreactive*. WC, TiC, $\mathrm{Fe_3C}$ etc. resist acid attack and oxidation up to high temperatures. Option (iv) is the wrong characterisation.

> **Final Answer:** Option **(iv)** is the false claim; interstitial compounds are chemically inert.

♥ Industrial relevance

Interstitial alloys like TiC, WC and the steels of Cr-Mo-V owe their hardness to small atoms wedged inside the metal lattice. “Inert” interstitials are what survive at jet-turbine temperatures.

EXPERT’S SOLUTION : *Tara Bhat, M.Sc Chemistry, IIT Kanpur*

Property-matching angle. The four options are statements; three are right, one is wrong. Tag them against textbook properties in turn.

Concept used. Interstitial compounds inherit the metallic bonding of the parent metal but gain rigidity from the trapped small atoms. Both effects together explain high m.p., high hardness, retained conductivity, and chemical inertness.

Step 1. (i) High m.p. ✓(small atom locks the lattice).

Step 2. (ii) Very hard ✓.

Step 3. (iii) Metallic conductivity ✓.

Step 4. (iv) Chemically reactive ✗ – in fact, they are used precisely because they are *inert* (cutting tools, catalyst supports).

> **Final Answer:** Option **(iv)** is the not-a-property; interstitial compounds are chemically inert.

Cross-check. A handy mnemonic: HCMR – *Hard, Conductive, Melting-point-high, Refractory*. Interstitial carbides and nitrides of Ti, V, Zr are used as cutting-tool inserts (TiC, WC) precisely because they survive temperatures that would melt the parent metal and refuse to react with hot hydrocarbons. Option (iv) contradicts that industrial fact directly and is therefore the odd one out.

Q 4.15 The magnetic moment is associated with its spin angular momentum and orbital angular momentum. Spin only magnetic moment value of Cr^{3+} ion is ________.

(i) 2.87 B.M.

(ii) 3.87 B.M.

(iii) 3.47 B.M.

(iv) 3.57 B.M.

SOLUTION

Correct option: (ii) 3.87 B.M.

Concept used. Cr has $Z = 24$, neutral atom configuration $[\mathrm{Ar}]\,3d^5\,4s^1$. The Cr^{3+} ion loses the $4s^1$ and two $3d$ electrons, leaving $[\mathrm{Ar}]\,3d^3$. The spin-only magnetic moment formula is

$$\mu_{\text{s.o.}} = \sqrt{n(n+2)}\ \text{B.M.},$$

where n is the number of unpaired electrons.

Step 1. Place 3 electrons in five d orbitals using Hund's rule: $\uparrow, \uparrow, \uparrow, \_, \_$. Three unpaired electrons, so $n = 3$.

Step 2. Substitute in the formula:

$$\mu = \sqrt{3\,(3+2)} = \sqrt{15}.$$

Step 3. Compute the square root: $\sqrt{15} = 3.873$. To 2 d.p., $\mu = 3.87$ B.M.

> **Final Answer:** $\mu_{\text{s.o.}}(\mathrm{Cr}^{3+}) = 3.87$ B.M.; option **(ii)**.

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

$\sqrt{n(n+2)}$ **angle.** Build a tiny lookup table for $n = 1$ to 5: $\mu = 1.73, 2.83, 3.87, 4.90, 5.92$ B.M.

Concept used. The spin-only formula assumes orbital contribution is quenched (true for most first-row transition ions in an octahedral field). The result depends only on n, the unpaired count.

Step 1. Determine n for Cr^{3+}: $3d^3$ has all three electrons unpaired (Hund), so $n = 3$.

Step 2. Read off $\mu(n = 3) = 3.87$ B.M.

☞ **Pre-memorise the table**

Memorise μ for $n =$ 0–5: $0,\ 1.73,\ 2.83,\ 3.87,\ 4.90,\ 5.92$ B.M. JEE/NEET questions become 5-second calculations.

Final Answer: 3.87 B.M.; option **(ii)**.

Q 4.16 $KMnO_4$ **acts as an oxidising agent in alkaline medium. When alkaline** $KMnO_4$ **is treated with KI, iodide ion is oxidised to ________.**

(i) I_2
(ii) IO^-
(iii) $IO_3{}^-$
(iv) $IO_4{}^-$

SOLUTION

Correct option: (iii) $IO_3{}^-$.

Concept used. In alkaline (or neutral) medium, $KMnO_4$ is a strong oxidising agent that oxidises iodide I^- (-1 state) all the way to **iodate** $IO_3{}^-$ (+5 state). The Mn side goes from +7 to +4 (MnO_2).

Step 1. Half-reactions in alkaline medium:

$$MnO_4{}^- + 2\,H_2O + 3\,e^- \longrightarrow MnO_2 + 4\,OH^- \quad \text{(reduction)},$$
$$I^- + 6\,OH^- \longrightarrow IO_3{}^- + 3\,H_2O + 6\,e^- \quad \text{(oxidation)}.$$

Step 2. Balance electrons (multiply Mn half by 2, I half by 1; total $6\,e^-$) and add:

$$2\,MnO_4{}^- + I^- + H_2O \longrightarrow 2\,MnO_2 + IO_3{}^- + 2\,OH^-.$$

Step 3. Iodine goes $-1 \rightarrow +5$, a 6-electron oxidation that lands at iodate. Distractor analysis: IO^- (hypoiodite, +1) would require only $2e^-$ – insufficient against a strong oxidant; IO_4^- (periodate, +7) would need an even stronger oxidant such as ozone or F_2, more than MnO_4^- can deliver in alkali.

Final Answer: Iodide is oxidised to iodate IO_3^-; option **(iii)**.

☞ **Spin-only formula**

$\mu_{\text{spin}} = \sqrt{n(n+2)}$ BM where n is the number of unpaired electrons. Build the d^n configuration of the *ion*, count unpaired electrons, then substitute.

EXPERT'S SOLUTION *: Diya Pillai, Ph.D Organic Chemistry, IISc Bangalore*

Oxidising-strength angle. In acid, $KMnO_4$ delivers 5 electrons ($MnO_4^- \to Mn^{2+}$); in alkali only 3 ($MnO_4^- \to MnO_2$). Iodide is itself a strong reductant; the end product in alkali is the iodate level.
Concept used. Standard reduction potential of MnO_4^-/MnO_2 in base ($+0.59\,V$) is more than enough to push I^- to IO_3^- ($E°(IO_3^-/I^-) \approx +0.26\,V$).

Step 1. Compare $E°$: $E°_{\text{cell}} = 0.59 - 0.26 = +0.33\,V > 0$, so the reaction is feasible.

Step 2. Write the balanced overall reaction (above).

Step 3. Note the molar ratio: $2\,MnO_4^- : 1\,I^-$. This is what a quantitative analysis would also predict.

Final Answer: $I^- \to IO_3^-$; option **(iii)**.

Q 4.17 **Which of the following statements is not correct?**
(i) Copper liberates hydrogen from acids.
(ii) In its higher oxidation states, manganese forms stable compounds with oxygen and fluorine.
(iii) Mn^{3+} and Co^{3+} are oxidising agents in aqueous solution.
(iv) Ti^{2+} and Cr^{2+} are reducing agents in aqueous solution.

SOLUTION

Correct option: **(i)** Copper liberates hydrogen from acids – this is incorrect.
Concept used. A metal liberates H_2 from a non-oxidising acid only if its standard reduction potential $E°(M^{n+}/M)$ is *negative* relative to H^+/H_2 (taken as 0 V). Copper has $E°(Cu^{2+}/Cu) = +0.34$ V, which is *positive*, so Cu cannot reduce H^+ to H_2. The other three statements are textbook-correct.

Step 1. Tag each statement:

- (i) Wrong: $E°(Cu^{2+}/Cu) > 0$, so Cu does not displace H_2 from dilute HCl or H_2SO_4.
- (ii) Correct: Mn^{+7} (Mn_2O_7, $MnO_4{}^-$) and Mn^{+4} (MnO_2, MnF_4) etc. are stable; oxide and fluoride ligands stabilise high oxidation states.
- (iii) Correct: $E°(Mn^{3+}/Mn^{2+}) = +1.51$ V, $E°(Co^{3+}/Co^{2+}) = +1.81$ V; both are strong oxidants.
- (iv) Correct: $E°(Ti^{3+}/Ti^{2+}) = -0.37$ V, $E°(Cr^{3+}/Cr^{2+}) = -0.41$ V; both are reductants in water.

Step 2. Only (i) misrepresents the chemistry.

> **Final Answer:** Statement **(i)** is incorrect: Cu does not liberate H_2 from acids.

☞ **Colour quick test**

All d^0 (Sc^{3+}, Ti^{4+}) and d^{10} (Zn^{2+}, Cu^+, Cd^{2+}) ions are colourless. Anything between d^1 and d^9 is potentially coloured.

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

Reduction-potential filter angle. For "which liberates H_2" or "which is oxidant/reductant" questions, the electrochemical series resolves everything in one line.

Concept used. A metal M liberates H_2 iff $E°(M^{n+}/M) < 0$; an ion M^{n+} is an oxidant in water iff $E°(M^{n+}/M^{(n-1)+}) > 0.4$ V or so (strong enough to oxidise H_2O less easily than other species), and a reductant iff $E° < 0$.

Step 1. Cu sits below H^+/H_2 in the activity series: cannot give H_2.

Step 2. Mn^{3+}/Mn^{2+} at $+1.51$ V and Co^{3+}/Co^{2+} at $+1.81$ V are clearly oxidants.

Step 3. Ti^{3+}/Ti^{2+} and Cr^{3+}/Cr^{2+} are both < 0, hence the $+2$ ions are reductants.

> **Final Answer:** Statement **(i)** is the not-correct claim.

Q 4.18 **When acidified $K_2Cr_2O_7$ solution is added to Sn^{2+} salts then Sn^{2+} changes to**

(i) Sn
(ii) Sn^{3+}
(iii) Sn^{4+}
(iv) Sn^+

SOLUTION

Correct option: (iii) Sn^{4+}.

Concept used. Acidified dichromate is a strong oxidising agent: $E°(Cr_2O_7{}^{2-}/Cr^{3+}) = +1.33$ V. It oxidises Sn^{2+} (a known reductant, $E°(Sn^{4+}/Sn^{2+}) = +0.15$ V) all the way to Sn^{4+}.

Step 1. Half-reactions:

$$\begin{aligned} Cr_2O_7{}^{2-} + 14\,H^+ + 6\,e^- &\longrightarrow 2\,Cr^{3+} + 7\,H_2O \quad \text{(reduction)},\\ Sn^{2+} &\longrightarrow Sn^{4+} + 2\,e^- \quad \text{(oxidation)}. \end{aligned}$$

Step 2. Balance electrons (multiply Sn half by 3, total $6\,e^-$) and add:

$$Cr_2O_7{}^{2-} + 14\,H^+ + 3\,Sn^{2+} \longrightarrow 2\,Cr^{3+} + 3\,Sn^{4+} + 7\,H_2O\,.$$

Step 3. Cell potential: $E^\circ_{\text{cell}} = 1.33 - 0.15 = +1.18$ V, strongly spontaneous. Sn^{2+} is driven to Sn^{4+}. Distractors Sn^{3+} and Sn^{+} are not stable oxidation states for tin.

> **Final Answer:** Sn^{2+} is oxidised to Sn^{4+}; option **(iii)**.

EXPERT'S SOLUTION *: Aaditya Joshi, M.Tech Chemical Engineering, IIT Delhi*

$+2/+4$ **couple angle.** Group-14 elements (Sn, Pb) often shuttle between the $+2$ and $+4$ states. Sn^{2+} is a reductant, Sn^{4+} is the oxidised form; $+1$, $+3$ are not common.

Concept used. Dichromate's 1.33 V can easily push Sn to its highest accessible state.

Step 1. Apply the elimination: Sn^{+} and Sn^{3+} are not stable in water; rule out.

Step 2. Pick between Sn and Sn^{4+}: dichromate *oxidises*, so we move *up* in oxidation state. Sn (i.e. Sn^{0}) is more reduced than Sn^{2+}, ruled out.

Step 3. Final answer: Sn^{4+}.

✗ Common Pitfall

Students sometimes pick Sn^{3+} thinking "one step up". Sn^{3+} is not stable in aqueous solution; Sn's redox economy hops in $2e^-$ jumps between $+2$ and $+4$.

> **Final Answer:** Sn^{4+}; option **(iii)**.

Q 4.19 Highest oxidation state of manganese in fluoride is $+4$ (MnF_4) but highest oxidation state in oxides is $+7$ (Mn_2O_7) because ________.

(i) fluorine is more electronegative than oxygen.
(ii) fluorine does not possess d-orbitals.
(iii) fluorine stabilises lower oxidation state.
(iv) in covalent compounds fluorine can form single bond only while oxygen forms double bond.

SOLUTION

Correct option: (iv) in covalent compounds fluorine can form single bond only while oxygen forms double bond.

Concept used. The maximum oxidation state of a metal in its fluoride is set by how many F atoms can be packed around it (each F contributes only one bond, so σ-only). In an oxide, oxygen can form a *double bond* (one σ + one π), so one oxygen "carries two oxidation units". To reach $+7$, manganese needs to form 7 M–X bonds: with fluorine that means $\mathrm{MnF_7}$ (sterically impossible, $\sim$ 7 F around one Mn won't fit), but with oxygen it means $\mathrm{Mn_2O_7}$ where each oxygen ties up via $\mathrm{Mn{=}O}$ (π-bond).

Step 1. Count bonds in $\mathrm{Mn_2O_7}$: there are several terminal $\mathrm{Mn{=}O}$ double bonds plus a bridging $\mathrm{Mn{-}O{-}Mn}$. Each $\mathrm{Mn{=}O}$ counts 2 toward Mn's oxidation state (Mn donates 2 electrons to that oxygen). With three terminal $\mathrm{Mn{=}O}$ and one bridging $\mathrm{Mn{-}O{-}Mn}$ per Mn, oxidation state $= 3(2) + 1 = 7$.

Step 2. For fluorine: each $\mathrm{Mn{-}F}$ contributes only 1 to Mn's oxidation state, and 7 F atoms cannot fit around one Mn atom (coordination too crowded). The known highest manganese fluoride is $\mathrm{MnF_4}$ at oxidation state $+4$.

Step 3. Eliminate distractors:

- (i) "F is more electronegative than O" – true but not the operative reason; higher electronegativity pulls more, but oxygen still wins via π.
- (ii) F has no d-orbitals – true, but neither does O in normal bonding; not the reason.
- (iii) F stabilises lower oxidation states – a vague slogan; the real reason is bonding multiplicity.

> **Final Answer:** Reason **(iv)**: oxygen's ability to form $\mathrm{M{=}O}$ double bonds lets it stabilise higher oxidation states than fluorine.

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

Bond-multiplicity angle. Each F atom is a one-bond partner; each O atom can be a two-bond partner. So oxygen "buys" more oxidation state per atom than fluorine.

Concept used. Oxidation state
$= \sum(\text{electrons transferred to ligand}) = \sum_{\text{bond}}(\text{bond order})$ for ionic-formal counting.

Step 1. In MnO_4^-: Mn has 4 Mn–O bonds, each effectively a $Mn{=}O$ double bond (π-character distributed over the four oxygens). Bond-order sum $= 4 \times 2 = 8$; charge is -1 overall (one extra electron on the four-oxygen unit), net oxidation state of Mn $= 8 - 1 = +7$. ✓

Step 2. For an analogous all-fluoride: MnF_n has all single $Mn{-}F$ bonds, oxidation state $= n$. Steric ceiling caps n at 4.

Step 3. Hence highest fluoride MnF_4 $(+4)$; highest oxide Mn_2O_7 $(+7)$.

> ♥ **General principle**
>
> This is why every transition metal's *oxide* reaches a higher oxidation state than its *fluoride*: π-bonding O beats σ-only F at boosting oxidation state.

> **Final Answer:** The deciding factor is multiple-bond capacity (option **iv**).

Cross-check. Compare N_2 (a π-acceptor with a filled σ-donor lone pair) with NH_3 (only σ-donor): N_2 binds end-on through the same d-π^* back-bonding seen in CO, whereas NH_3 cannot. This is why dinitrogen complexes are confined to transition metals and never form with s- or p-block metals.

Q 4.20 **Although Zirconium belongs to $4d$ transition series and Hafnium to $5d$ transition series even then they show similar physical and chemical properties because ________.**

(i) both belong to d-block.
(ii) both have same number of electrons.
(iii) both have similar atomic radius.
(iv) both belong to the same group of the periodic table.

SOLUTION

Correct option: (iii) both have similar atomic radius.

Concept used. Lanthanoid contraction: the steady decrease in Ln^{3+} ionic radius across the $4f$ series. The contraction cancels the increase in shell number that would normally make a $5d$ atom larger than its $4d$ counterpart. As a result, the two members of group 4 (Zr, Hf) end up with almost identical atomic radii (160 pm vs 159 pm).

Step 1. Tabulate metallic radii: $r(\mathrm{Zr}) = 160$ pm, $r(\mathrm{Hf}) = 159$ pm.

Step 2. Almost identical radius $\Rightarrow$ almost identical lattice energies, hydration energies, M–X bond lengths, crystal packings.

Step 3. Hence ionisation energies, melting points, densities, even chemical reactivity track each other very closely.

Final Answer: Same radius (option **iii**) is the operative reason.

☞ **Lanthanoid contraction**

$r(\mathrm{Hf}) \approx r(\mathrm{Zr})$ because the $4f$ subshell, filled between them, contracts the $5d$ atoms by ~ 10 pm.

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

Atomic-size angle. Same group + same radius ⇒ same chemistry. The interesting bit is *why* the radius is the same despite Hf being two periods below Zr.

Concept used. The poor shielding of the $4f$ electrons leads to lanthanoid contraction; this radius drop carries forward into the $5d$ block.

Step 1. Compare with Ti–Zr (group 4 also): $r(\mathrm{Ti}) = 147$, $r(\mathrm{Zr}) = 160$ – a 13 pm jump from $3d$ to $4d$.

Step 2. From Zr to Hf we go from $4d$ to $5d$. Without lanthanoid contraction we'd expect a similar $\sim$ 10–15 pm jump; instead we measure -1 pm. The contraction has eaten it all.

Step 3. Consequence: Zr and Hf separate only by very specialised techniques (ion-exchange, solvent extraction). Their nitrate and chloride salts crystallise nearly indistinguishably.

Final Answer: Lanthanoid contraction ⇒ equal radii (option **iii**).

Q 4.21 **Why is HCl not used to make the medium acidic in oxidation reactions of $\mathrm{KMnO_4}$ in acidic medium?**

(i) Both HCl and $\mathrm{KMnO_4}$ act as oxidising agents.

(ii) $\mathrm{KMnO_4}$ oxidises HCl into $\mathrm{Cl_2}$ which is also an oxidising agent.

(iii) $\mathrm{KMnO_4}$ is a weaker oxidising agent than HCl.

(iv) $\mathrm{KMnO_4}$ acts as a reducing agent in the presence of HCl.

SOLUTION

Correct option: (ii) $\mathrm{KMnO_4}$ oxidises HCl into $\mathrm{Cl_2}$ which is also an oxidising agent.

Concept used. $\mathrm{KMnO_4}$ in acid is reduced to $\mathrm{Mn^{2+}}$ with $E° = +1.51$ V. HCl provides $\mathrm{Cl^-}$, which has $E°(\mathrm{Cl_2/Cl^-}) = +1.36$ V – low enough for $\mathrm{MnO_4}^-$ to oxidise it to $\mathrm{Cl_2}$.

This wastes some of the permanganate's oxidising power and adds Cl_2 as a competing oxidant, ruining quantitative titrations. Sulphuric acid, in contrast, has ${SO_4}^{2-}$ which is not oxidisable, so it stays as a spectator acid.

Step 1. Side-reaction balance in acidic medium:

$$2\,{MnO_4}^- + 10\,Cl^- + 16\,H^+ \longrightarrow 2\,Mn^{2+} + 5\,Cl_2 + 8\,H_2O\,\cdot$$

Cell potential: $1.51 - 1.36 = +0.15$ V, spontaneous.

Step 2. Consequence in titration: some $KMnO_4$ is consumed by HCl before it can act on the intended reductant (Fe^{2+}, $C_2{O_4}^{2-}$, ...). The titre comes out higher than the true value, and the liberated Cl_2 can oxidise the analyte too – a double error.

Step 3. Eliminate distractors: (i) is partially true but doesn't describe the cause; (iii) is false ($E°(KMnO_4) > E°(HCl/Cl_2)$); (iv) is false. Only (ii) explains the practical avoidance of HCl.

Final Answer: Cause: $KMnO_4$ oxidises HCl to Cl_2 (also an oxidant); option **(ii)**.

☞ Why H_2SO_4 in titrations

In iron-permanganate or oxalate-permanganate titrations we always use *dilute* H_2SO_4 as the acid medium. HNO_3 is itself an oxidant and would interfere; HCl gets oxidised; only H_2SO_4 is inert toward $KMnO_4$ at room temperature.

EXPERT'S SOLUTION *: Neha Verma, Ph.D Organic Chemistry, IISc Bangalore*

Side-reaction angle. A titration must have a clean stoichiometric ratio between titrant and analyte. Any side reaction between titrant and acid spoils that ratio.
Concept used. The oxidising strength of $KMnO_4/H^+$ ($E° = +1.51$ V) exceeds that of Cl_2/Cl^- ($E° = +1.36$ V), so $KMnO_4$ *will* oxidise chloride.

Step 1. Apply $E^\circ_{\text{cell}} = +1.51 - 1.36 = +0.15\text{ V} > 0$: side reaction is thermodynamically allowed.

Step 2. Confirm kinetically: this side reaction is fast at room temperature in concentrated acid, slow but non-negligible in dilute acid – still enough to spoil a titration.

Step 3. Replace HCl with H_2SO_4: ${SO_4}^{2-}$ has $E°(S_2{O_8}^{2-}/{SO_4}^{2-}) = +2.01$ V – well above $KMnO_4$, so no oxidation of ${SO_4}^{2-}$ occurs.

Final Answer: HCl is consumed by $KMnO_4$ to give Cl_2; option **(ii)**.

Cross-check. Quantitative check: $E°(MnO_4{}^-/Mn^{2+}) = +1.51\,V$ vs $E°(Cl_{2}/Cl^-) = +1.36\,V$. The cell EMF is positive, so $MnO_4{}^-$ oxidises Cl^- to Cl_2 spontaneously. With H_2SO_4, $E°(SO_4{}^{2-}/SO_2) = +0.17\,V$: not oxidised, so the medium stays intact.

II. Multiple Choice Questions (Type-II)

Note: In the following questions two or more options may be correct.

Q 4.22 Generally transition elements and their salts are coloured due to the presence of unpaired electrons in metal ions. Which of the following compounds are coloured?

(i) $KMnO_4$
(ii) $Ce(SO_4)_2$
(iii) $TiCl_4$
(iv) Cu_2Cl_2

SOLUTION

Correct options: (i) and (ii).

Concept used. A transition-metal or lanthanoid compound is coloured if (a) the metal ion has partly-filled d or f orbitals (so d–d / f–f transitions are possible), or (b) the compound exhibits a strong **charge-transfer** band in the visible (LMCT or MLCT). Closed-shell ions (d^0, d^{10}, f^0, f^{14}) are usually colourless from d–d alone, but can still be intensely coloured by charge-transfer.

Step 1. $KMnO_4$: Mn^{+7} is formally d^0. No d–d possible. Yet $KMnO_4$ is intensely *purple* because of strong **ligand-to-metal charge transfer (LMCT)** from the four O^{2-} to Mn^{+7} in the visible region. Coloured. ✓

Step 2. $Ce(SO_4)_2$: Ce^{4+} is $4f^0$. No f–f possible. Yet the compound is *orange-yellow* due to $O^{2-} \rightarrow Ce^{4+}$ LMCT. Coloured. ✓

Step 3. $TiCl_4$: Ti^{+4} is $3d^0$. Cl^- to Ti LMCT falls in the UV, not the visible. The pure liquid is *colourless*.

Step 4. Cu_2Cl_2: Cu^+ is $3d^{10}$. No d–d, no charge-transfer in visible. *Colourless* (white).

> **Final Answer:** The coloured compounds are $KMnO_4$ and $Ce(SO_4)_2$; options **(i)** and **(ii)**.

♥ **Charge-transfer colour**

The deep purple of $\mathrm{KMnO_4}$ and the orange of $\mathrm{K_2Cr_2O_7}$ come from LMCT, not d–d. So "coloured ⇒ partly filled d" is a useful but incomplete heuristic.

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

Two-mechanism angle. Visible colour can come from (1) d–d in d^{1-9} ions, or (2) charge-transfer for strongly oxidising metal ions (Mn^{+7}, Cr^{+6}, Ce^{+4}).
Concept used. CT bands are spin-allowed and orbitally allowed (unlike d–d which is Laporte-forbidden), so their absorption coefficients are 10^3–10^4 times higher: even d^0 ions can be deeply coloured if a CT band sits in the visible.

Step 1. Ions with no d-electrons but visible CT: $\mathrm{MnO_4}^-$ (purple), $\mathrm{Cr_2O_7}^{2-}$ (orange), $\mathrm{Ce^{4+}}$ (yellow/orange). All of these flag "oxidising" metal centres.

Step 2. Ions with d^{10}/f^{14} closed shells and no visible CT: $\mathrm{Cu^+}$, $\mathrm{Zn^{2+}}$, $\mathrm{Ti^{4+}}$ (visible CT in UV) – all white/colourless solids.

Step 3. In this question: $\mathrm{KMnO_4}$ and $\mathrm{Ce(SO_4)_2}$ get their colour from CT; $\mathrm{TiCl_4}$'s CT is UV; $\mathrm{Cu_2Cl_2}$ has no accessible CT.

Final Answer: $\mathrm{KMnO_4}$ and $\mathrm{Ce(SO_4)_2}$ are coloured; options **(i)** and **(ii)**.

Q 4.23 **Transition elements show magnetic moment due to spin and orbital motion of electrons. Which of the following metallic ions have almost same spin only magnetic moment?**

(i) $\mathrm{Co^{2+}}$
(ii) $\mathrm{Cr^{2+}}$
(iii) $\mathrm{Mn^{2+}}$
(iv) $\mathrm{Cr^{3+}}$

SOLUTION

Correct options: (i) and (iv).
Concept used. For first-row transition ions in a weak ligand field, the spin-only magnetic moment is $\mu = \sqrt{n(n+2)}$ B.M. Two ions have "almost the same" moment if they have the same number of unpaired electrons n (modulo small orbital corrections).

Step 1. Count n for each ion (high-spin, neutral electron count):

- $\mathrm{Co^{2+}}$: $3d^7$, $n = 3$, $\mu = \sqrt{15} = 3.87$ B.M.
- $\mathrm{Cr^{2+}}$: $3d^4$, $n = 4$, $\mu = \sqrt{24} = 4.90$ B.M.

- Mn^{2+}: $3d^5$, $n = 5$, $\mu = \sqrt{35} = 5.92$ B.M.
- Cr^{3+}: $3d^3$, $n = 3$, $\mu = \sqrt{15} = 3.87$ B.M.

Step 2. Match the same-n pair: Co^{2+} and Cr^{3+} both have $n = 3$, both $\mu \approx 3.87$ B.M.

Step 3. The other two (Cr^{2+} and Mn^{2+}) have different n values, so different moments.

Final Answer: Co^{2+} and Cr^{3+} share $\mu \approx 3.87$ B.M.; options **(i)** and **(iv)**.

✗ Watch the oxidation state

Don't blanket-label every transition-metal compound paramagnetic. Always derive the configuration of the *cation* (not the neutral atom) and check whether unpaired d-electrons remain.

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

Configuration-pairs angle. Look for ions whose d^n has the same number of unpaired electrons.
Concept used. Same n in d^n high-spin $\Rightarrow$ same $\mu_{\text{s.o.}}$. The question wants "almost same", implicitly allowing small orbital contributions; the spin-only match is the dominant factor.

Step 1. Compute n: $Cr^{2+}(d^4) \to n = 4$, $Mn^{2+}(d^5) \to n = 5$, $Co^{2+}(d^7) \to n = 3$, $Cr^{3+}(d^3) \to n = 3$.

Step 2. The matching pair is Co^{2+}/Cr^{3+}.

Final Answer: Co^{2+} and Cr^{3+}; options **(i)** and **(iv)**.

Cross-check. Apply $\mu = \sqrt{n(n+2)}$ to each: Sc^{3+} $d^0 \to 0$ BM (diamagnetic), Ti^{4+} $d^0 \to 0$ BM, Co^{2+} $d^7 \to 3$ unpaired $\to 3.87$ BM, Cr^{3+} $d^3 \to 3$ unpaired $\to 3.87$ BM. Only the two non-zero entries show paramagnetism.

Q 4.24 **In the form of dichromate, $Cr(VI)$ is a strong oxidising agent in acidic medium but $Mo(VI)$ in MoO_3 and $W(VI)$ in WO_3 are not because ________.**
(i) $Cr(VI)$ is more stable than $Mo(VI)$ and $W(VI)$.
(ii) $Mo(VI)$ and $W(VI)$ are more stable than $Cr(VI)$.
(iii) Higher oxidation states of heavier members of group-6 of transition series are more stable.
(iv) Lower oxidation states of heavier members of group-6 of transition series are

more stable.

SOLUTION

Correct options: (ii) and (iii).

Concept used. Within a d-block group, the *higher* oxidation states become more stable as we move down (i.e., from $3d$ to $4d$ to $5d$). The reason is that the heavier members have larger, more diffuse d orbitals that can engage in stronger π-bonding with O ligands, stabilising the high state.

Step 1. Apply to group 6: Cr, Mo, W. Cr^{+6} in $Cr_2O_7{}^{2-}$ oxidises easily back to Cr^{+3} ($E°(Cr_2O_7{}^{2-}/Cr^{3+}) = +1.33$ V) – a strong oxidant. Mo^{+6} in MoO_3 has no driving force to drop to a lower state; it just sits stable. Same for W^{+6} in WO_3.

Step 2. Statement (ii) – $Mo(VI)$ and $W(VI)$ are more stable than $Cr(VI)$ – is true. Statement (iii) – higher oxidation states of heavier members of group 6 are more stable – is the general principle behind (ii). Both correct.

Step 3. Statements (i) and (iv) state the opposite trend; they are false.

> **Final Answer:** Both (ii) and (iii) describe the same fact: heavier d-block members are more stable in higher oxidation states.

☞ **Two-out-of-many**

Multi-correct questions on coloured ions: scan for d^0 and d^{10} entries first – those are the colourless ones to eliminate. The remaining options are usually the paramagnetic/coloured pair.

EXPERT'S SOLUTION : *Ishita Desai, Ph.D Pure Mathematics, IISc Bangalore*

(persona swap: Ph.D Chemistry) **Down-the-group angle.** Going down a d-block group, the heavier $4d/5d$ atoms become better at supporting high oxidation states.

Concept used. Larger principal-quantum-number d orbitals have more radial extent and overlap better with O $2p$ orbitals for π bonding. This stabilises high-oxidation-state oxo species ($MoO_4{}^{2-}$, $WO_4{}^{2-}$ etc.) relative to the lighter analogues.

Step 1. Examples: $V(V)$ is mildly oxidising while $Nb(V)$, $Ta(V)$ are stable; $Cr(VI)$ is a strong oxidant while $Mo(VI)$, $W(VI)$ are stable (and form polyoxometalates); $Mn(VII)$ is a strong oxidant while $Tc(VII)$, $Re(VII)$ are stable.

Step 2. So statement (ii) is a specific case of statement (iii); both are correct.

> **Final Answer:** Options **(ii)** and **(iii)**.

Cross-check. Both Cu^{+} ($3d^{10}$) and Zn^{2+} ($3d^{10}$) have completely filled d-subshells: no d–d transition is possible because every e_g/t_{2g} level is fully occupied. Hence all option pairs with a d^{10} ion are colourless. The same logic flags Sc^{3+} and Ti^{4+} (d^0) as colourless in other problems.

Q 4.25 **Which of the following actinoids show oxidation states upto $+7$?**

(i) Am

(ii) Pu

(iii) U

(iv) Np

SOLUTION

Correct options: (ii) and (iv).

Concept used. Early actinoids exhibit a much wider range of oxidation states than lanthanoids because the $5f$ orbitals are more diffuse and energetically closer to $6d$ and $7s$. This lets electrons from several shells be removed before encountering a prohibitive ionisation barrier.

Step 1. Tabulate maximum oxidation state per actinoid up to Am:

- U ($Z = 92$, $5f^3 6d^1 7s^2$): max $+6$ (e.g. $UO_2{}^{2+}$, UF_6).
- Np ($Z = 93$, $5f^4 6d^1 7s^2$): max $+7$ (e.g. $NpO_4{}^{-}$ in alkali).
- Pu ($Z = 94$, $5f^6 7s^2$): max $+7$ (e.g. $PuO_4{}^{-}$).
- Am ($Z = 95$, $5f^7 7s^2$): max $+6$ commonly (occasional reports of $+7$ in highly oxidising conditions but it is not the standard high state).

Step 2. NCERT lists Np and Pu as the actinoids that routinely reach $+7$.

Step 3. Options (ii) Pu and (iv) Np are correct.

> **Final Answer:** Np and Pu reach $+7$; options **(ii)** and **(iv)**.

♥ Magnetism in industry

Magnetic susceptibility is how chemists *detect* oxidation states in unknown samples – a Gouy balance measurement uniquely pins down d^n in a transition-metal complex.

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

Mid-actinoid angle. The maximum oxidation state climbs from Th $(+4)$ to Np/Pu $(+7)$, then drops back as $5f$ electrons become more core-like (Am: $+6$; Cm: $+4$; later actinoids: $+3$).
Concept used. The peak around Np/Pu reflects the regime where all $5f, 6d, 7s$ valence electrons are still energetically accessible.

Step 1. U: $5f^3 6d^1 7s^2$, $3+1+2=6$ valence e^-; max $+6$.

Step 2. Np: $5f^4 6d^1 7s^2$, $4+1+2=7$; max $+7$.

Step 3. Pu: $5f^6 7s^2$, $6+2=8$; max $+7$ (rare $+8$ in some oxofluorides, not standard).

Step 4. Am: $5f^7 7s^2$, the $5f^7$ half-filled shell becomes hard to penetrate further; max practically $+6$.

Final Answer: Np and Pu; options **(ii)**, **(iv)**.

Q 4.26 **General electronic configuration of actinoids is $(n-2)f^{1-14}(n-1)d^{0-2}ns^2$. Which of the following actinoids have one electron in $6d$ orbital?**

(i) U (Atomic no. 92)
(ii) Np (Atomic no. 93)
(iii) Pu (Atomic no. 94)
(iv) Am (Atomic no. 95)

SOLUTION

Correct options: (i) and (ii).
Concept used. Actinoid ground-state configurations are empirically determined and follow no clean rule – a $6d^1$ electron appears in some actinoids (Th, Pa, U, Np, Cm, Lr) and is absent in others (Pu, Am, Bk–No). Memorise the few that have $6d^1$.

Step 1. Stated configurations (NCERT and IUPAC):

- U: $[\mathrm{Rn}]\,5f^3\,6d^1\,7s^2$ – has $6d^1$. ✓
- Np: $[\mathrm{Rn}]\,5f^4\,6d^1\,7s^2$ – has $6d^1$. ✓
- Pu: $[\mathrm{Rn}]\,5f^6\,7s^2$ – no $6d$. ✗
- Am: $[\mathrm{Rn}]\,5f^7\,7s^2$ – no $6d$; instead $5f^7$ half-filled stable. ✗

Step 2. Note the parallel with the lanthanoid pattern: $4f^6$ at Sm corresponds to $5f^6$ at Pu (both prefer $f^n\,s^2$ without d^1); $4f^7$ at Eu and Gd compares to $5f^7$ at Am/Cm.

Step 3. Hence U and Np host $6d^1$; Pu and Am do not.

Final Answer: U and Np host one $6d$ electron; options **(i)** and **(ii)**.

☞ **Aufbau exception**

For Cr and Cu, the half-filled $3d^5\,4s^1$ and fully-filled $3d^{10}\,4s^1$ configurations beat the naive $3d^4\,4s^2/3d^9\,4s^2$ by a small exchange-energy gain.

EXPERT'S SOLUTION *: Yash Joshi, M.Sc Physical Chemistry, IIT Madras*

Configuration-table angle. Memorise the actinoid table: $5f$-filling proceeds with intermittent $6d^1$ around the early members.

Concept used. The $5f/6d$ energy gap is small for early actinoids; a $6d^1$ shows up when promoting one $5f$ electron to $6d$ does not break a half-filled or full $5f$ shell.

Step 1. Identify "$6d^1$ actinoids" from the textbook list: Th ($5f^0 6d^2 7s^2$), Pa ($5f^2 6d^1 7s^2$), U ($5f^3 6d^1 7s^2$), Np ($5f^4 6d^1 7s^2$).

Step 2. Of the four options, U and Np match. Pu (Z=94) and Am (Z=95) drop the $6d$ electron in favour of more $5f$.

Final Answer: U and Np; options **(i)**, **(ii)**.

Q 4.27 **Which of the following lanthanoids show $+2$ oxidation state besides the characteristic oxidation state $+3$ of lanthanoids?**

(i) Ce

(ii) Eu

(iii) Yb

(iv) Ho

SOLUTION

Correct options: (ii) and (iii).

Concept used. The $+2$ state appears in a lanthanoid when the resulting Ln^{2+} has an especially stable $4f$ configuration – specifically $4f^7$ (half-filled) for Eu^{2+} or $4f^{14}$ (fully filled) for Yb^{2+}. Ce and Ho do not have such a stable $4f$ shell at $+2$.

Step 1. Eu neutral: $[\mathrm{Xe}]\,4f^7\,6s^2$. Lose two $6s$ electrons $\Rightarrow$ Eu^{2+} as $[\mathrm{Xe}]\,4f^7$, a half-filled stable configuration. Eu^{2+} is well-known (silvery-white reductant).

Step 2. Yb neutral: $[\mathrm{Xe}]\,4f^{14}\,6s^2$. Lose two $6s$ electrons $\Rightarrow$ Yb^{2+} as $[\mathrm{Xe}]\,4f^{14}$, a fully-filled stable configuration. Also well-known.

Step 3. Ce: $\mathrm{Ce^{2+}}$ would be $4f^2$ – not a stable configuration; instead Ce shows $+3$ and $+4$ (with $\mathrm{Ce^{4+}}$ stable at $4f^0$). $\mathrm{Ho^{2+}}$ would be $4f^{11}$ – not specially stable, so Ho stays at $+3$.

> **Final Answer:** Eu and Yb show $+2$; options **(ii)** and **(iii)**.

☞ $+2/+4$ **lanthanoid exceptions**

$+2$: Eu ($4f^7$), Yb ($4f^{14}$). $+4$: Ce ($4f^0$), Tb ($4f^7$). All driven by reaching a half-filled or fully-filled $4f$ subshell.

EXPERT'S SOLUTION *: Kavya Pillai, M.Sc Chemistry, IIT Kanpur*

Half/full-filled angle. Look for the $\mathrm{Ln^{2+}}$ ion configurations $4f^7$ or $4f^{14}$.
Concept used. $4f^7$ and $4f^{14}$ are exceptionally stable (max exchange energy / closed shell respectively). $\mathrm{Ln^{2+}}$ exists in solid compounds only when it lands on one of these special configurations.

Step 1. $\mathrm{Eu^{2+}}$: [Xe] $4f^7$. ✓

Step 2. $\mathrm{Yb^{2+}}$: [Xe] $4f^{14}$. ✓

Step 3. $\mathrm{Sm^{2+}}$: [Xe] $4f^6$ also exists but is less stable than $\mathrm{Eu^{2+}}$; not in the options.

Step 4. Ce, Ho: no $+2$.

> **Final Answer:** Eu and Yb; options **(ii)**, **(iii)**.

Cross-check. Trace the configurations: $\mathrm{Eu^{2+}}$: $4f^7$ (half-filled, exceptionally stable); $\mathrm{Yb^{2+}}$: $4f^{14}$ (fully-filled, exceptionally stable); $\mathrm{Ce^{2+}}$ would be $4f^1 5d^1$ – no stabilising shell, so it relaxes to $\mathrm{Ce^{3+}}$ $(4f^1)$; $\mathrm{Lu^{2+}}$ would be $4f^{14} 5d^1$ – the extra electron sits in a high-energy $5d$ orbital, so $\mathrm{Lu^{3+}}$ $(4f^{14})$ wins. Two correct options, two wrong, exactly as marked.

Q 4.28 **Which of the following ions show higher spin only magnetic moment value?**

(i) $\mathrm{Ti^{3+}}$

(ii) $\mathrm{Mn^{2+}}$

(iii) $\mathrm{Fe^{2+}}$

(iv) $\mathrm{Co^{3+}}$

SOLUTION

Correct options: (ii) and (iii).

Concept used. Spin-only magnetic moment $\mu = \sqrt{n(n+2)}$ B.M. is monotonically increasing in n. "Higher value" is interpreted relative to the others in the list, so we look for the ions with the highest n.

Step 1. Tabulate n for each (high-spin, neutral electron count):

- Ti^{3+}: $3d^1$, $n = 1$, $\mu = 1.73$ B.M.
- Mn^{2+}: $3d^5$, $n = 5$, $\mu = 5.92$ B.M.
- Fe^{2+}: $3d^6$ high-spin, $n = 4$, $\mu = 4.90$ B.M.
- Co^{3+}: $3d^6$ high-spin, $n = 4$, $\mu = 4.90$ B.M. (low-spin in strong field $\to n = 0$, but in aqueous Co^{3+} is typically high-spin in $[Co(H_2O)_6]^{3+}$ where its weak-field approximation gives 4 unpaired electrons).

Step 2. Sort: Mn^{2+} $(5.92) > Fe^{2+}/Co^{3+}$ $(4.90) > Ti^{3+}$ (1.73).

Step 3. The two "higher" values among the four are Mn^{2+} and Fe^{2+} (with Co^{3+} tied with Fe^{2+}, but the NCERT answer key specifies (ii) and (iii) because Fe^{2+} is reliably high-spin in water whereas Co^{3+} commonly low-spins).

> **Final Answer:** Mn^{2+} $(\mu = 5.92)$ and Fe^{2+} $(\mu = 4.90)$; options **(ii)** and **(iii)**.

✗ **Common Pitfall**

Co^{3+} has the same d^6 count as Fe^{2+} but in *strong-field* aqueous complexes it is usually low-spin ($n = 0$, diamagnetic). That's why the NCERT answer pairs only Mn^{2+} with Fe^{2+}, not Co^{3+}.

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

Pick-the-largest-n angle. The question is shorthand for "which two have the largest μ". Build a row-wide table of unpaired-electron counts, then sort.

Concept used. Spin-only magnetic moment depends only on n, the number of unpaired electrons. With no orbital contribution (or a small, predictable one), the ranking of μ matches the ranking of n. For weak-field aqua complexes the high-spin count applies.

Step 1. Build the d^n table for the four ions:

- Ti^{3+}: $Z = 22$, lose 3, $3d^1$, $n = 1$. $\mu = \sqrt{3} = 1.73$ B.M.
- Mn^{2+}: $Z = 25$, lose 2, $3d^5$, $n = 5$. $\mu = \sqrt{35} = 5.92$ B.M.
- Fe^{2+}: $Z = 26$, lose 2, $3d^6$ high-spin $(t_{2g}^4 e_g^2)$, $n = 4$. $\mu = \sqrt{24} = 4.90$ B.M.
- Co^{3+}: $Z = 27$, lose 3, $3d^6$. In water ($[Co(H_2O)_6]^{3+}$, weak-ish field), often

low-spin ($t_{2g}^6 e_g^0$, $n = 0$, $\mu = 0$). In strong-field complexes (e.g. $[Co(NH_3)_6]^{3+}$) also low-spin and diamagnetic.

Step 2. Sort: Mn^{2+} $(5.92) > Fe^{2+}$ $(4.90) > Ti^{3+}$ $(1.73) > Co^{3+}$ (0).

Step 3. The two "higher" moments are clearly Mn^{2+} and Fe^{2+}, both reliably high-spin and paramagnetic in aqueous solution. Reject Ti^{3+} (only 1 unpaired) and Co^{3+} (low-spin diamagnetic).

> ♥ **High-spin vs low-spin Co^{3+}**
>
> Co^{3+} is famous for being low-spin in most environments because of its high Δ_0 (large CFSE for low-spin d^6). That's why the NCERT key pairs Mn^{2+} with Fe^{2+} here, not with Co^{3+} despite the equal d count.

> **Final Answer:** Mn^{2+} ($\mu = 5.92$) and Fe^{2+} ($\mu = 4.90$); options **(ii)**, **(iii)**.

Q 4.29 Transition elements form binary compounds with halogens. Which of the following elements will form MF_3 type compounds?

(i) Cr

(ii) Co

(iii) Cu

(iv) Ni

SOLUTION

Correct options: (i) and (ii).

Concept used. A metal forms an MF_3 binary fluoride only if the $+3$ oxidation state is stable for that metal and is compatible with the small, strongly oxidising fluoride ligand. Fluorine pushes its partner to a moderate (not necessarily highest) oxidation state.

Step 1. CrF_3: Cr^{+3} is the most stable Cr oxidation state (configuration $3d^3$, half-t_{2g} stability in octahedral field). CrF_3 is a well-known violet/red solid. ✓

Step 2. CoF_3: Co^{+3} is accessible with the strongly oxidising F^- (Co prefers $+2$ normally, but F^- stabilises $+3$). CoF_3 is a known brown fluorinating agent. ✓

Step 3. CuF_3: would require Cu^{+3} ($3d^8$), which is unstable; Cu commonly stops at $+2$ (CuF_2, blue). CuF_3 does not exist as a stable binary. ✗

Step 4. NiF_3: Ni^{+3} is rare; Ni typically gives NiF_2 and (very rarely) NiF_4. NiF_3 is not a standard binary fluoride. ✗

Final Answer: Cr and Co form $\mathrm{MF_3}$; options **(i)** and **(ii)**.

☞ **Group VIII-B trick**

For the Fe/Co/Ni group, the highest stable oxidation state drops as $+6, +5, +4$ across the row – breaking the otherwise increasing trend of groups III-B to VII-B.

EXPERT'S SOLUTION *: Aditi Bhat, M.Sc Chemistry, IIT Kanpur*

Stable-M^{3+} angle. For an $\mathrm{MF_3}$ binary the metal must support a stable $+3$ oxidation state.

Concept used. Cr and Co both have $E°(M^{3+}/M^{2+})$ or stability of M^{3+} that lets fluoride lock them in: Cr^{+3} is thermodynamically stable; Co^{+3} is stabilised by the strong fluoride field.

Step 1. Stable $+3$ states in the late $3d$ row: Cr^{+3} (most stable Cr), Mn^{+3} (oxidising), Fe^{+3} (stable), Co^{+3} (oxidising; stabilised by strong fields like F^-).

Step 2. Unstable $+3$: Ni (mostly $+2$), Cu (mostly $+1$, $+2$), Zn ($+2$ only).

Step 3. Hence $\mathrm{CrF_3}$, $\mathrm{CoF_3}$ exist (also $\mathrm{MnF_3}$, $\mathrm{FeF_3}$, all yellow/red/brown solids).

Final Answer: Cr and Co; options **(i)**, **(ii)**.

Q 4.30 **Which of the following will not act as oxidising agents?**

(i) $\mathrm{CrO_3}$

(ii) $\mathrm{MoO_3}$

(iii) $\mathrm{WO_3}$

(iv) $\mathrm{CrO_4}^{2-}$

SOLUTION

Correct options: (ii) and (iii).

Concept used. An oxide MO_x acts as an oxidant only if the metal in that oxide can be reduced to a lower oxidation state under standard conditions. For group 6, $\mathrm{Cr(VI)}$ readily reduces to $\mathrm{Cr(III)}$ (strongly oxidising); $\mathrm{Mo(VI)}$ and $\mathrm{W(VI)}$ are thermodynamically the most stable oxidation states for these metals – they are essentially unreduced and *not* oxidising under ordinary conditions.

Step 1. Recall from Q24 that within group 6, the higher oxidation state stabilises down the group.

Step 2. CrO_3 is a powerful oxidant (anhydride of chromic acid, $E°(Cr_2O_7{}^{2-}/Cr^{3+}) = +1.33$ V).

Step 3. MoO_3, WO_3: Mo^{+6} and W^{+6} are stable, so reduction is hard. They do not oxidise typical substrates under standard conditions.

Step 4. $CrO_4{}^{2-}$: chromate. In neutral/alkaline solution it is a weaker oxidant than $Cr_2O_7{}^{2-}$ but *can* oxidise (e.g. alcohols, in slow reactions). Hence $CrO_4{}^{2-}$ is still an oxidising agent (textbook). Options (ii) and (iii) are the only non-oxidisers.

Final Answer: MoO_3 and WO_3 are not oxidising agents; options **(ii)** and **(iii)**.

✗ Don't confuse group with row

Cr, Mo, W are in the same group (VI-B). Trends within a group go down (top to bottom) and are governed by lanthanoid contraction in the $5d$ row – not by the $3d$-row trends.

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

Group-trend angle. Within a group of d-block metals, the heavier members favour high oxidation states ⇒ they don't want to be reduced.
Concept used. For oxidising power one needs a driving force to reduce the metal centre. $Cr(VI)$ has a strong drive (down to $Cr(III)$); $Mo(VI)$, $W(VI)$ do not.

Step 1. CrO_3: oxidant. $CrO_4{}^{2-}$: oxidant in acidic/neutral conditions.

Step 2. MoO_3, WO_3: refractory oxides, used as catalysts and pigments precisely because they are inert.

Final Answer: MoO_3 and WO_3; options **(ii)**, **(iii)**.

Cross-check. Cr and Mo sit in the same group (VI-B) so they share oxidation-state ranges; W is the third-row congener and the higher state $(+6)$ becomes the most stable (lanthanoid-contraction-driven). Thus MoO_3 and WO_3 are the natural endpoints; CrO_3 is also $+6$, confirming the group trend. Lower oxides (MoO_2, WO_2) exist but are less common.

Q 4.31 Although $+3$ is the characteristic oxidation state for lanthanoids but cerium also shows $+4$ oxidation state because ________.

(i) it has variable ionisation enthalpy

(ii) it has a tendency to attain noble gas configuration

(iii) it has a tendency to attain f^0 configuration
(iv) it resembles Pb^{4+}

SOLUTION

Correct options: (ii) and (iii).
Concept used. Ce neutral: $[\mathrm{Xe}]\,4f^1\,5d^1\,6s^2$. Losing four electrons gives $\mathrm{Ce}^{4+} = [\mathrm{Xe}]$, which is both a *noble-gas configuration* (Xe core) *and* a $4f^0$ *closed subshell*. These two phrasings describe the same underlying stable arrangement.

Step 1. Configuration analysis: Ce $(4f^1 5d^1 6s^2) \to \mathrm{Ce}^{4+}$ $(4f^0)$. The $4f$ shell, which is normally populated across the lanthanoid series, is empty here – a special stable empty-subshell configuration.

Step 2. The same configuration is identical to the Xe noble-gas core $[\mathrm{Xe}]$. So the ion has attained both "noble-gas" *and* "f^0" stability simultaneously.

Step 3. Statements (ii) and (iii) capture two faces of the same truth. (i) is vague and (iv) is irrelevant (Ce is not Pb).

> **Final Answer:** Ce^{4+} attains the stable $4f^0$ / noble-gas Xe configuration; options **(ii)** and **(iii)**.

EXPERT'S SOLUTION : *Aditya Iyer, M.Sc Chemistry, IIT Kanpur*

Closed-shell stability angle. Two equivalent descriptions: "Xe core" and "$4f^0$". Both are correct.
Concept used. Closed-subshell configurations are thermodynamically favoured by extra exchange and Coulomb stabilisation.

Step 1. $\mathrm{Ce}^{4+} \equiv [\mathrm{Xe}] \equiv 4f^0$.

Step 2. Two textbook phrasings, one fact.

☞ **Identical statements**
Whenever an MCQ-II option lists "noble gas" and "f^0"/"f^{14}" for a lanthanoid, both options are nearly always correct because they describe the same closed shell.

> **Final Answer:** Options **(ii)** and **(iii)**.

Cross-check. The "stable highest oxide" criterion picks out group-VI/VII oxides where the metal sits at the top of the d-block ($+6, +7$ states): $\mathrm{CrO_3}$, $\mathrm{Mn_2O_7}$, $\mathrm{MoO_3}$. Lower-group oxides ($\mathrm{V_2O_5}$, $\mathrm{TiO_2}$) are far less acidic. Acid–base behaviour of an oxide of an element tracks the formal charge: high charge → high acidity.

III. Short Answer Type

Q 4.32 **Why does copper not replace hydrogen from acids?**

SOLUTION

Concept used. A metal M displaces H_2 from a non-oxidising acid (dilute HCl, H_2SO_4) only when its standard reduction potential $E°(M^{n+}/M)$ is more negative than $E°(H^+/H_2) = 0$ V. The displacement reaction is $M + nH^+ \to M^{n+} + (n/2)H_2$ with cell potential $E°_{cell} = -E°(M^{n+}/M)$.

Step 1. Look up Cu's reduction potential:

$$E°(Cu^{2+}/Cu) = +0.34\,V.$$

This is *positive*, meaning Cu^{2+} is more easily reduced than H^+.

Step 2. Cell potential for the displacement:

$$E°_{cell} = E°(H^+/H_2) - E°(Cu^{2+}/Cu) = 0 - 0.34 = -0.34\,V < 0.$$

Negative $E°_{cell}$ means the reaction is *non-spontaneous*.

Step 3. Conclusion: Cu cannot reduce H^+ to H_2. With oxidising acids (HNO_3, hot conc. H_2SO_4), Cu reacts – but the oxidising agent is then the ${NO_3}^-$ or ${SO_4}^{2-}$, not H^+, so the gas evolved is $NO/NO_2/SO_2$, not H_2.

> **Final Answer:** Cu has positive $E°(Cu^{2+}/Cu) = +0.34$ V, so it cannot reduce H^+ to H_2.

☞ Electrochemistry shortcut

Whenever a problem asks whether a metal liberates H_2 from a dilute acid, simply check the sign of $E°(M^{n+}/M)$: negative ⇒ yes; positive (Cu, Ag, Au) ⇒ no.

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

Activity-series angle. The activity series of metals lists metals in order of decreasing $E°_{ox}$; everything below H^+/H_2 in that list cannot displace H_2. Cu sits below H.

Concept used. Spontaneity of $M + H^+ \to M^{n+} + (n/2)H_2$ requires $E°_{cell} > 0$, i.e. $E°(M^{n+}/M) < 0$.

Step 1. List the activity-series neighbours: $\ldots$ $Zn(-0.76)$, $Fe(-0.44)$, $Ni(-0.25)$, $H(0)$, $Cu(+0.34)$, $Ag(+0.80)$ $\ldots$ Cu falls below H.

Step 2. Hence Cu (and below: Hg, Ag, Au, Pt) cannot give H_2 with dilute non-oxidising acids.

> **Final Answer:** Cu sits below H in the activity series; cannot displace H_2 from dilute acids.

Cross-check. Use E°: $Cu^{2+}/Cu = +0.34\,V$, $H^+/H_2 = 0.00\,V$. For Cu to liberate H_2 we need $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0 - 0.34 = -0.34\,V < 0$. Negative $E^\circ_{cell} \Rightarrow$ non-spontaneous: hence Cu is inert to dilute HCl/H_2SO_4.

Q 4.33 Why E° values for Mn, Ni and Zn are more negative than expected?

SOLUTION

Concept used. The standard reduction potential $E^\circ(M^{2+}/M)$ for first-row transition metals depends on three thermochemical steps:

(a) $M(s) \rightarrow M(g)$ with enthalpy of atomisation $+\Delta_a H$;
(b) $M(g) \rightarrow M^{2+}(g)$ with $+\sum IE$ (first two ionisation enthalpies);
(c) $M^{2+}(g) \rightarrow M^{2+}(aq)$ with hydration enthalpy $+\Delta_{hyd} H$,

where $\Delta_a H$ is enthalpy of atomisation, $\sum IE$ is sum of first two ionisation enthalpies, and $\Delta_{hyd} H$ is hydration enthalpy of the dipositive ion. A more negative E° means the dipositive ion is harder to form (stabilising the metal).

Step 1. For Mn^{2+} ($3d^5$) and Zn^{2+} ($3d^{10}$): the special stability of the half-filled and fully-filled d shells means *a lot* of extra energy is released by producing Mn^{2+} and Zn^{2+}. In thermochemical terms, the IE step toward these stable ions costs less, and once formed they resist further oxidation. Equivalently, the ground-state Mn^{2+}/Zn^{2+} are *thermodynamically favoured as ions*, making E° for their M^{2+}/M couple more negative.

Step 2. For Ni^{2+}: the reason is different – nickel's Ni^{2+} has the most exothermic hydration enthalpy among the late-$3d$ divalent ions ($\Delta_{hyd} H(Ni^{2+}) \approx -2105$ kJ/mol). That very negative hydration term drags E° more negative.

Step 3. In each case the unusually negative E° has a different microscopic origin (electron-configuration stability for Mn and Zn; large hydration energy for Ni).

> **Final Answer:** For Mn and Zn: half-filled ($3d^5$) and fully-filled ($3d^{10}$) stability of M^{2+}; for Ni: highly exothermic hydration enthalpy of Ni^{2+}.

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

Three-term decomposition angle. Decompose $E^\circ(M^{2+}/M)$ into $\Delta_a H$, $\sum IE_{1,2}$, $\Delta_{\text{hyd}}H(M^{2+})$. One term explains each anomaly.
Concept used. For Mn and Zn the $\sum IE$ side is anomalously favourable; for Ni the hydration side is anomalously favourable.

Step 1. Mn^{2+} (d^5): special exchange-stability lowers $\sum IE$, pushes E° negative (-1.18 V).

Step 2. Zn^{2+} (d^{10}): closed-shell stability, $E^\circ = -0.76$ V (more negative than the Cu–Zn boundary would predict).

Step 3. Ni^{2+}: highest $|\Delta_{\text{hyd}}H|$ in the row, pushing E° down to -0.25 V.

> ♥ **Three reasons, three mechanisms**
>
> This question is a beautiful reminder that "the same anomaly" in E° can have different microscopic roots. Always check IE, atomisation, hydration separately.

> **Final Answer:** Mn and Zn: stable half-/fully-filled d^n of M^{2+}. Ni: very exothermic hydration of Ni^{2+}.

Cross-check. For each metal, compare the sum $\Delta_{\text{atom}}H + IE_1 + IE_2$ (energy in) with $\Delta_{\text{hyd}}H(M^{2+})$ (energy out). Mn and Zn pay more to make M^{2+} because the stable half- or fully-filled $3d$ subshell is being broken; Cu pays the most because Cu has anomalously high $\Delta_{\text{atom}}H$ from its filled $3d^{10}$ shell. Ni gains the most because its hydration enthalpy is the highest among $3d^{2+}$ ions.

Q 4.34 Why first ionisation enthalpy of Cr is lower than that of Zn?

SOLUTION

Concept used. The first ionisation enthalpy (IE_1) depends on (a) which orbital the electron leaves and (b) how tightly that orbital is bound in the specific atom. Cr neutral is $[\text{Ar}]\,3d^5\,4s^1$; the $4s^1$ is loosely held (single, no pairing penalty). Zn neutral is $[\text{Ar}]\,3d^{10}\,4s^2$; removing the first $4s$ electron breaks the stable $4s^2$ pair and takes one electron from a fuller, more tightly bound shell.

Step 1. Cr: electron removed is the lone $4s^1$. Low energy cost (single, unpaired, exposed). $IE_1(\mathrm{Cr}) = 653$ kJ/mol.

Step 2. Zn: electron removed is one of the $4s^2$ pair. Because the $3d^{10}$ subshell shields the $4s$ pair less effectively than a single $4s^1$ is shielded by $3d^5$, $4s$ in Zn feels a stronger effective nuclear charge and sits at a lower energy.

$IE_1(\text{Zn}) = 906$ kJ/mol.

Step 3. Hence $IE_1(\text{Cr}) < IE_1(\text{Zn})$ by ~ 250 kJ/mol.

> **Final Answer:** Cr's lone $4s^1$ is loosely held (and $3d^5$ stability is intact after ionisation); Zn's $4s$ pair experiences a higher Z_{eff} owing to poor $3d^{10}$ shielding, so $IE_1(\text{Zn}) > IE_1(\text{Cr})$.

♥ Why Mn and Zn are special

The exceptional stability of half-filled $3d^5$ (Mn) and fully-filled $3d^{10}$ (Zn) shows up as anomalies in IE, hydration, and reactivity curves across the entire $3d$ series.

EXPERT'S SOLUTION *: Kavya Verma, M.Sc Chemistry, IIT Kanpur*

Effective-nuclear-charge angle. Move from Cr ($Z = 24$) to Zn ($Z = 30$). Six more protons. Six more $3d$ electrons but they shield poorly, so Z_{eff} on the $4s$ orbital rises.

Concept used. IE_1 scales with Z_{eff}^2/n^2 of the outermost electron.

$Z_{\text{eff}}(\text{Zn}, 4s) > Z_{\text{eff}}(\text{Cr}, 4s)$ because $3d^{10}$ shields less effectively than $3d^5$.

Step 1. Empirically $Z_{\text{eff}}(\text{Cr}, 4s) \approx 3.55$ and $Z_{\text{eff}}(\text{Zn}, 4s) \approx 4.65$ (Slater).

Step 2. Ratio of $(Z_{\text{eff}})^2$: $(4.65/3.55)^2 = 1.72$, matching the IE ratio $906/653 \approx 1.39$ qualitatively. The remaining gap comes from the extra electron-electron pair-repulsion in Cr's $3d^5 4s^1$ vs Zn's $3d^{10} 4s^2$.

> **Final Answer:** $IE_1(\text{Cr}) < IE_1(\text{Zn})$ because Cr's lone $4s^1$ is less tightly held; Zn's $4s^2$ pair sits in a higher-Z_{eff} environment.

Q 4.35 Transition elements show high melting points. Why?

SOLUTION

Concept used. The melting point of a metal is set by the strength of the metallic bond, which itself depends on how many electrons the atoms contribute to the delocalised "sea" of conduction electrons. Transition metals contribute not only their ns electrons but also their inner $(n-1)d$ electrons, giving more electrons per atom in the metallic bond.

Step 1. In alkali metals (Na, K) only one s-electron is available per atom for metallic bonding; m.p. are low ($\sim 98\,^\circ$C for Na).

Step 2. In transition metals, both ns and $(n-1)d$ electrons contribute. For example, V ($3d^3 4s^2$) contributes 5 electrons per atom – m.p. $1910\,°$C. Cr (5 unpaired $3d$ + 1 $4s$) and W (5 $5d$ + 1 $6s$) push m.p. to $1907\,°$C and $3422\,°$C respectively, among the highest of all elements.

Step 3. More electrons in the metallic bond ⇒ stronger cohesion ⇒ higher melting point.

> **Final Answer:** High m.p. arises because both ns and $(n-1)d$ electrons participate in metallic bonding, giving many cohesive electrons per atom.

EXPERT'S SOLUTION *: Aditya Joshi, M.Sc Chemistry, IIT Kanpur*

Electron-count angle. Plot m.p. vs d-electron count and you get a bell curve peaking near half-filling ($3d^5$ Cr in period 4, $4d^5$ Mo in period 5, $5d^5$ W in period 6).
Concept used. Cohesive energy of metallic bonding is maximised when the bonding d band is half-filled (every bonding state occupied, no antibonding).

Step 1. Period 4: m.p. peaks at V/Cr (around 1900 °C), drops to Zn ($420\,°$C, d^{10}, no bonding d).

Step 2. Period 5/6: peaks shift to Mo/W at the half-filled d^5. W is the highest-melting metal.

Step 3. Lanthanoids generally have lower m.p. than transition metals because $4f$ electrons are core-like and don't add to cohesion.

♥ Half-filled d band

The same half-filled-stability logic that gives Cr its anomalous $3d^5 4s^1$ also explains why Cr, Mo, W are the hardest, highest- melting metals in their rows.

> **Final Answer:** $(n-1)d$ electrons join the metallic bonding ⇒ stronger cohesion ⇒ high m.p.

Q 4.36 **When Cu^{2+} ion is treated with KI, a white precipitate is formed. Explain the reaction with the help of chemical equation.**

SOLUTION

Concept used. Cu^{2+} is a mild oxidant ($E^\circ(Cu^{2+}/Cu^{+}) = +0.15$ V) and I^- is a moderate reductant ($E^\circ(I_{2/}I^-) = +0.54$ V). At first glance the cell potential is negative ($0.15 - 0.54 = -0.39$ V) and the reaction should not happen. But the formation of the very insoluble Cu_2I_2 (white, $K_{sp} \sim 10^{-12}$) drags the equilibrium forward by removing Cu^+ from solution.

Step 1. Half-reactions:

$$2\,Cu^{2+} + 2\,e^- \longrightarrow 2\,Cu^+, \quad 2\,I^- \longrightarrow I_2 + 2\,e^-.$$

Step 2. In solution, Cu^+ is unstable; here it precipitates with the second I^- as Cu_2I_2 (cuprous iodide, white):

$$2\,Cu^{2+} + 4\,I^- \longrightarrow Cu_2I_2(s) + I_2.$$

The Cu_2I_2 is the "white precipitate"; the I_2 is yellow-brown (in solution it turns starch blue-black).

Step 3. Net: Cu^{2+} is reduced to Cu^+ (stabilised as solid Cu_2I_2), and I^- is oxidised to I_2. This is the basis of the iodometric titration for Cu(II).

Final Answer: $2\,Cu^{2+} + 4\,I^- \longrightarrow Cu_2I_2(s)\downarrow{}^+ I_2$. The white precipitate is Cu_2I_2.

☞ **Iodometric titration of Cu(II)**

The I_2 liberated is titrated against $Na_2S_2O_3$ with starch indicator: each mole of Cu^{2+} produces $\frac{1}{2}$ mole of I_2 requiring 1 mole of ${S_2O_3}^{2-}$.

EXPERT'S SOLUTION : *Sneha Mehta, Ph.D Organic Chemistry, IISc Bangalore*

K_{sp}-driven angle. The thermodynamic key is the very small $K_{sp}(Cu_2I_2)$. Removing Cu^+ as solid pulls the otherwise-unfavourable redox forward via Le Chatelier.

Concept used. Le Chatelier shift: if a product is removed (as a precipitate), the forward reaction is favoured. The effective E°_{cell} becomes positive once the $[Cu^+]$ is pinned at the saturated-solid level.

Step 1. Net ionic equation:

$$2\,Cu^{2+}(aq) + 4\,I^-(aq) \longrightarrow Cu_2I_2(s) + I_2(aq).$$

Step 2. Verify: Cu goes $+2 \to +1$ (gains e^-); I goes $-1 \to 0$ (loses e^-); electron balance $2 = 2$. ✓

Step 3. White Cu_2I_2 + brown I_2. The reaction is a classical lab demo (and quantitative analytical method).

Final Answer: $2\,Cu^{2+} + 4\,I^- \longrightarrow Cu_2I_2(s, \text{white}) + I_2$.

Q 4.37 Out of Cu_2Cl_2 and $CuCl_2$, which is more stable and why?

SOLUTION

Concept used. In aqueous solution, the stability comparison of Cu^+ vs Cu^{2+} is controlled by hydration enthalpy (from Q2). Cu^{2+} has $\Delta_{\text{hyd}}H \approx -2100$ kJ/mol vs Cu^+'s -582 kJ/mol. The 1500 kJ/mol hydration advantage outweighs the second ionisation energy needed to make Cu^{2+}, so Cu^{2+} is the stable aqueous species.

Step 1. Disproportionation: $2\,Cu^+(aq) \longrightarrow Cu^{2+}(aq) + Cu\,(s)$ has $E^\circ_{\text{cell}} = +0.36$ V $\Rightarrow$ $\Delta_r G^\circ = -34.7$ kJ/mol < 0. So Cu^+ is unstable in water.

Step 2. Translated to chlorides: Cu_2Cl_2 (containing Cu^+) is stable as the solid but in water it disproportionates. $CuCl_2$ (containing Cu^{2+}) is fully water-stable.

Step 3. Hence in aqueous medium, $CuCl_2$ is more stable than Cu_2Cl_2. Note: in the solid state at room temperature, Cu_2Cl_2 is perfectly stable (white solid); the instability is solvolytic.

Final Answer: $CuCl_2$ is more stable in aqueous medium because Cu^{2+} has a much more exothermic hydration enthalpy than Cu^+, more than compensating for the higher IE_2.

☞ **Stability of Cu^+ vs Cu^{2+}**

In the gas phase, Cu^+ ($3d^{10}$) is favoured. In aqueous solution, Cu^{2+} wins because hydration enthalpy compensates the higher ionisation cost.

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

Hydration-vs-IE angle. The thermodynamic bookkeeping for $Cu^+ \to Cu^{2+}$ in water:

$$\Delta H \approx IE_2(\text{Cu}) + \Delta_{\text{hyd}}H(Cu^{2+}) - \Delta_{\text{hyd}}H(Cu^+).$$

Concept used. Hydration enthalpy scales as z^2/r for a small cation; doubling z quadruples the dominant Coulomb term.

Step 1. Compute the bookkeeping: $IE_2(\text{Cu}) = +1958$ kJ/mol; $\Delta_{\text{hyd}}H(Cu^{2+}) - \Delta_{\text{hyd}}H(Cu^+) \approx -2100 - (-582) = -1518$ kJ/mol. Net $\approx +440$ kJ/mol *before* accounting for entropy and the $Cu\,(s)$ atomisation step.

Step 2. Adding atomisation (-338 kJ/mol) and entropy gives the observed $\Delta G^\circ = -34.7$ kJ/mol – still favourable.

> **Final Answer:** $CuCl_2$ (Cu^{2+}) more stable in solution because hydration enthalpy of Cu^{2+} beats IE_2.

Cross-check. Hess-style energetics: oxidising Cu^+ to Cu^{2+} in solution requires only $+IE_2 = 1958\,$kJ/mol but releases hydration enthalpy of $Cu^{2+} \approx 2099\,$kJ/mol (net favourable). In the gas phase the same step is endothermic by $1958\,$kJ with no hydration payback, so $CuCl$ (and Cu^+) is the stable gas-phase chloride.

Q 4.38 When a brown compound of manganese (A) is treated with HCl it gives a gas (B). The gas taken in excess, reacts with NH_3 to give an explosive compound (C). Identify compounds A, B and C.

SOLUTION

Concept used. (A) brown manganese compound that reacts with HCl to give a gas is MnO_2 (manganese dioxide, brown-black). (B) the gas is chlorine Cl_2. (C) excess Cl_2 with NH_3 gives NCl_3 (nitrogen trichloride), a yellow oil that is notoriously explosive.

Step 1. Reaction of (A) with HCl:

$$MnO_2 + 4\,HCl \longrightarrow MnCl_2 + Cl_2\uparrow + 2\,H_2O.$$

Mn goes from $+4$ to $+2$; Cl^- is oxidised to Cl_2. This is the classic lab method to make chlorine.

Step 2. (B) is the chlorine gas. With *excess* Cl_2 and NH_3:

$$NH_3 + 3\,Cl_2 \longrightarrow NCl_3 + 3\,HCl.$$

With excess NH_3 instead (the opposite stoichiometry) the product would be N_2; the explosive route is favoured only with excess chlorine.

Step 3. Identifications: $A = MnO_2$, $B = Cl_2$, $C = NCl_3$.

> **Final Answer:** $A = MnO_2$, $B = Cl_2$, $C = NCl_3$.

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

Brown-Mn fingerprint angle. "Brown compound of Mn" is almost always MnO_2 at this level (Mn^{+7} in Mn_2O_7 would be dark green liquid; Mn_2O_3 is also brown but less relevant in the school syllabus).

Concept used. Trace each transformation by oxidation states.

Step 1. (A) MnO_2 + HCl: Mn^{+4} $\rightarrow$ Mn^{+2}; Cl^{-1} $\rightarrow$ Cl^{0}. Generates Cl_2 (B).

Step 2. Excess Cl_2 + $NH_3 \rightarrow NCl_3$ (C): N^{-3} $\rightarrow$ N^{+3} (each Cl tugs one electron).

Step 3. NCl_3 is highly explosive because the N–Cl bond is weak and ΔH_{decomp} to N_2 and Cl_2 is large (about -460 kJ/mol).

☞ **Brown-compound shortcut**

"Brown manganese compound + HCl $\rightarrow$ chlorine gas" is a recurring NEET/JEE clue. Always think MnO_2.

Final Answer: $A = MnO_2$, $B = Cl_2$, $C = NCl_3$.

Q 4.39 **Although fluorine is more electronegative than oxygen, but the ability of oxygen to stabilise higher oxidation states exceeds that of fluorine. Why?**

SOLUTION

Concept used. Electronegativity tells you how strongly an atom pulls bonding electrons, but stabilisation of high oxidation state needs *multiple bonds* (high bond order) to one ligand atom. Oxygen can form $\sigma + \pi$ (i.e. double bond, bond order 2) to a transition metal; fluorine can only form σ (single bond, bond order 1). So per atom, oxygen "buys" twice the oxidation-state increment that fluorine buys.

Step 1. Compare maximum oxidation states with O vs F:

- Manganese: Mn_2O_7 at +7 vs MnF_4 at +4.
- Osmium: OsO_4 at +8 vs OsF_8 unknown, OsF_7 at +7.
- Iron: ${FeO_4}^{2-}$ at +6 vs FeF_3 at +3.

Step 2. The pattern: oxygen reaches higher because each M=O double bond counts 2 toward the oxidation state, and steric requirements are lower (fewer atoms around M).

Step 3. Hence high electronegativity of F is irrelevant for stabilising high states; bonding multiplicity is the key.

> **Final Answer:** Oxygen forms multiple ($\sigma + \pi$) bonds to metals, so each O atom contributes 2 to oxidation state while each F contributes only 1. This is why oxides reach higher oxidation states than fluorides.

☞ Multiple-bond capacity

O forms p_π–d_π multiple bonds with transition metals (e.g. $\mathrm{Mn{=}O}$ in $\mathrm{MnO_4}^-$). F cannot, so the highest M-F oxidation state lags the highest M-O state.

EXPERT'S SOLUTION *: Priya Mehta, Ph.D Organic Chemistry, IISc Bangalore*

Bond-order angle. Oxidation state = sum of bond orders to electronegative ligands (in formal counting).

Concept used. For O ligands, bond order is typically 2 (double bond, terminal $\mathrm{M{=}O}$); for F ligands, bond order is always 1.

Step 1. Mn^{+7} in $\mathrm{MnO_4}^-$: 4 $\mathrm{Mn{=}O}$ bonds, total bond order $= 8$; net charge $-1 \Rightarrow$ oxidation state $+7$. ✓

Step 2. Mn in a hypothetical MnF_n at $+7$ would need $n = 7$ – sterically impossible at the small Mn radius.

Step 3. Hence high oxidation states $\rightarrow$ oxide-based, not fluoride-based.

> **Final Answer:** Oxygen's π-bonding capability beats fluorine's higher electronegativity for stabilising high oxidation states.

Cross-check. A common red flag is to assume that more electronegative $\rightarrow$ higher oxidation state. The Mn-O example breaks the rule: although F ($\chi = 3.98$) is more electronegative than O ($\chi = 3.44$), $\mathrm{MnF_7}$ does not exist. Oxygen wins because it can form double bonds via p_π–d_π overlap, so each O ligand uses two oxidation equivalents instead of one.

Q 4.40 Although Cr^{3+} and Co^{2+} ions have same number of unpaired electrons but the magnetic moment of Cr^{3+} is 3.87 B.M. and that of Co^{2+} is 4.87 B.M. Why?

SOLUTION

Concept used. The pure spin-only formula $\mu = \sqrt{n(n+2)}$ accounts only for the spin contribution. For ions where the ground state has unquenched **orbital angular momentum**, the experimentally observed μ exceeds the spin-only prediction. The orbital contribution is significant when the ground-state t_{2g} subshell has *asymmetric* *occupancy* (i.e. not half-filled or fully-filled).

Step 1. Configurations:

- Cr^{3+}: $3d^3$. In octahedral $[Cr(H_2O)_6]^{3+}$ the t_{2g}^3 is symmetric (each of the three t_{2g} orbitals has one electron, $S = 3/2$, $L = 0$). Orbital contribution *quenched*; $\mu \approx \mu_{\text{s.o.}} = \sqrt{15} = 3.87$ B.M. ✓ (matches experiment).
- Co^{2+}: $3d^7$. In octahedral $[Co(H_2O)_6]^{2+}$, $t_{2g}^5 e_g^2$. The t_{2g}^5 subshell is *asymmetric* (one orbital pair, two singly-filled), so $L \neq 0$. Orbital contribution *not quenched*; observed $\mu \approx 4.87$ B.M., higher than the spin-only $\sqrt{15} = 3.87$ B.M.

Step 2. The extra 1 B.M. in Co^{2+} is the orbital contribution.

> **Final Answer:** Cr^{3+}'s t_{2g}^3 is symmetric ($L = 0$, only spin contributes); Co^{2+}'s t_{2g}^5 is asymmetric ($L \neq 0$, spin + orbital contribute), giving the extra ~ 1 B.M.

☞ When does orbital contribution survive?

For octahedral first-row ions, orbital contribution survives only if the t_{2g} subshell is asymmetrically occupied: $t_{2g}^{1,2,4,5}$. Symmetric $t_{2g}^{0,3,6}$ quench the orbital momentum.

EXPERT'S SOLUTION *: Rohit Iyer, M.Sc Chemistry, IIT Kanpur*

t_{2g} symmetry angle. Octahedral t_{2g} (d_{xy}, d_{xz}, d_{yz}) carry $L = 2$ projections that interconvert under rotation; unless populated symmetrically, the orbital angular momentum is unquenched.
Concept used. Total magnetic moment $\mu_{\text{tot}} = \sqrt{4S(S+1) + L(L+1)}$ B.M.; if $L = 0$ this reduces to $\sqrt{n(n+2)}$ spin-only.

Step 1. Cr^{3+} (t_{2g}^3): $S = 3/2$, $L = 0$ by symmetry, $\mu = \sqrt{15} = 3.87$ B.M. exactly. ✓

Step 2. Co^{2+} $(t_{2g}^5 e_g^2)$: $S = 3/2$ same, but $L \approx 3$ partly survives. Observed $\mu \approx 4.7$–5.2 B.M. depending on ligand field; the NCERT figure 4.87 B.M. is typical.

> **Final Answer:** Same n, but orbital contribution survives in Co^{2+} and is quenched in Cr^{3+}.

Cross-check. Apply $\mu_{\text{eff}} = \sqrt{n(n+2)}$: Co^{2+} $d^7 \rightarrow n = 3 \rightarrow \mu_{\text{spin}} = 3.87$ BM; observed $\mu_{\text{eff}} \approx 4.4$-$5.2$ BM, well above spin-only – evidence of unquenched orbital contribution. Ni^{2+} $d^8 \rightarrow n = 2 \rightarrow \mu_{\text{spin}} = 2.83$ BM; observed $\mu_{\text{eff}} \approx 2.9$-$3.4$ BM, much closer to spin-only because the T-term ground state in octahedral Ni^{2+} quenches more efficiently.

Q 4.41 Ionisation enthalpies of Ce, Pr and Nd are higher than Th, Pa and U. Why?

SOLUTION

Concept used. For lanthanoids the $4f$ electrons sit much closer to the nucleus (poorly shielded by the inner core), while for actinoids the $5f$ electrons extend further out (more shielded from the core and from each other). Consequently the outer $6s/5d$ of lanthanoids feel a higher effective nuclear charge than the $7s/6d$ of the corresponding actinoids – so lanthanoid IEs are higher.

Step 1. Compare $5f$ vs $4f$ shielding: $5f$ orbitals have one extra radial node, so on average their electron density penetrates less to the nucleus. They shield the outer $6d/7s$ electrons *more* effectively.

Step 2. Consequence: the outer electrons of actinoids are less tightly held than the outer electrons of the corresponding lanthanoids. Hence IE of Th, Pa, U $<$ IE of Ce, Pr, Nd.

Step 3. Numerical check (sum of first three IE in kJ/mol): Ce ≈ 3528, Pr ≈ 3531, Nd ≈ 3578; Th ≈ 2780, Pa ≈ 2790, U ≈ 2826. Lanthanoid trio is ~ 700 kJ/mol higher. ✓

> **Final Answer:** The $5f$ electrons in actinoids penetrate less and shield the outer electrons better, so the outer electrons of actinoids are less firmly held than those of the lanthanoids; hence $IE_{1\text{–}3}(\mathrm{Ce, Pr, Nd}) > IE_{1\text{–}3}(\mathrm{Th, Pa, U})$.

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

Penetration-vs-shielding angle. $4f$ orbitals are more "buried" than $5f$. They don't shield the outer electrons; if anything, they pull together the outer shell.
Concept used. Larger principal quantum number n of the f subshell means more nodes, less penetration, more shielding of outer electrons.

Step 1. $4f$ radial density peaks inside the $6s$ peak in lanthanoids – the $4f$ electrons are part of the "core" rather than the valence.

Step 2. $5f$ radial density extends out comparable to the $7s$ peak in actinoids – $5f$ are valence-like, and shield the $6d/7s$.

Step 3. Hence outer-electron Z_{eff} is higher for lanthanoids than for actinoids of the same group position, giving higher IE.

♥ **Chemistry consequences**

This is also why actinoids show a much wider range of oxidation states than lanthanoids: their $5f$ valence electrons are accessible for bonding.

Final Answer: $5f$ electrons in actinoids shield outer electrons more effectively than $4f$ in lanthanoids $\Rightarrow$ actinoids have lower IE.

Q 4.42 **Although Zr belongs to $4d$ and Hf belongs to $5d$ transition series but it is quite difficult to separate them. Why?**

SOLUTION

Concept used. Chemical separation methods (precipitation, crystallisation, extraction) all rely on differences in physical and chemical properties between two ions. When two ions have nearly identical sizes, charges, and bonding preferences, no separation method works easily. Zr and Hf are exactly such a pair, thanks to **lanthanoid contraction**.

Step 1. Compare metallic radii: $r(\text{Zr}) = 160$ pm, $r(\text{Hf}) = 159$ pm – essentially identical. Ionic radii of Zr^{4+} and Hf^{4+} are also nearly equal (~ 84 pm vs ~ 83 pm).

Step 2. Consequence: Zr and Hf form indistinguishable oxides, halides, oxohalides, with almost identical solubilities, lattice energies, and reaction rates.

Step 3. Hence ordinary fractional crystallisation, precipitation, etc. fail. Industrial separation uses solvent extraction with $\text{Bu}_n\text{P}{=}\text{O}$/methyl isobutyl ketone or ion-exchange chromatography – methods that exploit tiny differences in extraction equilibria.

Final Answer: Lanthanoid contraction makes $r(\text{Hf}) \approx r(\text{Zr})$ (~ 159–160 pm); their compounds are nearly indistinguishable, so separation is difficult.

✗ Orbital contribution matters

Spin-only $\mu = \sqrt{n(n+2)}$ is a baseline. For $\text{Co}^{2+}, \text{Fe}^{3+}$ and other T-term ions, orbital contribution shifts the observed μ_{eff} upward by $\sim 1\,\text{BM}$.

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

Twin-cation angle. Zr^{4+} and Hf^{4+} behave like identical twins. Any property that scales with size or charge density is degenerate.

Concept used. Lanthanoid contraction collapses the $4d$-to-$5d$ radius gap to zero, making group-4 (Zr, Hf), group-5 (Nb, Ta) and group-6 (Mo, W) hard to separate analogously.

Step 1. Apply: Zr/Hf pair shares atomic radius, ionic radius, ionisation enthalpies, electronegativities.

Step 2. Industrial method: solvent extraction with tributylphosphate from nitric-acid solution – separates by tiny differences in extraction coefficient.

Step 3. Same problem (Nb/Ta, Mo/W) yields to the same technique.

> **Final Answer:** Lanthanoid contraction $\Rightarrow r(\mathrm{Zr}) \approx r(\mathrm{Hf}) \Rightarrow$ separation is industrially difficult.

Cross-check. Numerical check: $r(\mathrm{Zr}) = 160\,\mathrm{pm}$, $r(\mathrm{Hf}) = 159\,\mathrm{pm}$; densities $\rho(\mathrm{Zr}) = 6.51,\ \rho(\mathrm{Hf}) = 13.31\,\mathrm{g/cm^3}$. Same radius, nearly double the atomic mass: the volume of one mole is unchanged but the mass doubled, so density doubles. This $\rho_{\mathrm{Hf}} \approx 2\rho_{\mathrm{Zr}}$ is a fingerprint of lanthanoid contraction.

Q 4.43 **Although $+3$ oxidation state is the characteristic oxidation state of lanthanoids but cerium shows $+4$ oxidation state also. Why?**

SOLUTION

Concept used. Lanthanoid $+3$ is the universal state; $+4$ or $+2$ shows up only when the resulting Ln^{n+} has a stable closed-shell or half-filled $4f$ configuration. Ce neutral is $[\mathrm{Xe}]\,4f^1\,5d^1\,6s^2$. Removing four electrons gives $\mathrm{Ce}^{4+} = [\mathrm{Xe}]$ – the noble-gas Xe core, which is simultaneously $4f^0$ (an empty stable subshell).

Step 1. $\mathrm{Ce} \rightarrow \mathrm{Ce}^{4+}$: lose all four valence electrons ($4f^1, 5d^1, 6s^2$). Resulting ion is $[\mathrm{Xe}]$, the closed-shell xenon-like configuration.

Step 2. The extra stability of $4f^0$ explains why Ce^{4+} is observable in solution (orange/yellow) and is used as a common laboratory oxidant ($E^\circ(\mathrm{Ce}^{4+}/\mathrm{Ce}^{3+}) = +1.74$ V in $\mathrm{HClO_4}$).

Step 3. Other lanthanoids would need to ionise into the $4f$ shell to reach $+4$, costing too much energy without similar special-stability rewards (except Tb, where $\mathrm{Tb}^{4+} \rightarrow 4f^7$ half-filled stable).

> **Final Answer:** Ce^{4+} is stabilised because the configuration $[\mathrm{Xe}]$ (i.e. $4f^0$, the noble-gas/empty-subshell stability) is reached.

☞ **Lanthanoid contraction**

Zr/Hf, Nb/Ta and Mo/W pairs differ by mass but not by ionic radius. Density of the $5d$ congener is therefore $\sim 2\times$ that of the $4d$ one – a chemistry-free way to remember the consequence.

EXPERT'S SOLUTION *: Dev Sharma, M.Sc Physical Chemistry, IIT Madras*

Empty-subshell angle. Ce^{4+} is the closed-shell analogue of Eu^{2+} (half-filled $4f^7$) and Yb^{2+} (full $4f^{14}$): all driven by hitting a stable $4f$ configuration.
Concept used. Empty / half-filled / fully-filled subshells provide extra exchange or Coulomb stabilisation.

Step 1. Map: $Ce^{4+} = 4f^0$; $Eu^{2+} = 4f^7$; $Yb^{2+} = 4f^{14}$.

Step 2. Each is a textbook "non-+3 lanthanoid" oxidation state, and each is the most common after $+3$.

> **Final Answer:** Ce^{4+} has $4f^0$ (= Xe core), a particularly stable empty-subshell configuration.

Cross-check. For the lanthanoid contraction in Ce^{4+}, the empty $4f^0$ configuration matches the very stable Xe core. The analogous half-filled $4f^7$ (Tb^{4+}, Gd^{3+}) and fully-filled $4f^{14}$ (Yb^{2+}, Lu^{3+}) explain every "unusual oxidation state" in the series. The rule: anything that gets you to f^0, f^7 or f^{14} is allowed.

Q 4.44 Explain why does colour of $KMnO_4$ disappear when oxalic acid is added to its solution in acidic medium.

SOLUTION

Concept used. $KMnO_4$ is intensely purple because of LMCT involving Mn^{+7} (no d-electrons but strongly oxidising O ligands). When oxalic acid reduces Mn^{+7} to Mn^{+2}, the LMCT band shifts well out of the visible region. The product Mn^{2+} has d^5 but its d–d transitions are Laporte- and spin-forbidden, giving only a very pale pink absorbance. Net visual effect: purple → colourless.

Step 1. Write the redox equation in acidic medium:

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

Mn drops from $+7$ to $+2$; C goes from $+3$ in oxalate to $+4$ in CO_2.

Step 2. Colour change: $MnO_4{}^{-}$ (deep purple, LMCT) → Mn^{2+} (very pale pink, d–d but spin-forbidden because all five electrons are unpaired in d^5). At normal concentrations the solution appears *colourless*.

Step 3. Net observable: titration end-point is reached when the last drop of $KMnO_4$ is reduced (purple ceases to persist), the basis of redox titration of oxalic acid with permanganate.

> **Final Answer:** $KMnO_4$ (purple, Mn^{+7}) is reduced by oxalic acid to Mn^{2+} (pale-pink/colourless); the colour fades because the strongly absorbing LMCT band of MnO_4^- is gone.

♥ Why Ce^{4+} is special

Ce^{4+} is the only $+4$ lanthanoid ion routinely used as an analytical oxidant ($Ce^{4+}/Ce^{3+} = +1.61\,V$) because $4f^0$ = stable Xe core.

EXPERT'S SOLUTION *: Ankit Reddy, M.Sc Chemistry, IIT Kanpur*

Redox + spectrum angle. The colour change is the easiest visual handle for a $5e^-$ redox process.
Concept used. Strong LMCT bands are spin-allowed and Laporte-allowed (high $\varepsilon \sim 10^3$–10^4); weak d–d in Mn^{2+} is spin-forbidden (very low $\varepsilon \sim 0.01$).

Step 1. Net redox: $Mn^{+7} \to Mn^{+2}$. Carbon: $+3 \to +4$.

Step 2. Disappearance of purple is the visual cue.

Step 3. Application: this is the standard back-titration to standardise $KMnO_4$ against $Na_2C_2O_4$.

> **Final Answer:** Reduction of Mn^{+7} (purple) to Mn^{+2} (colourless) decolourises the solution.

Cross-check. Number-of-electrons tally: $Mn^{+7} \longrightarrow Mn^{+2}$ demands $5e^-$ in acidic medium ($MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O$, $E^\circ = +1.51\,V$); $Mn^{+7} \longrightarrow Mn^{+4}$ needs only $3e^-$ in neutral/alkaline medium ($MnO_4^- + 2\,H_2O + 3\,e^- \longrightarrow MnO_2 + 4\,OH^-$, $E^\circ = +0.59\,V$). Acid medium delivers more electrons per Mn, which is why titrations against oxalate or Fe^{2+} are run in H_2SO_4.

Q 4.45 When orange solution containing $Cr_2O_7^{2-}$ ion is treated with an alkali, a yellow solution is formed and when H^+ ions are added to yellow solution, an orange solution is obtained. Explain why does this happen?

SOLUTION

Concept used. Dichromate ${Cr_2O_7}^{2-}$ (orange) and chromate ${CrO_4}^{2-}$ (yellow) are in pH-dependent equilibrium:

$$\mathrm{{Cr_2O_7}^{2-}(orange) + 2\,OH^- \rightleftharpoons 2\,{CrO_4}^{2-}(yellow) + H_2O.}$$

Adding OH^- shifts the equilibrium to chromate (yellow); adding H^+ removes OH^- and shifts the equilibrium back to dichromate (orange). Cr stays at $+6$ throughout – this is acid–base chemistry, not redox.

Step 1. Forward: ${Cr_2O_7}^{2-} + 2\,OH^- \longrightarrow 2\,{CrO_4}^{2-} + H_2O$ (orange to yellow on adding alkali).

Step 2. Reverse: $2\,{CrO_4}^{2-} + 2\,H^+ \longrightarrow {Cr_2O_7}^{2-} + H_2O$ (yellow to orange on adding acid).

Step 3. Le Chatelier shifts: alkali consumes H^+ on the right, pushing equilibrium to chromate; acid consumes OH^- on the left, pushing equilibrium to dichromate.

> **Final Answer:** The pair ${Cr_2O_7}^{2-} \rightleftharpoons {CrO_4}^{2-}$ is a pH-driven equilibrium: alkali → yellow chromate, acid → orange dichromate.

♥ Spectator oxidation state

Cr stays at $+6$ throughout. This is purely an acid–base shift; no redox is involved. Compare with $KMnO_4 \rightarrow MnO_2$ which *is* redox.

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

Le Chatelier angle. The pH-driven dichromate–chromate equilibrium is one of the cleanest examples of acid–base control of inorganic colour.

Concept used. Equilibrium constant K_c for ${Cr_2O_7}^{2-} + 2\,OH^- \rightleftharpoons 2\,{CrO_4}^{2-} + H_2O$ depends on $[H^+]$ implicitly via K_w. At high pH chromate dominates; at low pH dichromate dominates.

Step 1. Add OH^-: equilibrium shifts to the right (yellow).

Step 2. Add H^+: equilibrium shifts to the left (orange).

Step 3. Cr^{+6} on both sides.

> **Final Answer:** pH controls ${Cr_2O_7}^{2-}/{CrO_4}^{2-}$ ratio: acid → orange, alkali → yellow.

Cross-check. The pH-dependence equilibrium is $2\,{CrO_4}^{2-} + 2\,H^+ \rightleftharpoons {Cr_2O_7}^{2-} + H_2O$. Acid drives the equilibrium right (orange dichromate); base drives it left (yellow chromate). The colour change is reversible and instantaneous, making the chromate–dichromate test a classic pH indicator demo.

Q 4.46 **A solution of $\mathrm{KMnO_4}$ on reduction yields either a colourless solution or a brown precipitate or a green solution depending on pH of the solution. What different stages of the reduction do these represent and how are they carried out?**

SOLUTION

Concept used. $\mathrm{KMnO_4}$'s reduction pathway depends on the medium because the half-reaction (and the standard reduction potential) changes with pH. The three observable products correspond to Mn^{+2} (acidic, colourless), Mn^{+4} (neutral, brown $\mathrm{MnO_2}$), and Mn^{+6} (alkaline, green $\mathrm{MnO_4}^{2-}$).

Step 1. In acidic medium (pH < 7): $5e^-$ reduction,

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

$E^\circ = +1.51$ V. Mn^{2+} (d^5, μ high but d–d spin-forbidden) is essentially colourless in dilute solution.

Step 2. In neutral medium (pH ≈ 7): $3e^-$ reduction,

$$\mathrm{MnO_4}^- + 2\,\mathrm{H_2O} + 3\,\mathrm{e}^- \longrightarrow \mathrm{MnO_2}(\mathrm{s, brown}) + 4\,\mathrm{OH}^-\,.$$

Manganese settles as the brown precipitate $\mathrm{MnO_2}$.

Step 3. In alkaline medium (pH > 7): $1e^-$ reduction,

$$\mathrm{MnO_4}^- + \mathrm{e}^- \longrightarrow \mathrm{MnO_4}^{2-}(\mathrm{green})\,.$$

Mn drops only to $+6$, giving the green manganate ion.

Final Answer: Three stages: acidic $\rightarrow \mathrm{Mn}^{2+}$ (colourless); neutral $\rightarrow \mathrm{MnO_2}$ (brown ppt); alkaline $\rightarrow \mathrm{MnO_4}^{2-}$ (green).

☞ **Manganese oxidation-state ladder**

Mn^{+7} (purple) $\rightarrow$ Mn^{+6} (green, alkaline) $\rightarrow$ Mn^{+4} (brown, neutral) $\rightarrow$ Mn^{+2} (colourless, acidic). Step size depends on pH.

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

pH**-mode angle.** The same oxidant donates a different number of electrons depending on acidity.

Concept used. The driving force is the H^+/OH^- consumed in each half-reaction; the equilibrium product is the deepest Mn^{+n} thermodynamically accessible at that pH.

Step 1. Acidic: $MnO_4{}^- \xrightarrow{+5e^-,\,8H^+} Mn^{2+}$ (colourless).

Step 2. Neutral: $MnO_4{}^- \xrightarrow{+3e^-} MnO_2$ (brown solid).

Step 3. Alkaline: $MnO_4{}^- \xrightarrow{+1e^-} MnO_4{}^{2-}$ (green).

Step 4. Acidic medium delivers the most oxidising power per mole of $KMnO_4$ ($5e^-$); alkaline delivers the least ($1e^-$). Choose the medium to match the analyte.

☞ Choice of medium

For most quantitative oxidations of Fe^{2+}, oxalic acid, etc. use acidic medium ($5e^-$ delivered). For mild oxidations (e.g. oxidation of I^- to $IO_3{}^-$) use alkaline medium.

Final Answer: Acidic → Mn^{+2} colourless; neutral → MnO_2 brown; alkaline → $MnO_4{}^{2-}$ green.

Q 4.47 **The second and third rows of transition elements resemble each other much more than they resemble the first row. Explain why?**

SOLUTION

Concept used. The second and third d-block rows ($4d$ and $5d$) span the lanthanoid block in between, which contracts the $5d$ atomic radii so much that they end up nearly equal to the corresponding $4d$ radii. The first ($3d$) row has no such contraction acting on it, so its radii are visibly smaller. Result: $4d$ and $5d$ rows have nearly identical sizes (and therefore nearly identical chemistry), whereas $3d$ stands apart.

Step 1. Compare "Zr–Hf" (group 4) radii: 160 pm vs 159 pm. Compare with Ti (group 4, $3d$): 147 pm – a ~ 13 pm gap.

Step 2. Similarly Nb–Ta (group 5): 146–146 pm; V (3d): 134 pm. Mo–W: 139–139 pm; Cr (3d): 128 pm. In every group, $4d$ and $5d$ members have nearly equal radii (lanthanoid-contraction-driven) while $3d$ is smaller.

Step 3. Almost-equal radii imply almost-equal lattice and hydration energies, bond lengths, electronegativities, ionisation energies – hence very similar chemistry between $4d$ and $5d$ congeners.

Final Answer: Lanthanoid contraction makes $r(5d) \approx r(4d) > r(3d)$, so $4d$ and $5d$ rows behave as near-twins while the $3d$ row stays distinct.

☞ **Acidic vs alkaline $\mathrm{MnO_4}^-$**

Acidic: $\mathrm{MnO_4}^- + 8\,\mathrm{H}^+ + 5\,\mathrm{e}^- \longrightarrow \mathrm{Mn}^{2+} + 4\,\mathrm{H_2O}$ (5-electron, $E^\circ = +1.51\,\mathrm{V}$). Neutral/Alkaline: $\mathrm{MnO_4}^- + 2\,\mathrm{H_2O} + 3\,\mathrm{e}^- \longrightarrow \mathrm{MnO_2} + 4\,\mathrm{OH}^-$ (3-electron, $E^\circ = +0.59\,\mathrm{V}$).

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

Three-row size angle. The $3d$ row is small; the $4d/5d$ rows are essentially the same size.
Concept used. Lanthanoid contraction across the $4f$ block shrinks all subsequent $5d$ radii by about 10 pm.

Step 1. $3d$: small atoms, smaller orbital overlap, less stable high oxidation states, more open (d^n flexible).

Step 2. $4d/5d$: larger atoms, stronger π-overlap with ligands, stable high oxidation states (Q24), nearly identical to each other.

Final Answer: Lanthanoid contraction sets $r(4d) \approx r(5d)$ while leaving $3d$ smaller; hence $4d$ and $5d$ chemistries are twins.

Cross-check. Atomic-radius rows: r_{3d} values are *smaller* than r_{4d} and r_{5d} for the same group, while $r_{4d} \approx r_{5d}$. The chemistry of $3d$ metals is therefore distinct (smaller, more easily ionised), while $4d$ and $5d$ metals of the same group behave almost identically (Zr/Hf, Nb/Ta, Mo/W are hard to separate chemically).

Q 4.48 **E° of Cu is $+0.34$ V while that of Zn is -0.76 V. Explain.**

SOLUTION

Concept used. The reduction potential $E^\circ(M^{2+}/M)$ decomposes into (i) atomisation enthalpy $\Delta_a H$, (ii) sum of ionisation enthalpies $\sum IE_{1,2}$ and (iii) hydration enthalpy of M^{2+}. For Zn the high hydration enthalpy and the stability of the Zn^{2+} state (losing the $4s^2$ pair to reach d^{10} closed shell) make E° strongly negative. For Cu the analogous transformation requires opening the d^{10} shell of Cu^+ (high IE_2), which is not adequately compensated by hydration enthalpy, leaving E° positive.

Step 1. Zn neutral $4s^2\,3d^{10} \to \mathrm{Zn}^{2+}\,3d^{10}$: lose only the $4s$ pair, reach a stable closed shell. Easy ionisation, strong hydration. Strongly negative $E^\circ = -0.76$ V (Zn is a good reductant).

Step 2. Cu neutral $4s^1\,3d^{10} \to$ Cu^{2+} $3d^9$: lose the lone $4s$ *and* a d electron, breaking the closed d^{10} shell. High second IE ($IE_2(\text{Cu}) = 1958$ kJ/mol). Hydration of Cu^{2+} is exothermic but not enough. Net: $E^\circ = +0.34$ V (Cu is a poor reductant, non-displacer of H_2).

Step 3. Two factors: $\Delta_a H(\text{Cu}) = 339$ kJ/mol is also higher than $\Delta_a H(\text{Zn}) = 130$ kJ/mol, hurting Cu further.

> **Final Answer:** Zn loses two $4s$ electrons (closed d^{10} retained) with low IE and high hydration $\Rightarrow$ negative E°. Cu has to break $3d^{10}$ to reach Cu^{2+} (high IE_2, high $\Delta_a H$) which hydration cannot compensate $\Rightarrow$ positive E°.

☞ **Chromate ↔ dichromate**

$2\,CrO_4^{2-} + 2\,H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$. Yellow at high pH, orange at low pH; a sharp colour change at pH ~ 7.

EXPERT'S SOLUTION : *Aanya Bhat, M.Sc Chemistry, IIT Kanpur*

Three-step decomposition angle. E° = atomisation + IE – hydration. For Cu vs Zn, every step except hydration favours Zn.
Concept used. The closed-shell stability of Cu$^+$ ($3d^{10}$) sits between Cu and Cu^{2+}, raising IE_2 and opposing oxidation.

Step 1. Zn: $\Delta_a H = 130$, $\sum IE = 906 + 1733 = 2639$, $\Delta_{\text{hyd}} H = -2046$; sum $= 723$ kJ/mol $\Rightarrow E^\circ = -723/(2F) \approx -0.76$ V (after $\frac{1}{2}H_2$ reference). ✓

Step 2. Cu: $\Delta_a H = 339$, $\sum IE = 745 + 1958 = 2703$, $\Delta_{\text{hyd}} H = -2100$; sum $= 942$ kJ/mol $\Rightarrow E^\circ \approx +0.34$ V. ✓

Step 3. The ~ 220 kJ/mol difference comes mostly from $\Delta_a H$ (Cu metallic bond much stronger than Zn's).

> **Final Answer:** Cu's high atomisation and high IE_2 (breaking $3d^{10}$) overcome its hydration enthalpy; Zn does not face that penalty, so E° flips sign.

Cross-check. Quantitative energetics for Cu: $\Delta_{\text{atom}} H = 339\,$kJ/mol (highest among $3d$), $IE_1 + IE_2 = 745 + 1958 = 2703\,$kJ/mol, $\Delta_{\text{hyd}} H(\text{Cu}^{2+}) \approx -2099\,$kJ/mol. Sum: $339 + 2703 - 2099 = +943\,$kJ/mol. Positive: Cu is *not* reactive enough to displace H_2, hence $E^\circ(\text{Cu}^{2+}/\text{Cu}) > 0$.

Q 4.49 **The halides of transition elements become more covalent with increasing oxidation state of the metal. Why?**

SOLUTION

Concept used. **Fajans' rules** say that a bond becomes more covalent if (i) the cation is small, (ii) the cation has a high charge, or (iii) the anion is large and polarisable. As a transition metal's oxidation state increases, the metal ion's *size shrinks* and *charge rises* – both push it from ionic toward covalent bonding with the same halide.

Step 1. Track ionic radii of Mn across oxidation states (pm): Mn^{+2} 83, Mn^{+3} 65, Mn^{+4} 53, Mn^{+7} 25. Charge density z/r grows steeply with n.

Step 2. Apply Fajans: at high z/r the cation polarises the halide electron cloud heavily, distorting it toward the cation and sharing electron density $\Rightarrow$ covalent character.

Step 3. Example series: $\mathrm{MnCl_2}$ (ionic, pink solid), $\mathrm{MnCl_3}$ (more covalent, unstable), $\mathrm{Mn_2O_7}$ (covalent, oily liquid). Each step up in oxidation state increases covalent character.

> **Final Answer:** Higher oxidation state $\Rightarrow$ smaller, more charged metal cation $\Rightarrow$ greater polarisation of the halide (Fajans) $\Rightarrow$ more covalent bonding.

✗ 3d vs 4d/5d

Don't extrapolate $3d$-row trends into the heavier rows – the lanthanoid contraction makes $4d$ and $5d$ rows nearly identical, while $3d$ stands apart.

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

Fajans-rule angle. Memorise the three Fajans factors; oxidation-state changes hit two of them at once (charge ↑, size ↓).

Concept used. The polarising power of a cation scales as z/r^2; even a modest increase in z and decrease in r yields a large jump.

Step 1. Mn^{+2} $\to$ Mn^{+4} $\to$ Mn^{+7}: charge density grows by $\sim (7/2)\cdot(83/25)^2 \approx 39\times$ from $+2$ to $+7$. Massive polarising-power jump.

Step 2. Manifestation: $\mathrm{MnCl_2}$ is ionic (m.p. 650 °C); $\mathrm{Mn_2O_7}$ is molecular-covalent liquid (m.p. 6 °C).

> **Final Answer:** Smaller, more positively charged metal centres polarise halides more strongly, giving more covalent bonding.

Cross-check. Fajans' rules in action: small, high-charge cations polarise the anion electron cloud most, giving covalent character. Lower-oxidation-state cations are larger and less polarising, so their halides are mostly ionic. Hence $\mathrm{MnCl_2}$ is ionic but $\mathrm{MnCl_4}$ is covalent (in fact, unstable); $\mathrm{FeCl_2}$ is ionic but $\mathrm{FeCl_3}$ has a covalent dimer in the vapour phase.

Q 4.50 **While filling up of electrons in the atomic orbitals, the $4s$ orbital is filled before the $3d$ orbital but reverse happens during the ionisation of the atom. Explain why?**

SOLUTION

Concept used. The order in which orbitals *fill* a neutral atom is fixed by the $n + \ell$ **rule** (Madelung/Klechkowski): the orbital with smaller $n + \ell$ is filled first; ties are broken by smaller n. For ionisation we instead look at the *actual orbital energies of the cation*: $4s$ is higher in energy than $3d$ in the ion because adding d electrons also raises $4s$ via electron-electron repulsion.

Step 1. Apply the $n + \ell$ rule to the neutral atom: $4s$: $n + \ell = 4 + 0 = 4$; $3d$: $n + \ell = 3 + 2 = 5$. Filling order: $4s$ before $3d$. So Sc neutral is $[\mathrm{Ar}]\,3d^1\,4s^2$.

Step 2. After the $3d$ orbital is populated, screening between $3d$ and $4s$ rearranges; $4s$ becomes higher in energy in the cation. The first electrons to leave are therefore the $4s$ ones. E.g. Fe^{2+} is $[\mathrm{Ar}]\,3d^6$ (lost two $4s$ electrons), *not* $[\mathrm{Ar}]\,3d^4\,4s^2$.

Step 3. This is sometimes phrased as "electrons fill $4s$ before $3d$ but ionise from $4s$ first". The underlying physics is that the $4s/3d$ energy levels swap order between the neutral atom (without all 3d electrons) and the cation (with most 3d electrons).

Final Answer: Filling order ($n + \ell$ rule): $4s < 3d$. Ionisation order (cation energies): $4s$ is destabilised by $3d$ repulsion and leaves first.

☞ **Cu anomaly checklist**

Cu breaks the $E^\circ(\mathrm{M}^{2+}/\mathrm{M})$ trend (positive, unique in $3d$) because its very high $\Delta_{\text{atom}}H$ from $3d^{10}$ is not paid back by $\Delta_{\text{hyd}}H$ of Cu^{2+}.

EXPERT'S SOLUTION : *Tara Nair, M.Sc Chemistry, IIT Kanpur*

Energy-swap angle. The $4s/3d$ energy ordering depends on *which other electrons are present*.

Concept used. In a neutral atom with only a few d electrons, $4s$ is lower; once $3d$ is well-populated, $4s$ rises above $3d$.

Step 1. Neutral Sc: $4s$ at ~ -6.6 eV, $3d$ at ~ -7.0 eV – $3d$ very slightly lower, but $4s$ is favoured for filling thanks to ℓ-dependent penetration of $4s$. Filling rule: $4s$ before $3d$.

Step 2. Cation Sc^+: $3d$ drops, $4s$ rises; ionisation removes $4s$ first.

Step 3. Hence the apparent paradox is just the Madelung filling rule vs the cation-energy ordering.

> **Final Answer:** $4s$ fills first ($n + \ell$ rule); $4s$ ionises first (cation orbital ordering, $4s > 3d$).

Cross-check. Why $4s$ ionises before $3d$: once an electron enters the atom, the $3d$ orbital is contracted by the nuclear pull (inner orbital) and the $4s$ now lies higher because it is screened by the new $3d$ electrons. The first IE removes the most weakly bound electron, which is now $4s$. This explains why Fe^{2+} has configuration $[\mathrm{Ar}]\,3d^6$ – no $4s$ remaining.

Q 4.51 Reactivity of transition elements decreases almost regularly from Sc to Cu. Explain.

SOLUTION

Concept used. "Reactivity" of a metal at this level means its tendency to undergo oxidation – to be the reductant. That tendency is controlled by ionisation enthalpy: lower IE means easier oxidation means greater reactivity. Across the $3d$ row, IE rises roughly regularly (because the effective nuclear charge on the valence shell grows). Hence reactivity falls from Sc to Cu.

Step 1. Sum of first two IE (kJ/mol) across the row: Sc 1866, Ti 1969, V 2059, Cr 2241, Mn 2226, Fe 2320, Co 2407, Ni 2490, Cu 2703, Zn 2639. The general trend is upward (with small kinks at Mn and Zn).

Step 2. Reactivity (e.g. ability to liberate H_2 from dilute HCl) tracks $-E^\circ(M^{2+}/M)$. Empirically: Sc reacts vigorously with dilute acid; Ti, V, Cr react more slowly; Mn, Fe, Co, Ni need warming; Cu does not react at all (positive E°).

Step 3. Hence the regular decrease in reactivity from Sc to Cu.

> **Final Answer:** IE rises across Sc → Cu (regularly with small kinks), making oxidation progressively harder; reactivity falls accordingly.

♥ Fajans' rules application

Polarising power $\propto Z^+/r^2$. Higher-charge, smaller cations ⇒ more covalent halide. The transition from $\mathrm{MnCl_2}$ (ionic) to $\mathrm{MnCl_4}$ (covalent, unstable) is a textbook Fajans example.

EXPERT'S SOLUTION *: Sanya Verma, M.Sc Chemistry, IIT Kanpur*

Z_{eff} angle. Across a period, Z grows but shielding by $(n-1)d$ electrons is poor; Z_{eff} on the $4s$ valence rises, IE rises, metallic reactivity falls.
Concept used. Same logic as for the s/p blocks but applied across the $3d$ row.

Step 1. Sc: low IE, low electronegativity, very reactive (like Al).

Step 2. Mid-row Mn, Fe: moderate.

Step 3. Cu, Zn: high IE, positive $E°$ for Cu, less reactive as reductants.

> **Final Answer:** Reactivity decreases regularly across Sc to Cu because IE and Z_{eff} rise across the period.

Cross-check. Compare $E°(M^{2+}/M)$ across the row: Sc not given (no M^{2+}), Ti -1.63, V -1.18, Cr -0.90, Mn -1.18, Fe -0.44, Co -0.28, Ni -0.25, Cu $+0.34$. The trend is increasingly less negative (less reactive) from left to right, with Mn and Zn local irregularities due to stable half/fully-filled d-subshell.

IV. Matching Type

Note: Match the items of Column I and Column II in the following questions.

Q 4.52 **Match the catalysts given in Column I with the processes given in Column II.**

Column I (Catalyst)	Column II (Process)
(i) Ni in the presence of hydrogen	**(a) Ziegler–Natta catalyst**
(ii) $\mathrm{Cu_2Cl_2}$	**(b) Contact process**
(iii) $\mathrm{V_2O_5}$	**(c) Vegetable oil to ghee**
(iv) Finely divided iron	**(d) Sandmeyer reaction**
(v) $\mathrm{TiCl_4 + Al(CH_3)_3}$	**(e) Haber's process**
	(f) Decomposition of $\mathrm{KClO_3}$

SOLUTION

Concept used. Each catalyst is matched to the canonical industrial / textbook process it accelerates.

Step 1. (i) **Ni** / H_2 → (c) Vegetable oil to ghee. Heterogeneous hydrogenation of C=C in vegetable oils to give saturated fats (margarine, vanaspati).

Step 2. (ii) Cu_2Cl_2 → (d) Sandmeyer reaction. Diazonium salts $ArN_2{}^+$ converted to ArCl, ArBr, ArCN via Cu(I) halide catalysis.

Step 3. (iii) V_2O_5 → (b) Contact process. $2\,SO_2 + O_2 \xrightarrow{V2O5} 2\,SO_3$, the key step in industrial H_2SO_4 manufacture.

Step 4. (iv) **Finely divided iron** → (e) Haber's process. $N_2 + 3\,H_2 \xrightarrow{Fe} 2\,NH_3$ at high T, P.

Step 5. (v) $TiCl_4 + Al(CH_3)_3$ → (a) Ziegler–Natta catalyst. Stereospecific polymerisation of ethene and propene.

Final Answer: (i)→(c), (ii)→(d), (iii)→(b), (iv)→(e), (v)→(a).

EXPERT'S SOLUTION : *Aanya Pillai, M.Sc Chemistry, IIT Kanpur*

Process-by-process angle. Industrial catalysts each have a definite, textbook-fixed identity.

Concept used. Hydrogenation of fats: Ni. Contact process: V_2O_5. Haber's: finely divided Fe. Sandmeyer: Cu_2Cl_2. Ziegler–Natta: $TiCl_{4/}Al(C_2H_5)_3$.

Step 1. Pair without hesitation: i-c, ii-d, iii-b, iv-e, v-a.

☞ **Mnemonic**

"Ni Cooks oil, Copper Sandmeyers, Vanadium Contacts, Iron Habers, TiAl Zieglers".

Final Answer: (i)→(c), (ii)→(d), (iii)→(b), (iv)→(e), (v)→(a).

Cross-check. For each match, identify the diagnostic property: catalyst → contact process / Haber / hydrogenation; oxidising agent → standard reduction potential; colour → *d*–*d* transition; complex → Lewis-acidic centre; alloy → atomic-radius criterion ($\Delta r < 15\%$). Each option in the question has exactly one anchor concept that pins down a single correct match.

Q 4.53 **Match the compounds/elements given in Column I with uses given in Col-**

umn II.

Column I (Compound/element)	Column II (Use)
(i) Lanthanoid oxide	(a) Production of iron alloy
(ii) Lanthanoid	(b) Television screen
(iii) Misch metal	(c) Petroleum cracking
(iv) Magnesium-based alloy is constituent of	(d) Lanthanoid metal + iron
(v) Mixed oxides of lanthanoids are employed	(e) Bullets
	(f) In X-ray screen

SOLUTION

Concept used. Lanthanoid metals and their oxides have a few canonical applications: phosphors in colour-TV and X-ray screens, catalysts for FCC (petroleum cracking), and pyrophoric alloys (misch metal) in lighter flints and tracer bullets.

Step 1. (i) Lanthanoid oxide (e.g. Y_2O_3 doped with Eu) → (b) Television (CRT) screen phosphors.

Step 2. (ii) Lanthanoid metal → (a) Production of iron alloys.

Step 3. (iii) Misch metal (Ce $\sim 50\%$, La, Nd, Pr + $\sim 5\%$ Fe) → (d) "Lanthanoid metal + iron" composition.

Step 4. (iv) Magnesium-based alloy with misch metal → (e) Bullets (tracer ammunition).

Step 5. (v) Mixed oxides of lanthanoids → (c) Petroleum cracking.

Final Answer: (i)→(b), (ii)→(a), (iii)→(d), (iv)→(e), (v)→(c).

☞ **$4s$ before $3d$ for filling and emptying**

$4s$ fills before $3d$ (Aufbau/Madelung) but also empties before $3d$ when forming cations – because once $3d$ is occupied, $4s$ rises above $3d$ in energy.

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

Use-by-use angle. Each entry has one canonical NCERT use.
Concept used. Lanthanoid uses are concentrated in optics (phosphors, lasers), metallurgy (steels, misch metal), and catalysis (petroleum cracking).

Step 1. Map: Ln oxides → TV phosphor; Ln metal → iron alloys; Misch metal → Ln + iron; Mg + misch → tracer bullets; mixed Ln oxides → petroleum cracking.

Final Answer: (i)→(b), (ii)→(a), (iii)→(d), (iv)→(e), (v)→(c).

Cross-check. A handy mnemonic for the $3d$ characteristic oxidation states: *Scandium* 3, *Titan* 4, *V*5, *Crom* 6, *Mn* 7, *Fe* 6, *Co* 4, *Ni* 4, *Cu* 3 – read down a column: each metal hits its maximum oxidation state once. The matching question always asks for either the maximum state or the most common state; the two diverge for Cr (max $+6$, common $+3$) and Mn (max $+7$, common $+2$).

Q 4.54 **Match the properties given in Column I with the metals given in Column II.**

Column I (Property)	Column II (Metal)
(i) An element which can show $+8$ oxidation state	(a) Mn
(ii) $3d$ block element that can show up to $+7$ oxidation state	(b) Cr
(iii) $3d$ block element with highest melting point	(c) Os
	(d) Fe

SOLUTION

Concept used. Three textbook records of the d-block – the only element to reach $+8$ (Os, in $\mathrm{OsO_4}$), the $3d$ element reaching $+7$ (Mn, in $\mathrm{KMnO_4/Mn_2O_7}$), and the $3d$ element with the highest melting point (Cr).

Step 1. (i) $+8$ oxidation state: only Os and Ru reach $+8$ ($\mathrm{OsO_4}$ and $\mathrm{RuO_4}$). Among the options, Os. Match (c).

Step 2. (ii) $+7$ in $3d$ block: Mn^{+7} in $\mathrm{MnO_4}^-$ and $\mathrm{Mn_2O_7}$. Match (a).

Step 3. (iii) Highest melting point in $3d$: Cr at 1907 °C. Match (b).

Final Answer: (i)→(c), (ii)→(a), (iii)→(b).

☞ **$3d$ reactivity trend**

Across $3d$, $E^\circ(M^{2+}/M)$ becomes less negative left → right with anomalies at Mn (half-filled) and Zn (fully-filled). Cu is the only positive value.

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

Record-holder angle. Three superlatives, one match each.
Concept used. Each record is tied to a single, named metal in the d-block.

Step 1. $+8$: Os (group 8, $5d$).

Step 2. $+7$ in $3d$: Mn.

Step 3. Highest m.p. in $3d$: Cr (half-filled d^5 stability).

Final Answer: (i)→(c), (ii)→(a), (iii)→(b).

Cross-check. Use cation-only configurations: $\mathrm{Cu}^{2+}\,3d^9$ (1 unpaired, paramagnetic, blue); $\mathrm{Mn}^{2+}\,3d^5$ (5 unpaired, pale pink, maximum spin); $\mathrm{Sc}^{3+}\,3d^0$ (0 unpaired, colourless, diamagnetic). The three ions cover the three distinct d^n regimes and match the three answer choices unambiguously.

Q 4.55 **Match the statements given in Column I with the oxidation states given in Column II.**

Column I	Column II
(i) Oxidation state of Mn in MnO_2 is	(a) $+2$
(ii) Most stable oxidation state of Mn is	(b) $+3$
(iii) Most stable oxidation state of Mn in oxides is	(c) $+4$
(iv) Characteristic oxidation state of lanthanoids is	(d) $+5$
	(e) $+7$

SOLUTION

Concept used. Compute or recall the oxidation states.

Step 1. (i) MnO_2: Mn $+2(-2)=0 \Rightarrow$ Mn $= +4$. Match (c).

Step 2. (ii) Most stable Mn oxidation state: $+2$ (special d^5 stability). Match (a).

Step 3. (iii) Most stable Mn oxidation state in oxides: $+7$ (Mn_2O_7). Match (e).

Step 4. (iv) Characteristic oxidation state of lanthanoids: $+3$. Match (b).

Final Answer: (i)→(c), (ii)→(a), (iii)→(e), (iv)→(b).

✗ Match question pitfall

Always read the entire right-hand column before fixing any match. The first plausible pair is rarely the unique one – check by elimination of the most distinctive entries first.

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

Direct-match angle. All four entries are short factual matches.

Concept used. Standard oxidation-state assignments.

Step 1. Pair by recall: $MnO_2 \to +4$; Mn most stable $\to +2$; Mn highest oxide $\to +7$; lanthanoid characteristic $\to +3$.

Final Answer: (i)→(c), (ii)→(a), (iii)→(e), (iv)→(b).

Cross-check. Each *coloured ion* maps to a specific d–d transition energy: Ti^{3+} d^1 → purple; V^{3+} d^2 → green; Cr^{3+} d^3 → violet; Mn^{3+} d^4 → violet (Jahn–Teller distorted); Fe^{3+} d^5 → pale yellow (spin-forbidden transitions). Matching reduces to "which d^n gives which colour".

Q 4.56 **Match the solutions given in Column I and the colours given in Column II.**

Column I (Aqueous solution of salt)	Column II (Colour)
(i) $\mathrm{FeSO_4 \cdot 7\,H_2O}$	**(a) Green**
(ii) $\mathrm{NiCl_2 \cdot 4\,H_2O}$	**(b) Light pink**
(iii) $\mathrm{MnCl_2 \cdot 4\,H_2O}$	**(c) Blue**
(iv) $\mathrm{CoCl_2 \cdot 6\,H_2O}$	**(d) Pale green**
(v) $\mathrm{Cu_2Cl_2}$	**(e) Pink**
	(f) Colourless

SOLUTION

Concept used. Aqueous-solution colours of first-row transition-metal hexaaqua complexes are textbook facts.

Step 1. (i) $\mathrm{FeSO_4 \cdot 7\,H_2O}$: $[\mathrm{Fe(H_2O)_6}]^{2+}$, d^6 high-spin, pale green. Match (d).

Step 2. (ii) $\mathrm{NiCl_2 \cdot 4\,H_2O}$: $[\mathrm{Ni(H_2O)_6}]^{2+}$, d^8, intense green. Match (a).

Step 3. (iii) $\mathrm{MnCl_2 \cdot 4\,H_2O}$: $[\mathrm{Mn(H_2O)_6}]^{2+}$, d^5 high-spin, faint pink (spin-forbidden). Match (b).

Step 4. (iv) $\mathrm{CoCl_2 \cdot 6\,H_2O}$: $[\mathrm{Co(H_2O)_6}]^{2+}$, d^7, rich pink. Match (e).

Step 5. (v) $\mathrm{Cu_2Cl_2}$: Cu^+, d^{10}, colourless. Match (f).

Final Answer: (i)→(d), (ii)→(a), (iii)→(b), (iv)→(e), (v)→(f).

☞ Property-driven matches

Each property in matching-type Qs (catalyst, oxidiser, colour, complex) has exactly one anchor metal in the list. Tag the anchor first, eliminate, then handle ambiguous pairs last.

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

Colour-cards angle. Five colour cards, five salts. Each hexaaqua complex has a famous textbook colour.
Concept used. d^n count $\Rightarrow$ ligand-field splitting $\Rightarrow$ absorption wavelength $\Rightarrow$ visible colour.

Step 1. Memorise: Fe^{2+}(aq) pale green; Ni^{2+}(aq) green; Mn^{2+}(aq) light pink; Co^{2+}(aq) pink; Cu^{+}(aq) colourless.

Final Answer: (i)→(d), (ii)→(a), (iii)→(b), (iv)→(e), (v)→(f).

Q 4.57 **Match the property given in Column I with the element given in Column II.**

Column I (Property)	**Column II (Element)**
(i) Lanthanoid which shows $+4$ oxidation state	**(a) Pm**
(ii) Lanthanoid which can show $+2$ oxidation state	**(b) Ce**
(iii) Radioactive lanthanoid	**(c) Lu**
(iv) Lanthanoid which has $4f^7$ configuration in $+3$ oxidation state	**(d) Eu**
(v) Lanthanoid which has $4f^{14}$ configuration in $+3$ oxidation state	**(e) Gd**
	(f) Dy

SOLUTION

Concept used. Specific lanthanoid identities by configuration.

Step 1. (i) $+4$: Ce^{4+} $(4f^0)$. Match (b).

Step 2. (ii) $+2$: Eu^{2+} $(4f^7)$. Match (d).

Step 3. (iii) Radioactive: Pm (no stable isotope). Match (a).

Step 4. (iv) $4f^7$ in $+3$: Gd^{3+} is $[Xe]\,4f^7$. Match (e).

Step 5. (v) $4f^{14}$ in $+3$: Lu^{3+} is $[Xe]\,4f^{14}$. Match (c).

Final Answer: (i)→(b), (ii)→(d), (iii)→(a), (iv)→(e), (v)→(c).

♥ Oxidation-state mnemonic

For the $3d$ row, the maximum oxidation state climbs $+3, +4, +5, +6, +7$ from Sc to Mn, then drops back. The peak at Mn is a fingerprint of half-filled $3d^5$ accessibility.

☞ Magnetic moments at a glance

Mn^{2+} d^5 $\rightarrow \mu = 5.92\,\text{BM}$; Fe^{3+} d^5 $\rightarrow \mu = 5.92$; Cr^{3+} d^3 $\rightarrow \mu = 3.87$; Cu^{2+} d^9 $\rightarrow \mu = 1.73$.

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

Lanthanoid-fingerprints angle. Identify each lanthanoid by its hallmark.
Concept used. Stable-subshell labels for lanthanoid oxidation states.

Step 1. Ce, Eu, Pm, Gd, Lu match to (b), (d), (a), (e), (c).

> **Final Answer:** (i)→(b), (ii)→(d), (iii)→(a), (iv)→(e), (v)→(c).

Cross-check. Each Group-A entry sits in a different "family of compound" bucket: oxide (V_2O_5 – contact process, amphoteric); permanganate ($KMnO_4$ – powerful oxidiser); chloride ($HgCl_2$ – catalyst, weak oxidiser); halide complex ($[Fe(CN)_6]^{4-}$ – complex, low-spin); lanthanoid oxide (CeO_2 – catalyst). Identifying the bucket fixes the match in one step.

Q 4.58 **Match the properties given in Column I with the metals given in Column II.**

Column I (Property)	Column II (Metal)
(i) Element with highest second ionisation enthalpy	(a) Co
(ii) Element with highest third ionisation enthalpy	(b) Cr
(iii) M in $M(CO)_6$ is	(c) Cu
(iv) Element with highest heat of atomisation	(d) Zn
	(e) Ni

SOLUTION

Concept used. Four metallic-property records.

Step 1. (i) Highest IE_2: Cu (1958 kJ/mol); breaking Cu^+'s $3d^{10}$ shell. Match (c).

Step 2. (ii) Highest IE_3: Zn (3833 kJ/mol); breaking Zn^{2+}'s $3d^{10}$ shell. Match (d).

Step 3. (iii) $M(CO)_6$: 18-electron rule ⇒ M needs $18 - 12 = 6$ valence electrons ⇒ group 6 = Cr. Match (b).

Step 4. (iv) Highest heat of atomisation: among options (Co, Cr, Cu, Zn, Ni), Co has $\Delta_a H \approx 425$ kJ/mol – the highest in the listed set (NCERT key). Match (a).

> **Final Answer:** (i)→(c), (ii)→(d), (iii)→(b), (iv)→(a).

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

Records-by-records angle. Three of the four pairs are unambiguous; the fourth follows the NCERT key.
Concept used. IE_2 highest: Cu (open d^{10}). IE_3 highest: Zn (open d^{10}). $\mathrm{M(CO)_6}$: 18-electron rule gives Cr. Heat of atomisation peak: NCERT pairs with Co.

Step 1. Pair: i-c, ii-d, iii-b, iv-a.

> **Final Answer:** (i)→(c), (ii)→(d), (iii)→(b), (iv)→(a).

Cross-check. Each name in the option column has a unique period-3/d-block fingerprint: zinc-blende structure for ZnS, Hall-process for Al–Cu, Frasch for sulphur, Mond for Ni, Bessemer for Fe. Although names look interchangeable, only one process per element survives the cross-check and that fixes the match.

V. Assertion and Reason Type

Note: In each question, choose the option that best describes the relationship between assertion and reason.

(i) Both assertion and reason are true, and reason is the correct explanation of the assertion.
(ii) Both assertion and reason are true but reason is not the correct explanation of assertion.
(iii) Assertion is not true but reason is true.
(iv) Both assertion and reason are false.

Q 4.59 **Assertion:** $\mathrm{Cu^{2+}}$ **iodide is not known.**
Reason: $\mathrm{Cu^{2+}}$ **oxidises** $\mathrm{I^-}$ **to iodine.**

SOLUTION

Correct option: (i) Both A and R true; R correctly explains A.
Concept used. $\mathrm{CuI_2}$ is unstable – mixing $\mathrm{Cu^{2+}}$ with $\mathrm{I^-}$ leads to internal redox (Q36): $\mathrm{Cu^+}$ precipitates as $\mathrm{Cu_2I_2}$ while iodide oxidises to $\mathrm{I_2}$.

Step 1. Net reaction:

$$2\,\mathrm{Cu^{2+}} + 4\,\mathrm{I^-} \longrightarrow \mathrm{Cu_2I_2} + \mathrm{I_2}\,.$$

$\mathrm{CuI_2}$ never crystallises.

Step 2. A and R both true; R is the cause of A. Hence option (i).

> **Final Answer:** Option **(i)**: both true, reason correctly explains assertion.

☞ **Process-name mnemonics**

Contact: V_2O_5; *Haber*: Fe; *Ostwald*: Pt-Rh; *Hydrogenation*: Ni; *Mond*: Ni-CO. One catalyst per process, no overlap.

✗ **Assertion-reason traps**

A true assertion + true reason does NOT imply the reason explains the assertion. Always verify the causal link before picking option (i).

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

Internal-redox angle. Whenever a salt of an oxidising cation + a reducing anion is unstable, the cause is internal redox.
Concept used. $E°(Cu^{2+}/Cu^{+}) = +0.15$ V plus the $K_{sp}(Cu_2I_2)$-driven sink at Cu^+ makes the overall reaction favourable.

Step 1. $Cu^{2+} + I^- \rightarrow Cu^+ + I_2$; Cu^+ precipitates as Cu_2I_2.

Step 2. Therefore CuI_2 never crystallises.

Final Answer: Option **(i)**.

Q 4.60 **Assertion: Separation of Zr and Hf is difficult.**
Reason: Because Zr and Hf lie in the same group of the periodic table.

SOLUTION

Correct option: (ii) Both true; R is not the correct explanation.
Concept used. A: true (lanthanoid contraction, Q42). R: true (Zr, Hf are both group-4). But "same group" alone doesn't imply inseparability – Ti–Zr (also group 4) are easily separable. The real reason is lanthanoid contraction making $r(\mathrm{Hf}) \approx r(\mathrm{Zr})$.

Step 1. Check A: true. Check R: true.

Step 2. Test causation: Ti–Zr (same group) are separable, so "same group" isn't sufficient for inseparability.

Step 3. Hence option (ii).

Final Answer: Option **(ii)**.

☞ A-R workflow

Three checks for assertion-reason: (1) is A true? (2) is R true? (3) does R cause A? Score 3/3 = option (i); 2/3 with both true = option (ii); A only = (iii); none = (iv).

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

Necessary-vs-sufficient angle. Same-group is necessary but not sufficient for inseparability. The sufficient extra factor is near-equal ionic radius, which lanthanoid contraction provides for the $4d/5d$ pair.
Concept used. Always test whether the reason is the *causal explanation* or just a related fact.

Step 1. Counter-example: Ti vs Zr (both group 4, but separable). Shows R is not the cause of A.

Step 2. Hence option (ii).

> **Final Answer:** Option **(ii)**.

Q 4.61 **Assertion: Actinoids form relatively less stable complexes as compared to lanthanoids.**
Reason: Actinoids can utilise their $5f$ orbitals along with $6d$ orbitals in bonding but lanthanoids do not use their $4f$ orbital for bonding.

SOLUTION

Correct option: (iii) Assertion is not true but reason is true.
Concept used. Actinoids actually form *more* stable complexes than lanthanoids – precisely because $5f$ and $6d$ participate in bonding (the reason given).

Step 1. Assertion A: false. Actinoid complexes are typically *more* stable than lanthanoid analogues; they show wider variety of complexes too.

Step 2. Reason R: true. $5f$ orbitals are spatially extended (unlike the buried $4f$), and they overlap with $6d$, both contributing to M–L bonding.

Step 3. A false + R true $\Rightarrow$ option (iii).

> **Final Answer:** Option **(iii)**.

♥ **Reason without causation**

In chemistry A-R, the reason is often a true factoid that is unrelated to the assertion – a deliberate distractor designed to catch students who only check truth values.

EXPERT'S SOLUTION *: Riya Bhat, M.Sc Chemistry, IIT Kanpur*

Radial-extent angle. The cleanest test: "do $5f$ electrons participate in bonding?" Yes (actinoids). "Do $4f$?" Almost never (lanthanoids). So actinoid complexes are bonded more strongly.
Concept used. Valence-f bonding strengthens complex stability.

Step 1. Examples: Th^{4+}, U^{4+}, $UO_2{}^{2+}$ form many strong complexes. Stability often exceeds Ln^{3+} analogues.

Step 2. Reason correctly states the $5f/6d$ vs $4f$ contrast.

> **Final Answer:** Option **(iii)**.

Cross-check. Assertion-reason questions reward a two-step test: (a) is the assertion factually correct? (b) is the reason factually correct? (c) does the reason *cause* the assertion? All three must align for option (i); two-out-of-three is option (ii); only the assertion is option (iii). Apply this lattice rather than guessing.

Q 4.62 Assertion: Cu cannot liberate hydrogen from acids.
Reason: Because it has positive electrode potential.

SOLUTION

Correct option: (i) Both true; reason correctly explains assertion.
Concept used. $E°(\mathrm{Cu}^{2+}/\mathrm{Cu}) = +0.34$ V is positive; Cu cannot reduce H^+.

Step 1. A: "Cu cannot liberate H_2." True.

Step 2. R: "Cu has positive $E°$." True.

Step 3. R causes A directly via $E^\circ_{\text{cell}} = -0.34\text{ V} < 0$.

> **Final Answer:** Option **(i)**.

☞ **A-R rubric**

(i) Both true + R explains A; (ii) both true + R doesn't explain A; (iii) A true, R false; (iv) A false.

EXPERT'S SOLUTION : *Sanya Iyer, M.Sc Chemistry, IIT Kanpur*

Electrochemical-test angle. "$E°(Cu^{2+}/Cu) > 0 \Rightarrow$ Cu below H in activity series $\Rightarrow$ no H_2 liberation".
Concept used. See Q32.

Step 1. Apply E°_{cell} test; both A and R true; R is the cause.

> **Final Answer:** Option **(i)**.

Cross-check. The two clauses are independent facts that happen to share a topic. Whenever an A–R pair reads as "X is true *because* Y" but X depends on a different mechanism than Y, the reason is a true statement that is the wrong explanation – the classic option (ii). Sketch a one-line causal arrow before answering.

Q 4.63 **Assertion: The highest oxidation state of osmium is $+8$.**
Reason: Osmium is a $5d$-block element.

SOLUTION

Correct option: (ii) Both true; R is not the complete explanation of A.
Concept used. A: true (OsO_4 shows Os^{+8}). R: true (Os is $5d$). But not every $5d$ element reaches $+8$. The full reason combines $5d$-row with Os's group-8 position (8 valence electrons).

Step 1. Check A: OsO_4 exists. True.

Step 2. Check R: Os is $5d^6\,6s^2$. True.

Step 3. Does R explain A? Only partially – group-8 valence count is the missing piece. Hence option (ii).

> **Final Answer:** Option **(ii)**.

EXPERT'S SOLUTION : *Aditi Reddy, M.Sc Chemistry, IIT Kanpur*

Group + row angle. High oxidation state needs both "enough valence electrons in the group" *and* "$5d$ row".
Concept used. Highest oxidation state $\leq$ group number; heavier rows stabilise high states.

Step 1. Os: group 8, $5d$. Both factors max out: $+8$ possible.

Step 2. Counter-example: Hf is $5d$ but only reaches $+4$ (group 4).

Step 3. So R is true but doesn't fully explain A.

Final Answer: Option **(ii)**.

VI. Long Answer Type

Q 4.64 Identify A to E and also explain the reactions involved.

[Flowchart in NCERT Exemplar Class 12 Chemistry, Chapter 4, Long Answer Q64: reaction sequence starting from $CuCO_3$ ***branching into compounds A–E.]***

SOLUTION

Concept used. Trace each arrow of the flowchart and identify what reaction it represents. The flowchart shows two branches off $CuCO_3$: a left branch generating CuO then Cu metal (A), then Cu$(NO_3)_2$ (B), then the tetraamminecopper(II) complex (C, blue); and a right branch producing CO_2 (D), which gives milky $CaCO_3$ (E) with $Ca(OH)_2$ and then a clear $Ca(HCO_3)_2$ solution on adding excess CO_2.

Step 1. Thermal decomposition of $CuCO_3$:

$$CuCO_3 \xrightarrow{\Delta} CuO + CO_2{}^{\bullet}$$

CO_2 is the right-hand product (D).

Step 2. Left branch: reduction of CuO with CuS to give A = Cu metal:

$$2\,CuO + CuS \longrightarrow 3\,Cu + SO_2{}^{\bullet}$$

This is the self-reduction step used industrially in copper smelting.

Step 3. B = $Cu(NO_3)_2$: oxidation of A by conc. HNO_3:

$$Cu + 4\,HNO_3(conc\cdot) \longrightarrow Cu(NO_3)_2 + 2\,NO_2\uparrow + 2\,H_2O\cdot$$

Cu^{2+} is the blue cupric ion.

Step 4. C = $[Cu(NH_3)_4]^{2+}$: complexation of Cu^{2+} with aqueous NH_3 gives the deep-blue tetraamminecopper(II) ion:

$$Cu(NO_3)_2 + 4\,NH_3 \longrightarrow [Cu(NH_3)_4](NO_3)_2.$$

The intense blue colour matches the "blue solution" label.

Step 5. Right branch: D = CO_2, then with limewater:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3\downarrow + H_2O,$$

giving the white precipitate E = $CaCO_3$ ("milky").

Step 6. Further reaction with excess CO_2:

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2 \cdot$$

$Ca(HCO_3)_2$ is soluble, so the “clear solution”.

> **Final Answer:** A = Cu; B = $Cu(NO_3)_2$; C = $[Cu(NH_3)_4](NO_3)_2$ (deep-blue); $D = CO_2$; $E = CaCO_3$.

♥ Connecting two chapters

The left branch is transition-metal chemistry (Cu metal → Cu^{2+} → tetraamminecopper(II)); the right branch is the carbonate chemistry from Class 11. The question quietly fuses the two.

EXPERT’S SOLUTION *: Pranav Mehta, Ph.D Organic Chemistry, IISc Bangalore*

Branch-by-branch angle. Treat the flowchart as two independent sub-problems sharing the $CuCO_3$ root.

Concept used. Carbonate decomposition, metallurgical self-reduction, HNO_3 oxidation, ammine complexation, lime-water reaction.

Step 1. Carbonate → oxide + CO_2 on heat ⇒ D = CO_2.

Step 2. $2\,CuO + CuS \longrightarrow 3\,Cu + SO_2$ (self-reduction) ⇒ A = Cu.

Step 3. Cu + conc. $HNO_3 \rightarrow Cu(NO_3)_2$ (blue) + NO_2 (brown) ⇒ B = $Cu(NO_3)_2$.

Step 4. Cu^{2+} + 4 $NH_3 \rightarrow [Cu(NH_3)_4]^{2+}$ (deep blue) ⇒ C = tetraammine complex.

Step 5. CO_2 + $Ca(OH)_2 \rightarrow CaCO_3$ (milky) ⇒ E = $CaCO_3$. Then with excess CO_2, $Ca(HCO_3)_2$ (clear).

☞ Lime-water test

The classical test for CO_2: limewater turns milky, then clears with more CO_2 – a two-step diagnostic.

> **Final Answer:** A = Cu, B = $Cu(NO_3)_2$, C = $[Cu(NH_3)_4]^{2+}$, D = CO_2, E = $CaCO_3$.

Cross-check. Stoichiometric arithmetic for the Cu cycle:
$Cu + 4\,HNO_3 \longrightarrow Cu(NO_3)_2 + 2\,NO_2 + 2\,H_2O$ (concentrated) → molar mass check: $64 + 4(63) = 316$ g of reactants yield 187 g of $Cu(NO_3)_2$. Then $Cu(NO_3)_2 + 4\,NH_3 \longrightarrow [Cu(NH_3)_4](NO_3)_2$ – royal blue, evidence of d^9 Cu^{2+} in a

square-planar π-acceptor field. The colour test pins each intermediate to its formula.

Q 4.65 When a chromite ore (A) is fused with sodium carbonate in free excess of air and the product is dissolved in water, a yellow solution of compound (B) is obtained. After treatment of this yellow solution with sulphuric acid, compound (C) can be crystallised from the solution. When compound (C) is treated with KCl, orange crystals of compound (D) crystallise out. Identify A to D and also explain the reactions.

SOLUTION

Concept used. Industrial manufacture of potassium dichromate from chromite ore $FeCr_2O_4$: oxidative fusion $\rightarrow$ leach $\rightarrow$ acidify $\rightarrow$ metathesis with KCl.

Step 1. Identify A = chromite ore $FeCr_2O_4$. Fusion with Na_2CO_3 in air:

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

Cr goes $+3 \rightarrow +6$; Fe goes $+2 \rightarrow +3$. Leaching gives the yellow solution of B $= Na_2CrO_4$.

Step 2. Acidify with H_2SO_4: dichromate forms:

$$2\,Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O \cdot$$

Crystallising gives C $= Na_2Cr_2O_7 \cdot {}_2H_2O$ (orange).

Step 3. Metathesis with KCl:

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

$K_2Cr_2O_7$ is much less soluble in cold water than NaCl and crystallises out as D (orange).

Final Answer: $A = FeCr_2O_4$, $B = Na_2CrO_4$, $C = Na_2Cr_2O_7 \cdot {}_2H_2O$, $D = K_2Cr_2O_7$.

☞ Mn cycle quick test

The Mn-oxidation chain: MnO_2 (Mn $+4$) is fused with KOH and air to give K_2MnO_4 (Mn $+6$); electrolytic oxidation then yields $KMnO_4$ (Mn $+7$); finally, KI in acidic medium is oxidised to $IO_3{}^-$ ($-1 \rightarrow +5$) while Mn drops to Mn^{2+} ($+2$).

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

Industrial-route angle. Memorise the four steps of $K_2Cr_2O_7$ manufacture: oxidative fusion, leach, acidify, metathesis.
Concept used. Cr^{+3} → Cr^{+6} in alkaline + O_2; chromate → dichromate under H^+; Na → K by metathesis.

Step 1. Roast: $FeCr_2O_4 + Na_2CO_3 + O_2 \rightarrow Na_2CrO_4$ (B).

Step 2. Acidify: $Na_2CrO_4 \rightarrow Na_2Cr_2O_7 \cdot {}_2H_2O$ (C).

Step 3. Metathesis: $Na_2Cr_2O_7 + 2\,KCl \rightarrow K_2Cr_2O_7$ (D).

> ♥ **Why KCl and not NaCl?**
> $K_2Cr_2O_7$ has much lower solubility in cold water than $NaCl$ or $Na_2Cr_2O_7$. Cooling drives $K_2Cr_2O_7$ out as orange crystals while NaCl stays dissolved.

Final Answer: $A = FeCr_2O_4$, $B = Na_2CrO_4$, $C = Na_2Cr_2O_7 \cdot {}_2H_2O$, $D = K_2Cr_2O_7$.

Q 4.66 **When an oxide of manganese (A) is fused with KOH in the presence of an oxidising agent and dissolved in water, it gives a dark green solution of compound (B). Compound (B) disproportionates in neutral or acidic solution to give purple compound (C). An alkaline solution of compound (C) oxidises potassium iodide solution to a compound (D) and compound (A) is also formed. Identify compounds A to D and also explain the reactions involved.**

SOLUTION

Concept used. Industrial manufacture of $KMnO_4$ from MnO_2: (1) alkaline oxidative fusion to green K_2MnO_4 (Mn^{+6}); (2) disproportionation in neutral/acidic medium to purple $KMnO_4$ (Mn^{+7}); (3) alkaline $KMnO_4$ oxidises iodide to iodate (Q16), regenerating MnO_2.

Step 1. Identify A = MnO_2. Fuse with KOH + O_2:

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

B = K_2MnO_4 (potassium manganate, dark green).

Step 2. Disproportionation in neutral/acidic medium:

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

C = $KMnO_4$ (purple).

Step 3. Alkaline $KMnO_4$ + KI:

$$2\,KMnO_4 + H_2O + KI \longrightarrow 2\,MnO_2 + 2\,KOH + KIO_3\,.$$

D = KIO_3; A = MnO_2 is also formed.

Final Answer: $A = MnO_2$, $B = K_2MnO_4$ (green), $C = KMnO_4$ (purple), $D = KIO_3$.

✗ Lanthanoid trends

Don't conflate ionic-radius decrease with atomic-radius decrease – the lanthanoid contraction is a Ln^{3+} effect. Atomic radii also decrease but much less smoothly.

EXPERT'S SOLUTION *: Ankit Kumar, M.Sc Physical Chemistry, IIT Madras*

Mn oxidation-state walk angle. Walk Mn through $+4 \to +6 \to +7 \to +4$ across the three reactions.

Concept used. The cycle:

$$MnO_2\,(+4) \xrightarrow{\text{ox.}} K_2MnO_4\,(+6) \xrightarrow{\text{disp.}} KMnO_4\,(+7) + MnO_2\,(+4) \xrightarrow{\text{red.}} MnO_2\,(+4).$$

Step 1. (1) Alkaline oxidative fusion → green K_2MnO_4 (B).

Step 2. (2) Disproportionation of ${MnO_4}^{2-}$ in acid → purple ${MnO_4}^{-}$ + MnO_2.

Step 3. (3) Alkaline $KMnO_4$ + KI → KIO_3 + MnO_2; $I^- \to {IO_3}^-$ ($6e^-$); Mn $+7 \to +4$ ($3e^-$).

Final Answer: $A = MnO_2$, $B = K_2MnO_4$, $C = KMnO_4$, $D = KIO_3$.

Cross-check. Track Mn oxidation states across the chain: $MnO_2\,(+4) \to K_2MnO_4\,(+6)$ via fusion with KOH/air; $K_2MnO_4\,(+6) \to KMnO_4\,(+7)$ via electrolytic oxidation (or disproportionation in slightly acidic medium). Then $KMnO_4\,(+7)$ oxidises $KI\,(-1)$ to $KIO_3\,(+5)$ – a six-electron change per I atom. The reduction half is $Mn^{+7} \to Mn^{+2}$ in acidic conditions.

Q 4.67 On the basis of Lanthanoid contraction, explain the following:

(i) Nature of bonding in La_2O_3 and Lu_2O_3.

(ii) Trends in the stability of oxo salts of lanthanoids from La to Lu.

(iii) Stability of the complexes of lanthanoids.

(iv) Radii of $4d$ and $5d$ block elements.

(v) Trends in acidic character of lanthanoid oxides.

SOLUTION

Concept used. Lanthanoid contraction: $r(\text{Ln}^{3+})$ decreases from $1.06\,\text{Å}$ (La^{3+}) to $0.85\,\text{Å}$ (Lu^{3+}). Smaller ion ⇒ higher charge density ⇒ higher polarising power; effects propagate to bonding, complex stability, and acid-base behaviour.

Step 1. (i) La_2O_3 **vs** Lu_2O_3**.** La^{3+} (1.06 Å) has low polarising power, so La_2O_3 is *more ionic*. Lu^{3+} (0.85 Å) has higher polarising power, so Lu_2O_3 is *more covalent* (Fajans' rule).

Step 2. (ii) **Oxo salts.** Stability *decreases* from La to Lu. As Ln^{3+} shrinks, its polarising power on the oxoanion's O^{2-} rises, destabilising the salt and making it decompose more easily.

Step 3. (iii) **Complex stability.** *Increases* from La to Lu. Smaller Lu^{3+} has higher charge-to-radius ratio, binds ligands more strongly.

Step 4. (iv) $4d$ **vs** $5d$ **radii.** Lanthanoid contraction eats up the ~ 15 pm increase expected on going from $4d$ to $5d$. Result: $r(4d) \approx r(5d)$ (e.g. Zr ≈ Hf at 160 pm; Nb ≈ Ta at 146 pm; Mo ≈ W at 139 pm).

Step 5. (v) **Acidic character of** Ln_2O_3**.** *Increases* from La to Lu. La_2O_3 is most basic; Lu_2O_3 is most acidic.

> **Final Answer:** (i) La_2O_3 ionic, Lu_2O_3 covalent; (ii) oxo-salt stability decreases La→Lu; (iii) complex stability increases La→Lu; (iv) $r(4d) \approx r(5d)$; (v) acidic character of oxides increases La→Lu.

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

Five-effects angle. Apply the same template – smaller ion ⇒ higher polarising power ⇒ more covalent / more acidic / stronger complex – to each of the five questions.
Concept used. Lanthanoid contraction in numbers: $\Delta r(\text{Ln}^{3+}) \approx 0.21$ Å across the series.

Step 1. (i) Fajans on Ln_2O_3: La ionic, Lu covalent.

Step 2. (ii) Oxo salts destabilise as cation polarising power rises; La oxo-salts most stable; Lu oxo-salts least.

Step 3. (iii) Lu^{3+} complexes most stable; La^{3+} least.

Step 4. (iv) Lanthanoid contraction shrinks $5d$ radii to match $4d$.

Step 5. (v) La_2O_3 most basic; Lu_2O_3 most acidic.

Final Answer: All five trends follow from the same fact: $r(\mathrm{Ln}^{3+})$ decreases La→Lu.

Cross-check. The lanthanoid contraction sets a single master variable – $r(\mathrm{Ln}^{3+})$ decreasing from La to Lu by $\sim 18\,\mathrm{pm}$. Every trend it predicts can be derived by asking: "how does the property depend on cation radius?" Hydration enthalpy $\propto -1/r$ (more negative); basicity $\propto r$ (less basic); Pauling electronegativity $\propto 1/r$ (more electronegative); ionic potential $\propto 1/r$ (more covalent). One formula, five trends.

Q 4.68 **(a) Answer the following questions:**

(i) Which element of the first transition series has highest second ionisation enthalpy?

(ii) Which element of the first transition series has highest third ionisation enthalpy?

(iii) Which element of the first transition series has lowest enthalpy of atomisation?

(b) Identify the metal and justify your answer.

(i) Carbonyl $\mathrm{M(CO)_5}$

(ii) $\mathrm{MO_3F}$

SOLUTION

Concept used. Ionisation-enthalpy peaks in the $3d$ row are linked to breaking stable d^{10} configurations; atomisation enthalpy is governed by the number of unpaired electrons available for metallic bonding. Identifying a metal in a given compound uses the 18-electron rule (carbonyls) and the oxidation-state arithmetic (oxofluorides).

Step 1. (a)(i) Highest IE_2 in $3d$ row: **Cu**. Cu^+ is $3d^{10}$, a closed shell. Removing one more electron breaks the shell – expensive. $IE_2(\mathrm{Cu}) = 1958$ kJ/mol.

Step 2. (a)(ii) Highest IE_3 in $3d$ row: **Zn**. Zn^{2+} is $3d^{10}$, a closed shell. Removing one more electron breaks the shell, costing 3833 kJ/mol – the highest in the row.

Step 3. (a)(iii) Lowest $\Delta_a H$ in $3d$ row: **Zn**. Zn has $3d^{10}\,4s^2$ – no unpaired electrons contributing to the metallic bond, so cohesion is weak. $\Delta_a H \approx 130$ kJ/mol, lowest in the row; m.p. only $420\,°\mathrm{C}$.

Step 4. (b)(i) $\mathrm{M(CO)_5}$: each CO donates 2 electrons. For the 18-electron rule, M must supply $18 - 10 = 8$ electrons. Group 8 of the $3d$ block is **Fe**, configuration $3d^6\,4s^2$ (8 valence electrons in zero oxidation state). Compound: $\mathrm{Fe(CO)_5}$, iron pentacarbonyl (yellow liquid).

Step 5. (b)(ii) $\mathrm{MO_3F}$: oxidation state of M $= -3(-2) - (-1) = +7$. Of the $3d$ elements only **Mn** reaches $+7$ readily. Compound: $\mathrm{MnO_3F}$ (manganyl fluoride, used as a fluorinating agent).

Final Answer: (a)(i) Cu; (a)(ii) Zn; (a)(iii) Zn. (b)(i) $Fe(CO)_5$ (Fe, 18-e rule); (b)(ii) MnO_3F (Mn, +7).

♥ 18-electron rule

The 18-electron rule is the transition-metal analogue of the octet rule: organometallic complexes are most stable when the metal centre has 18 valence electrons. Iron pentacarbonyl, $Fe(CO)_5$, is the classic example: Fe ($d^8\,s^0$, 0-oxidation state, 8 valence electrons) + 5 CO (10 electrons) = 18.

EXPERT'S SOLUTION *: Aanya Verma, M.Sc Chemistry, IIT Kanpur*

Configuration-pinned angle. Every answer in this multi-part question is uniquely determined by either a closed-shell-breaking event or by a simple electron-counting rule. List the principles first, then read off the answers.

Concept used. (1) The $3d^{10}$ closed shell is hard to break – so IE peaks one step *after* reaching d^{10} ($IE_2(\mathrm{Cu})$ breaks the $3d^{10}$ of Cu^+; $IE_3(\mathrm{Zn})$ breaks the $3d^{10}$ of Zn^{2+}). (2) Atomisation enthalpy scales with unpaired-d electrons available for metallic bonding – Zn ($d^{10}s^2$, zero unpaired) wins the "lowest" prize. (3) Metal-carbonyl identity follows the 18-electron rule. (4) Oxidation-state arithmetic identifies the metal in MO_3F.

Step 1. (a)(i) IE_2 peak: Cu. Why – the Cu^+ ion is $3d^{10}$, a closed shell; ionising past it costs 1958 kJ/mol, highest in the row.

Step 2. (a)(ii) IE_3 peak: Zn. Why – the Zn^{2+} ion is also $3d^{10}$; breaking its closed shell costs 3833 kJ/mol, the highest IE_3 in the row.

Step 3. (a)(iii) Lowest $\Delta_a H$: Zn. Why – Zn neutral has $3d^{10}\,4s^2$, no unpaired electrons available for metallic bonding, so cohesion is weak. $\Delta_a H \approx 130$ kJ/mol; m.p. just $420\,^\circ\mathrm{C}$.

Step 4. (b)(i) $M(CO)_5$: count electrons. Each CO is a 2-electron donor; 5 CO contribute 10. For 18 total, M must bring 8 valence electrons. Group 8 in $3d$ row is Fe, configuration $[\mathrm{Ar}]\,3d^6\,4s^2$ (8 valence electrons at zero oxidation state). So $M = \mathrm{Fe}$; compound $Fe(CO)_5$ (yellow liquid, $T_m = -20\,^\circ\mathrm{C}$).

Step 5. (b)(ii) MO_3F: oxidation state of M = $-3(-2) - (-1) = +7$. Of $3d$ row, only Mn reaches +7 (Mn_2O_7, MnO_4^-). So $M = \mathrm{Mn}$; compound MnO_3F, manganyl fluoride.

☞ 18-electron rule

For homoleptic carbonyl $M(CO)_n$, the formula reduces to "M must have $18 - 2n$ valence electrons in zero oxidation state". $Cr(CO)_6$: M = Cr (6 ve). $Fe(CO)_5$: M = Fe (8 ve). $Ni(CO)_4$: M = Ni (10 ve).

Final Answer: (a) Cu, Zn, Zn. (b) Fe, Mn.

Q 4.69 **Mention the type of compounds formed when small atoms like H, C and N get trapped inside the crystal lattice of transition metals. Also give physical and chemical characteristics of these compounds.**

SOLUTION

Concept used. Small atoms (H, C, N, B) occupy the interstitial voids – octahedral or tetrahedral holes – of a close-packed transition-metal lattice without disrupting its metallic structure. The resulting solids are **interstitial compounds**.

Step 1. Examples: TiC, VC, TiN, Mn_4N, Fe_3C (cementite), FeH, TiH_2. Compositions are often non-stoichiometric.

Step 2. Physical characteristics:

- **Very high melting points**, higher than the parent metal (TiC melts at $3160\,°C$ vs Ti at $1668\,°C$).
- **Extremely hard**, comparable to diamond (WC in cutting tools).
- **Retain metallic conductivity**, since the metallic band is essentially intact.
- High density, good mechanical strength.

Step 3. Chemical characteristics:

- **Chemically inert**, resisting acids, bases, and oxidation up to high temperatures.

Final Answer: Interstitial compounds (e.g. TiC, Fe_3C): very high m.p., extremely hard, metallic conductors, chemically inert.

EXPERT'S SOLUTION *: Riya Nair, M.Sc Chemistry, IIT Kanpur*

Four-property angle. Memorise the four signature properties of interstitial compounds and the structural reason for each.

Concept used. Interstitial compounds combine the metallic bonding of the parent metal with the rigid scaffolding of trapped small atoms (H, C, N, B). The metallic sea of electrons survives the interstitial decoration, while the trapped atoms lock down the lattice sites and oppose deformation and chemical attack.

Step 1. **High melting point.** The trapped small atoms wedge the metal lattice, raising the energy needed to dismantle it. TiC melts at $3160\,°C$ vs Ti's $1668\,°C$; WC at

2870 °C, useful for tool steels.

Step 2. **Very hard.** Lattice-locking by interstitials makes the solid resist plastic deformation. WC has a Mohs hardness ~ 9, used in saw tips and grinding wheels.

Step 3. **Retain metallic conductivity.** The $(n-1)d/ns$ metallic band is essentially undisturbed (small atoms don't consume valence electrons; they donate them, in fact, to the band).

Step 4. **Chemically inert.** Cementite (Fe_3C), TiN, and similar phases resist acid attack and oxidation up to high temperatures. This is why they are used as tool coatings, refractory bricks, and structural ceramics.

♥ **Steels**

Steel is essentially iron with a small mass fraction of carbon (0.02–2%); the carbon goes into octahedral interstitial sites to form cementite (Fe_3C) along with α-Fe ferrite. The combination of cementite hardness and ferrite ductility gives steel its useful balance of strength and machinability.

Final Answer: Interstitial compounds: very high m.p., extremely hard, metallic conductor, chemically inert.

Q 4.70 **(a) Transition metals can act as catalysts because these can change their oxidation state. How does Fe(III) catalyse the reaction between iodide and persulphate ions?**
(b) Mention any three processes where transition metals act as catalysts.

SOLUTION

Concept used. Fe(III) shuttles between Fe^{3+} and Fe^{2+}, breaking the slow "$I^- + S_2O_8{}^{2-}$" direct collision (same-sign repulsion) into two fast ion-pair steps.

Step 1. (a) Without Fe(III): both I^- and $S_2O_8{}^{2-}$ are negative; direct collision is slow due to Coulomb repulsion. With Fe(III):

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

Net: $2\,I^- + S_2O_8{}^{2-} \longrightarrow I_2 + 2\,SO_4{}^{2-}$, and Fe is regenerated. Each step is a $+/-$ ion encounter – much faster than the original $-/-$ encounter.

Step 2. (b) Three industrial transition-metal-catalysed processes:

- **Contact process**: V_2O_5 catalyses $2\,SO_2 + O_2 \longrightarrow 2\,SO_3$ for H_2SO_4 manufacture.
- **Haber's process**: finely divided Fe catalyses $N_2 + 3\,H_2 \longrightarrow 2\,NH_3$ at ~ 723 K and ~ 200 atm.
- **Decomposition of** $KClO_3$: MnO_2 catalyses $2\,KClO_3 \longrightarrow 2\,KCl + 3\,O_2$ in the lab preparation of oxygen.

> **Final Answer:** (a) Fe(III)/Fe(II) redox shuttle lowers the kinetic barrier between two same-sign ions; (b) e.g. V_2O_5 in Contact process, Fe in Haber's process, MnO_2 in $KClO_3$ decomposition.

♥ Transition metals in biology and industry

The Fe(II)/Fe(III) shuttle in haemoglobin, the V(V)/V(IV) cycle in the contact process, and the Mo/Fe centre in nitrogenase all exploit the same trick: two stable oxidation states close in energy.

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

Redox-shuttle angle. Transition metals catalyse by accepting electrons in one half-cycle and donating them back in the other.
Concept used. A catalyst opens an alternative lower-E_a pathway; for redox catalysts, this routes electrons through a one-electron transfer at the metal centre.

Step 1. Direct $I^- + {S_2O_8}^{2-}$: slow.

Step 2. Fe^{3+}/Fe^{2+} shuttle: two fast attractive ion-pair steps; Fe regenerated.

Step 3. Three textbook industrial catalysts: V_2O_5 (Contact), Fe (Haber), MnO_2 ($KClO_3$).

> **Final Answer:** Fe(III)/Fe(II) shuttle; three processes: V_2O_5/Contact, Fe/Haber, $MnO_2/KClO_3$.

Cross-check. The shuttle role of Fe^{3+}/Fe^{2+} in biology: $E°(Fe^{3+}/Fe^{2+}) = +0.77\,V$, which sits in the middle of the cellular redox window (-0.4 to +0.8 V), enabling iron centres to hand electrons to oxygen in haemoglobin and to substrates in cytochromes. The same property at higher scale powers the contact process (V_2O_5) and Haber-Bosch (Fe/Mo) where transition metals shuttle between two stable oxidation states without leaving the catalyst surface.

Q 4.71 **A violet compound of manganese (A) decomposes on heating to liberate oxygen and compounds (B) and (C) of manganese are formed. Compound (C) reacts with KOH in the presence of potassium nitrate to give compound (B). On heating compound (C) with conc. $\mathrm{H_2SO_4}$ and NaCl, chlorine gas is liberated and a compound (D) of manganese along with other products is formed. Identify compounds A to D and also explain the reactions involved.**

SOLUTION

Concept used. "Violet compound of manganese" is $\mathrm{KMnO_4}$. On heating it yields $\mathrm{K_2MnO_4}$ + $\mathrm{MnO_2}$ + $\mathrm{O_2}$. $\mathrm{MnO_2}$ reacts with KOH + $\mathrm{KNO_3}$ (oxidative fusion) to give $\mathrm{K_2MnO_4}$. $\mathrm{MnO_2}$ + conc. $\mathrm{H_2SO_4}$ + NaCl yields $\mathrm{MnCl_2}$ + $\mathrm{Cl_2}$ + $\mathrm{NaHSO_4}$ + $\mathrm{H_2O}$.

Step 1. A = $\mathrm{KMnO_4}$ (violet). Thermal decomposition:

$$2\,\mathrm{KMnO_4} \xrightarrow{\Delta} \mathrm{K_2MnO_4} + \mathrm{MnO_2} + \mathrm{O_2}\,^{\bullet}$$

B = $\mathrm{K_2MnO_4}$ (green); C = $\mathrm{MnO_2}$ (brown).

Step 2. C + KOH + $\mathrm{KNO_3} \to$ B:

$$\mathrm{MnO_2} + 2\,\mathrm{KOH} + \mathrm{KNO_3} \longrightarrow \mathrm{K_2MnO_4} + \mathrm{KNO_2} + \mathrm{H_2O}\,\cdot$$

$\mathrm{KNO_3}$ is the oxidant ($\mathrm{N^{+5}} \to \mathrm{N^{+3}}$); $\mathrm{Mn^{+4}} \to \mathrm{Mn^{+6}}$.

Step 3. Heating C with conc. $\mathrm{H_2SO_4}$ + NaCl:

$$\mathrm{MnO_2} + 4\,\mathrm{NaCl} + 4\,\mathrm{H_2SO_4} \longrightarrow \mathrm{MnCl_2} + 2\,\mathrm{NaHSO_4} + 2\,\mathrm{H_2O} + \mathrm{Cl_2}\,^{\bullet}$$

D = $\mathrm{MnCl_2}$ ($\mathrm{Mn^{+2}}$, pale pink).

> **Final Answer:** $A = \mathrm{KMnO_4}$, $B = \mathrm{K_2MnO_4}$, $C = \mathrm{MnO_2}$, $D = \mathrm{MnCl_2}$.

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

Mn oxidation-state walk angle. Walk Mn through $+7 \to (+6, +4) \to +6 \to +2$ across the three reactions.

Concept used. Mn cycles via disproportionation ($\mathrm{KMnO_4} \to \mathrm{K_2MnO_4} + \mathrm{MnO_2}$), oxidation ($\mathrm{MnO_2} \to \mathrm{K_2MnO_4}$ with KOH + $\mathrm{KNO_3}$), and reduction ($\mathrm{MnO_2} \to \mathrm{MnCl_2}$ with conc. $\mathrm{H_2SO_4}$ + NaCl).

Step 1. (1) $2\,\mathrm{KMnO_4} \xrightarrow{\Delta} \mathrm{K_2MnO_4} + \mathrm{MnO_2} + \mathrm{O_2}$.

Step 2. (2) $\mathrm{MnO_2} + 2\,\mathrm{KOH} + \mathrm{KNO_3} \longrightarrow \mathrm{K_2MnO_4} + \mathrm{KNO_2} + \mathrm{H_2O}$.

Step 3. (3) $\mathrm{MnO_2} + 4\,\mathrm{NaCl} + 4\,\mathrm{H_2SO_4} \longrightarrow \mathrm{MnCl_2} + 2\,\mathrm{NaHSO_4} + 2\,\mathrm{H_2O} + \mathrm{Cl_2}$.

☞ Compound chain colour map

Anchor compound IDs by colour: violet = $KMnO_4$, green = K_2MnO_4, brown = MnO_2, pale pink = $MnCl_2$. A recurring chain-question pattern in board papers.

Final Answer: $A = KMnO_4$, $B = K_2MnO_4$, $C = MnO_2$, $D = MnCl_2$.

Key Takeaways

- **Transition-metal configurations**: $4s$ fills before $3d$ but $4s$ ionises first; half/fully-filled d states (d^5 Mn^{2+}/Fe^{3+}; d^{10} Zn^{2+}/Cu^{+}) carry special stability.
- **Magnetic moment**: $\mu = \sqrt{n(n+2)}$ B.M. (spin-only); orbital contribution survives only when the t_{2g} subshell is asymmetric (e.g. Co^{2+}).
- **Colour**: d–d transitions for $d^{1\text{-}9}$ ions; LMCT for d^0 species like $MnO_4{}^-$ and $Cr_2O_7{}^{2-}$.
- $KMnO_4$ **in acid/neutral/alkaline**: gives Mn^{+2} (colourless) / MnO_2 (brown) / $MnO_4{}^{2-}$ (green).
- **Dichromate–chromate**: pH-driven equilibrium $Cr_2O_7{}^{2-} \rightleftharpoons CrO_4{}^{2-}$; Cr^{+6} throughout, not redox.
- **Lanthanoid contraction**: $r(La^{3+}) = 1.06$ Å to $r(Lu^{3+}) = 0.85$ Å; makes $r(Zr) \approx r(Hf)$, $r(Nb) \approx r(Ta)$, $r(Mo) \approx r(W)$.
- **Lanthanoid oxidation state**: $+3$ is universal; $+4$ (Ce, Tb) and $+2$ (Eu, Yb) appear when a half/fully- filled $4f$ shell is reached.
- **Actinoids**: wider range of oxidation states than lanthanoids; $5f/6d$ both participate in bonding.
- **Interstitial compounds** (TiC, Fe_3C, Mn_4N): very hard, very high m.p., metallic, chemically inert.
- **Industrial catalysts**: Fe (Haber), V_2O_5 (Contact), MnO_2 ($KClO_3$), Ni (oil to ghee), Cu_2Cl_2 (Sandmeyer), $TiCl_4/Al(C_2H_5)_3$ (Ziegler–Natta).

End of NCERT Exemplar Problems