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Introduction

Overview

- Four series of d-block elements formed by filling 3d, 4d, 5d, and 6d electron shells.
- These series together make up the d-block elements.
- f-block elements fill 4f and 5f orbitals in two long periods.

Solved Examples

- **Ex 1:** Identify the block of element with electronic configuration $[\text{Ar}] 3d^5 4s^2$.
Answer: d-block (3d electrons filling).

Practice Set

- **Q1:** Which orbitals are filled in d-block elements?
A. s-orbitals
B. p-orbitals
C. d-orbitals
D. f-orbitals
- **Q2:** The f-block elements fill which orbitals?
A. 3d
B. 4f and 5f
C. 4d
D. 5d
- **Q3:** How many series of d-block elements are there?
A. Two
B. Three
C. Four
D. Five

Answer Key

- **Q1:** C - d-orbitals are filled in d-block elements.

- **Q2:** B - f-block elements fill 4f and 5f orbitals.
- **Q3:** C - There are four series of d-block elements.

Memory Aids

- D-block = last electron in d-orbital.
- f-block = filling 4f and 5f orbitals.
- Four d-block series: 3d, 4d, 5d, 6d.

Transition Elements

Position in Periodic Table

- Transition elements lie between s- and p-block elements in the long form of the periodic table.
- Called d-block elements because last electron enters d-orbital.

Solved Examples

- **Ex 1:** Identify the position of Fe in the periodic table.
Answer: Between s- and p-block, in d-block.

Practice Set

- **Q1:** Transition elements are located between which blocks?
A. s- and p-block
B. p- and f-block
C. s- and f-block
D. p- and d-block
- **Q2:** Why are transition elements called d-block elements?
A. Last electron enters s-orbital
B. Last electron enters p-orbital
C. Last electron enters d-orbital
D. Last electron enters f-orbital

- **Q3:** Which of the following is a transition element?
A. Na
B. Ca
C. Fe
D. Ne

Answer Key

- **Q1:** A - Transition elements lie between s- and p-block.
- **Q2:** C - Last electron enters d-orbital.
- **Q3:** C - Fe is a transition element.

Memory Aids

- Transition elements = d-block elements.
- Located between s- and p-block in periodic table.
- Last electron enters d-orbital.

Electronic Configurations of the d-Block Elements

General electronic configuration

- d-block elements have the general configuration $(n-1)d^{1-10} ns^{0-2}$.
- Electrons fill the $(n-1)d$ and ns orbitals progressively across the series.

Filled d-orbitals in Zn, Cd, Hg, and Cn

- Elements Zn, Cd, Hg, and Cn have configuration $(n-1)d^{10} ns^2$.
- Their d and s orbitals are completely filled in ground and common oxidation states.
- They are not considered transition elements due to fully filled d-orbitals.

Transition series

- d-block consists of four transition series based on the d-orbital being filled:
- 1st series (3d): Sc (21) to Zn (30)
- 2nd series (4d): Y (39) to Cd (48)
- 3rd series (5d): La (57), Hf (72) to Hg (80)
- 4th series (6d): Ac (89), Rf (104) to Cn (112)

➤ First (3d) Transition Series (Sc - Zn) :

At. No.	21	22	23	24	25	26	27	28	29	30
Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
E.C.	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$

➤ Second (4d) Transition Series (Y - Cd) :

At. No.	39	40	41	42	43	44	45	46	47	48
Element	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
E.C.	$4d^1 5s^2$	$4d^2 5s^2$	$4d^4 5s^1$	$4d^5 5s^1$	$4d^5 5s^2$	$4d^7 5s^1$	$4d^8 5s^1$	$4d^{10} 5s^0$	$4d^{10} 5s^1$	$4d^{10} 5s^2$

➤ Third (5d) Transition Series (La - Hg) :

At. No.	57	72	73	74	75	76	77	78	79	80
Element	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
E.C.	$5d^1 6s^2$	$4f^{14} 5d^2 6s^2$	$4f^{14} 5d^3 6s^2$	$4f^{14} 5d^4 6s^2$	$4f^{14} 5d^5 6s^2$	$4f^{14} 5d^6 6s^2$	$4f^{14} 5d^7 6s^2$	$4f^{14} 5d^9 6s^1$	$4f^{14} 5d^{10} 6s^1$	$4f^{14} 5d^{10} 6s^2$

➤ Fourth (6d) Transition Series (Ac - Cn) :

At. No.	89	104	105	106	107	108	109	110	111	112
Element	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn
E.C.	$6d^1 7s^2$	$5f^{14} 6d^2 7s^2$	$5f^{14} 6d^3 7s^2$	$5f^{14} 6d^4 7s^2$	$5f^{14} 6d^5 7s^2$	$5f^{14} 6d^6 7s^2$	$5f^{14} 6d^7 7s^2$	$5f^{14} 6d^9 7s^1$	$5f^{14} 6d^{10} 7s^1$	$5f^{14} 6d^{10} 7s^2$

Electron configuration pattern

- Transition elements fill d-orbitals progressively across each series.
- Example: Sc (21) has configuration $3d^1 4s^2$.
- 4th series includes filling 5f orbitals (actinides).
- Electron configurations explain chemical properties and trends of transition metals.

Solved Examples

- Ex 1:** Write the electronic configuration of Fe (Z=26).
 - Fe is in 1st transition series (3d).
 - Configuration: $[\text{Ar}] 3d^6 4s^2$.

- **Ex 2:** Identify if Zn is a transition element.
 - Zn configuration: $[\text{Ar}] 3d^{10} 4s^2$.
 - Fully filled d-orbitals, so not a transition element.

Practice Set

- **Q1:** What is the general electronic configuration of d-block elements?
 - A. $(n-1)d^{1-10} ns^{0-2}$
 - B. $ns^2 np^6$
 - C. $(n-1)f^{1-14} ns^2$
 - D. $ns^1 np^5$
- **Q2:** Which element is NOT considered a transition element?
 - A. Fe
 - B. Zn
 - C. Cu
 - D. Ni
- **Q3:** What is the electronic configuration of the 2nd transition series element Cd ($Z=48$)?
 - A. $[\text{Kr}] 4d^{10} 5s^2$
 - B. $[\text{Kr}] 4d^9 5s^2$
 - C. $[\text{Kr}] 4d^8 5s^2$
 - D. $[\text{Kr}] 4d^{10} 5s^1$

Answer Key

- **Q1:** A. $(n-1)d^{1-10} ns^{0-2}$ - Defines d-block filling pattern.
- **Q2:** B. Zn - Fully filled d-orbitals, not a transition element.
- **Q3:** A. $[\text{Kr}] 4d^{10} 5s^2$ - Cd has completely filled d and s orbitals.

Memory Aids

- Transition series order: 3d (Sc-Zn), 4d (Y-Cd), 5d (La/Hf-Hg), 6d (Ac/Rf-Cn).
- Zn, Cd, Hg, Cn: $d^{10} s^2$ configuration, not transition metals.
- Remember: Transition elements have incomplete d-orbitals in common oxidation states.

General Properties of Transition Elements

Metallic Characteristics

- High tensile strength, ductility, malleability, thermal & electrical conductivity.
- Metallic lustre common except Zn, Cd, Hg, Mn.
- Typical metallic structures at room temperature except Zn, Cd, Hg, Mn.

Physical Properties

- High melting and boiling points due to strong metallic bonding.
- High enthalpies of atomisation from strong atomic forces.
- Atomic and ionic sizes decrease across series; increase down groups.
- Lanthanoid contraction causes size anomalies.
- Ionisation enthalpy generally increases across series.

Chemical Properties

- Multiple oxidation states due to similar energy d-orbitals.
- Variable standard electrode potentials.
- Magnetic properties from unpaired electrons; paramagnetism increases with unpaired electrons.
- Formation of coloured ions via d-d transitions; exceptions with empty d-orbitals.
- Complex compound formation due to small size and electron acceptance.
- Catalytic activity from variable oxidation states and complex formation.
- Interstitial compounds form by small atoms fitting in metal lattices.
- Alloy formation facilitated by similar atomic sizes.

Property	Trends and Explanations	
Melting and boiling points	High due to involvement of greater number of electrons from $(n-1)d$ in addition to ns electrons in the interatomic metallic bonding (greater the number of valence electrons, stronger is the resultant bonding).	M^{2+}/M standard electrode potential
Enthalpies of atomisation	High due to strong interatomic interactions.	M^{3+}/M^{2+} standard electrode potential
Atomic and ionic sizes	<ul style="list-style-type: none"> Decreases in the series with increase in atomic number because of increased nuclear charge and ineffective shielding effect of d-electrons. Increases down the group but radii of third series are virtually the same as those of the corresponding members of second series due to lanthanoid contraction. The filling of $4f$ before $5d$ orbital results in a regular decrease in atomic radii called lanthanoid contraction. 	Magnetic properties
Ionisation enthalpies	<ul style="list-style-type: none"> Ionisation enthalpy increases from left to right in a series. The first ionisation enthalpies of Zn, Cd and Hg are very high because of fully filled configurations. Cr and Cu show unusually high values of second ionisation enthalpies due to disruption of d^5 and d^{10} configurations of M^+ ion respectively while that of Zn is low as it leads to stable d^{10} configuration. Third ionisation enthalpy of Mn is very high due to disruption of d^5 configuration while that of Fe is very small as it leads to d^5 configuration. 	Formation of coloured ions
Oxidation states	<ul style="list-style-type: none"> All transition elements except the first and last member of each series show variable oxidation states because difference of energy in the $(n-1)d$ and ns orbitals is very little and electrons from both the orbitals can be used for bond formation. The compounds in +2 and +3 oxidation states are mostly ionic. The highest oxidation state is equal to total number of s- and d-electrons. Maximum oxidation state increases from Sc to Mn and then decreases to Zn. 	Formation of complex compounds
		Catalytic properties
		Formation of interstitial compounds
		Alloy formation

Solved Examples

- Ex 1: Explain why transition metals have high melting points.
Strong metallic bonding due to many valence electrons involved in bonding.
- Ex 2: Why do transition metals form coloured ions?
Electrons jump between split d -orbitals absorbing visible light.

Practice Set

- Q1: Which element is NOT a typical transition metal?
A. Fe B. Zn C. Cr D. Ni
- Q2: What causes the magnetic properties in transition metals?
A. Paired electrons B. Unpaired electrons C. Full d -orbitals D. Empty s -orbitals
- Q3: Why do transition metals show multiple oxidation states?
A. Different s -orbitals B. Similar energy d -orbitals C. Large atomic size D. High ionisation energy

Answer Key

- Q1: B - Zn is a non-typical transition metal with full d -orbitals.
- Q2: B - Unpaired electrons cause magnetic properties.
- Q3: B - Similar energy d -orbitals allow multiple oxidation states.

Memory Aids

- Zn, Cd, Hg are pseudo transition metals (no typical d-block behavior).
- High melting points = strong metallic bonds + many valence electrons.
- Colour arises from d-d electron transitions.

Colour and d-d Transitions

Colour Origin

- Transition metal ions with unpaired d-electrons show colour due to d-d transitions.
- Empty d-orbitals (e.g., Sc^{3+} , Ti^{4+} , V^{5+} , Cr^{6+} , Mn^{7+}) are colourless.
- Charge transfer causes colour in ions like VO_2^+ (pale yellow), CrO_4^{2-} (deep yellow), MnO_4^- (intense purple).

Solved Examples

- Ex 1: Why is MnO_4^- intensely purple?
Charge transfer transitions absorb visible light strongly.

Practice Set

- Q1: Which ion is colourless due to empty d-orbitals?
A. Ti^{4+} B. Fe^{2+} C. Cu^{2+} D. Mn^{2+}
- Q2: What causes colour in VO_2^+ ions?
A. d-d transitions B. Charge transfer C. No colour D. Full d-orbitals
- Q3: Which ion shows intense purple colour?
A. CrO_4^{2-} B. MnO_4^- C. VO_2^+ D. Sc^{3+}

Answer Key

- Q1: A - Ti^{4+} has empty d-orbitals, no d-d transitions.
- Q2: B - Charge transfer causes colour in VO_2^+ .
- Q3: B - MnO_4^- is intensely purple due to charge transfer.

Memory Aids

- Empty d-orbitals = colourless ions.
- Charge transfer ions: VO_2^+ , CrO_4^{2-} , MnO_4^- .

Stability of Higher Oxidation State

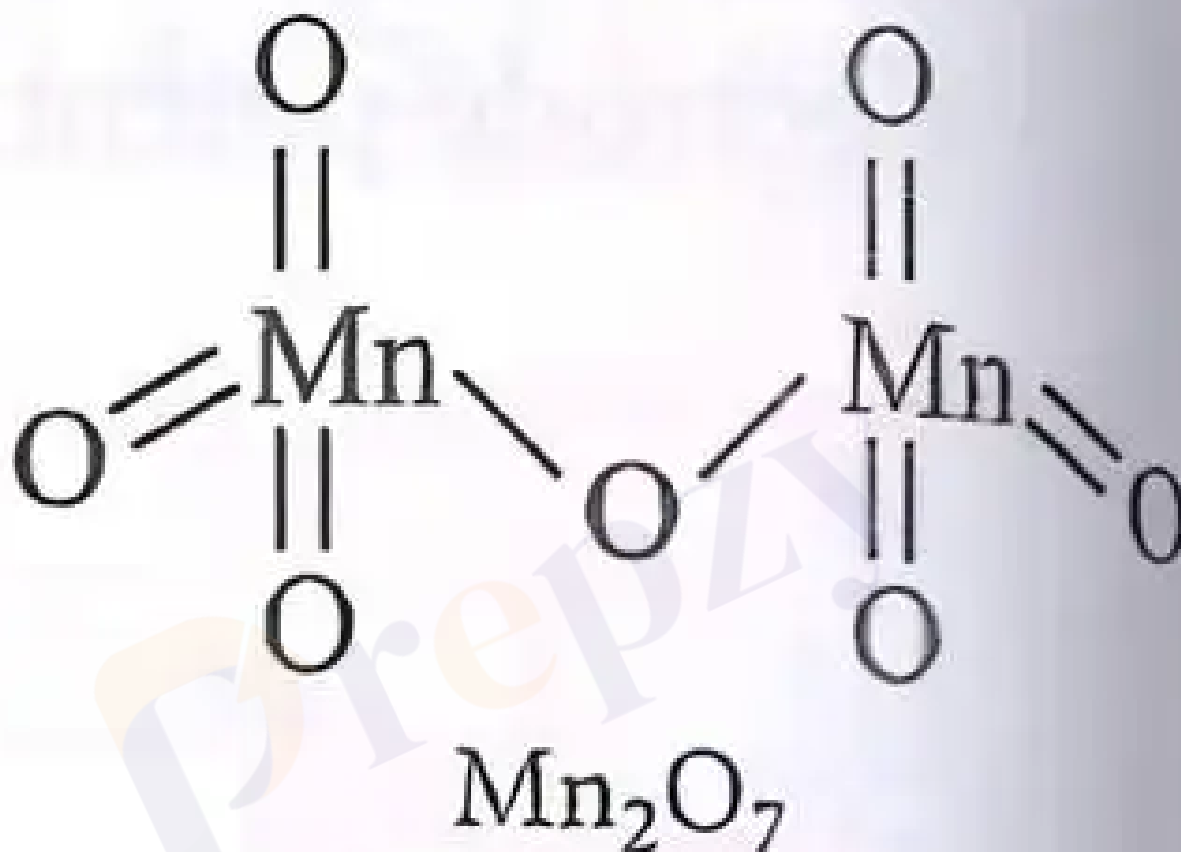
Halides

- Ti forms TiX_4 with oxidation state +4.
- Vanadium forms VF_5 (+5), chromium forms CrF_6 (+6).
- Mn does not form simple +7 halides; MnO_3F is known.
- Fluorine stabilises higher oxidation states via high lattice energy and bond enthalpy.
- CoF_3 stable due to high lattice enthalpy.
- VF_5 and CrF_6 stable due to high bond enthalpy.
- Vanadium pentahalide: only VF_5 known; others hydrolyse to VOX_3 .
- Cu(II) halides known except iodide; Cu^{2+} oxidises I^- to I_2 .
- Reaction: $2\text{Cu}^{2+}_{\text{aq}} + 4\text{I}^-_{\text{aq}} \rightarrow \text{Cu}_2\text{I}_{2\text{s}} + \text{I}_{2\text{s}}$
- Copper(I) compounds disproportionate: $2\text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{Cu}$
- Cu^{2+} more stable than Cu^+ in aqueous solution due to hydration enthalpy.

Oxides

- Highest oxidation number matches group number: Sc_2O_3 , TiO_2 , V_2O_5 , CrO_3 , Mn_2O_7 .
- No higher oxides beyond group 7 except Fe_2O_3 , Co_3O_4 .
- Oxocations like TiO^{2+} , VO_2^+ exist.

- Oxides more stable than fluorides at high oxidation states.
- Example: MnF_4 vs Mn_2O_7 .
- Oxygen forms multiple bonds, increasing oxide stability.
- Mn_2O_7 structure: each Mn tetrahedrally surrounded by O; Mn-O-Mn bridge present.
- Tetrahedral ions: VO_4^{3-} , CrO_4^{2-} , MnO_4^{3-} , MnO_4^{2-} , MnO_4^- .



Solved Examples

- Ex 1: Write the formula of the highest oxide of Mn.
Answer: Mn_2O_7
- Ex 2: Why are oxides more stable than fluorides at high oxidation states?
Oxygen forms multiple bonds with metals, increasing stability.

Practice Set

- Q1: Which halide shows highest oxidation state for vanadium?
A. VF_3 B. VF_4 C. VF_5 D. VCl_5
- Q2: What happens to copper(I) compounds in aqueous solution?
A. Stable B. Disproportionate C. Oxidised to Cu(II) D. Reduced to Cu metal
- Q3: Which oxide corresponds to Mn in +7 oxidation state?
A. MnO_2 B. Mn_2O_7 C. MnO_4^- D. MnO

Answer Key

- Q1: C - VF_5 is the only known pentahalide of vanadium(V).
- Q2: B - Copper(I) compounds disproportionate in aqueous solution.
- Q3: B - Mn_2O_7 is the highest oxide of Mn (+7 state).

Memory Aids

- Fluorides stabilise high oxidation states due to lattice and bond enthalpy.
- Cu(I) compounds disproportionate: $2\text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{Cu}$.
- Highest oxide formula matches group number for early transition metals.

Special Notes on Transition Elements

Key Points

- All transition elements are d-block elements.
- Zn, Cd, Hg are pseudo transition elements (not true transition metals).
- Anhydrous FeSO_4 and CuSO_4 are white due to no crystal field splitting despite unpaired electrons.
- Cu^{2+} ($3d^9$, $E^\circ = 0.34 \text{ V}$) is more stable than Cu^+ ($3d^{10}$, $E^\circ = 0.54 \text{ V}$) except with large anions.
- Examples: CuI more stable than CuI_2 , CuCN more stable than Cu(CN)_2 .
- W (atomic no. 74) has highest melting point (3410°C) among d-block; Hg (80) has lowest (-38.9°C).

Solved Examples

- Ex 1: Why are anhydrous FeSO_4 and CuSO_4 white?
No crystal field splitting in absence of water.
- Ex 2: Which d-block element has the highest melting point?
Answer: Tungsten (W), 3410°C .

Practice Set

- Q1: Which is NOT a true transition metal?
A. Fe B. Zn C. Ni D. Co
- Q2: Why is Cu^{2+} more stable than Cu^+ in aqueous solution?
A. Lower ionisation energy B. Higher hydration enthalpy C. Larger size D. More unpaired electrons
- Q3: Which element has the lowest melting point among d-block?
A. W B. Hg C. Fe D. Cu

Answer Key

- Q1: B - Zn is a pseudo transition metal.
- Q2: B - Cu^{2+} has higher hydration enthalpy stabilising it.
- Q3: B - Mercury (Hg) has the lowest melting point (-38.9°C).

Memory Aids

- Zn, Cd, Hg = pseudo transition metals.
- W highest melting point; Hg lowest in d-block.
- Cu^{2+} more stable than Cu^+ except with large anions.

Some Important Compounds of Transition Elements

Oxides and Oxoanions of Metals

- Transition metals form oxides with oxygen at high temperatures; formula MO up to Mn (except Sc).
- Highest oxidation number in oxides equals group number.
- Examples: Sc_2O_3 , Cr_2O_3 , TiO_2 , Mn_2O_7 , V_2O_5 .
- After Mn, only Fe_2O_3 and Co_3O_4 higher oxides known.
- Covalent character and acidic nature increase with metal oxidation state.
- Examples: V_2O_5 , Cr_2O_3 , Mn_2O_7 have low melting points; Mn_2O_7 is covalent green oil.
- Oxide acidity trend: V_2O_3 (basic), V_2O_4 (less basic), V_2O_5 (amphoteric).
- V_2O_5 reacts with alkali and acid:
 - $\text{V}_2\text{O}_5 + 6\text{NaOH} \rightarrow 2\text{Na}_3\text{VO}_4 + 3\text{H}_2\text{O}$
 - $\text{V}_2\text{O}_5 + 2\text{HCl} \rightarrow 2\text{VO}_2\text{Cl} + \text{H}_2\text{O}$
- CrO is basic; Cr_2O_3 amphoteric; CrO_3 and Mn_2O_7 acidic, forming acids in water:
 - $\text{CrO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CrO}_4$
 - $\text{Mn}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow 2\text{HMnO}_4$
 - $2\text{CrO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{Cr}_2\text{O}_7$

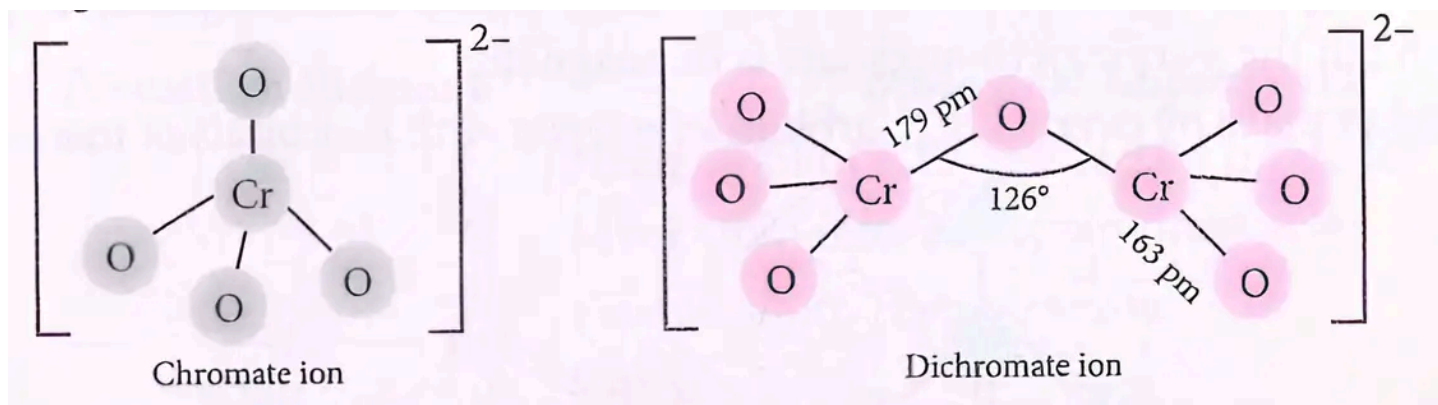
Potassium Dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$)

Preparation

- Obtained by fusion of chromite ore (FeCr_2O_4):
- $4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \rightarrow 8\text{Na}_2\text{CrO}_4 + \text{Fe}_2\text{O}_3 + 8\text{CO}_2$
- $\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{KCl} \rightarrow \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NaCl}$

Structure

- Chromate ion (CrO_4^{2-}) is tetrahedral.
- Dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) consists of two tetrahedra sharing one corner; Cr-O-Cr bond angle 126° .



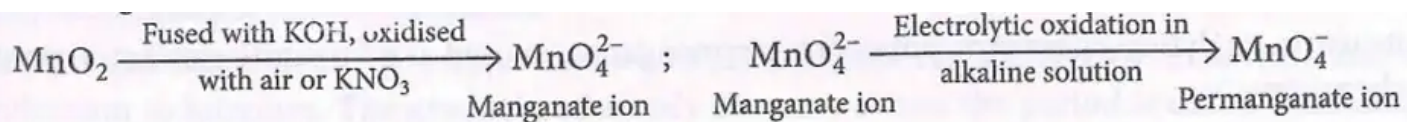
Properties

- Orange crystals, moderately soluble in cold water, readily soluble in hot water.
- In aqueous solution, equilibrium between dichromate and chromate ions:
 - $\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{CrO}_4^{2-} + 2\text{H}^+$
- In alkaline medium, equilibrium shifts forward (yellow solution): $\text{Cr}_2\text{O}_7^{2-} + 2\text{OH}^- \rightarrow 2\text{CrO}_4^{2-} + \text{H}_2\text{O}$
- In acidic medium, equilibrium shifts backward (orange solution): $2\text{CrO}_4^{2-} + 2\text{H}^+ \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$
- Strong oxidising agent in acidic medium:
 - $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$
 - Oxidises I^- to I_2 , H_2S to S , Sn^{2+} to Sn^{4+} , Fe^{2+} to Fe^{3+} .
- Chromyl chloride test: Metal chloride + $\text{K}_2\text{Cr}_2\text{O}_7$ + conc. $\text{H}_2\text{SO}_4 \rightarrow$ red vapours of CrO_2Cl_2 .
- Reaction: $\text{K}_2\text{Cr}_2\text{O}_7 + 4\text{KCl} + 6\text{H}_2\text{SO}_4 \rightarrow 2\text{CrO}_2\text{Cl}_2 + 6\text{KHSO}_4 + 3\text{H}_2\text{O}$

Potassium Permanganate (KMnO_4)

Preparation

- Prepared from pyrolusite ore (MnO_2): $2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 \rightarrow 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$
- K_2MnO_4 converted to KMnO_4 by:
 - Electrochemical oxidation: $\text{MnO}_4^{2-} \rightarrow \text{MnO}_4^- + \text{e}^-$ (green to purple)
 - In acidic/neutral medium, manganate disproportionates: $3\text{MnO}_4^{2-} + 4\text{H}^+ \rightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}$
- Commercially prepared by alkaline fusion of MnO_2 followed by electrolytic oxidation.

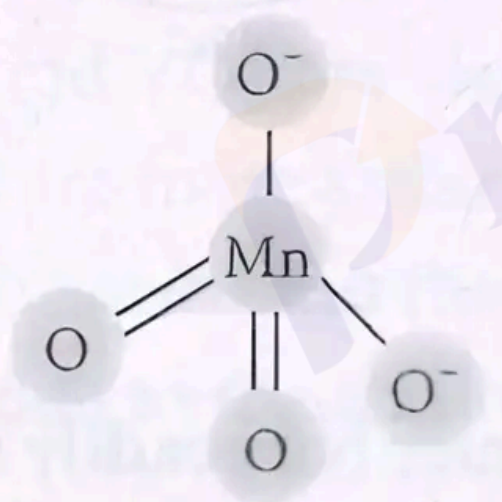


Laboratory Preparation

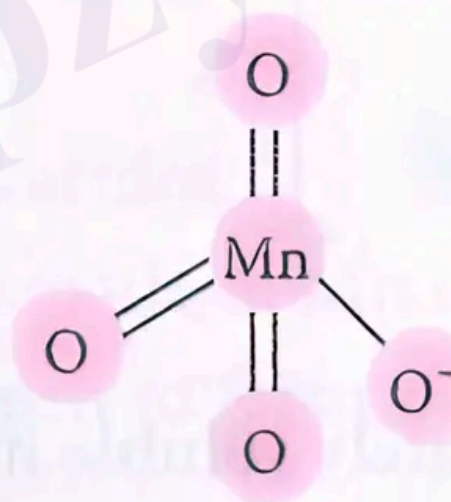
- Mn^{2+} salt oxidised by peroxodisulphate: $2\text{Mn}^{2+} + 5\text{S}_2\text{O}_8^{2-} + 8\text{H}_2\text{O} \rightarrow 2\text{MnO}_4^- + 10\text{SO}_4^{2-} + 16\text{H}^+$

Structure

- Manganate and permanganate ions are tetrahedral.
- Manganate (green) is paramagnetic (1 unpaired electron); permanganate (purple) is diamagnetic.
- π -bonding via overlap of oxygen p-orbitals with manganese d-orbitals.



Tetrahedral manganate ion (green)



Tetrahedral permanganate ion (purple)

Properties

- Dark purple crystals, sparingly soluble in water, decomposes at 513 K: $2\text{KMnO}_4 \rightarrow \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$
- Strong oxidising agent in acidic and alkaline medium.

- In acidic medium: $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
- Oxidises I^- to I_2 , Fe^{2+} to Fe^{3+} , oxalate to CO_2 , H_2S to S , sulphite to sulphate, nitrite to nitrate.
- In neutral/faintly alkaline medium: $\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$
- Used in volumetric titrations with dilute H_2SO_4 (not HCl or HNO_3).

Uses

- Analytical chemistry and organic synthesis oxidant.
- Bleaching of wool, cotton, silk, and textiles.
- Decolourisation of oils.

Biological importance of some transition elements :

Transition Element	Biological Importance
Fe	Haemoglobin (Oxygen carrier in blood) Myoglobin (Stores oxygen in muscle)
Cu	Plastocyanin, Haemocyanin
Co	Vitamin B ₁₂
Zn	Carbonic anhydrase

The Inner Transition Elements (f-Block)

Definition and Series

- Elements with last electron entering f-orbital are f-block or inner transition elements.
- Consist of lanthanoids (14 elements after lanthanum) and actinoids (14 elements after actinium).

Lanthanoids Overview

Electronic Configurations

- Common outer configuration: $6s^2$
- Variable 4f electron occupancy: $4f^n$ (n=1 to 14)
- Most stable oxidation state: +3 (tripositive ions)

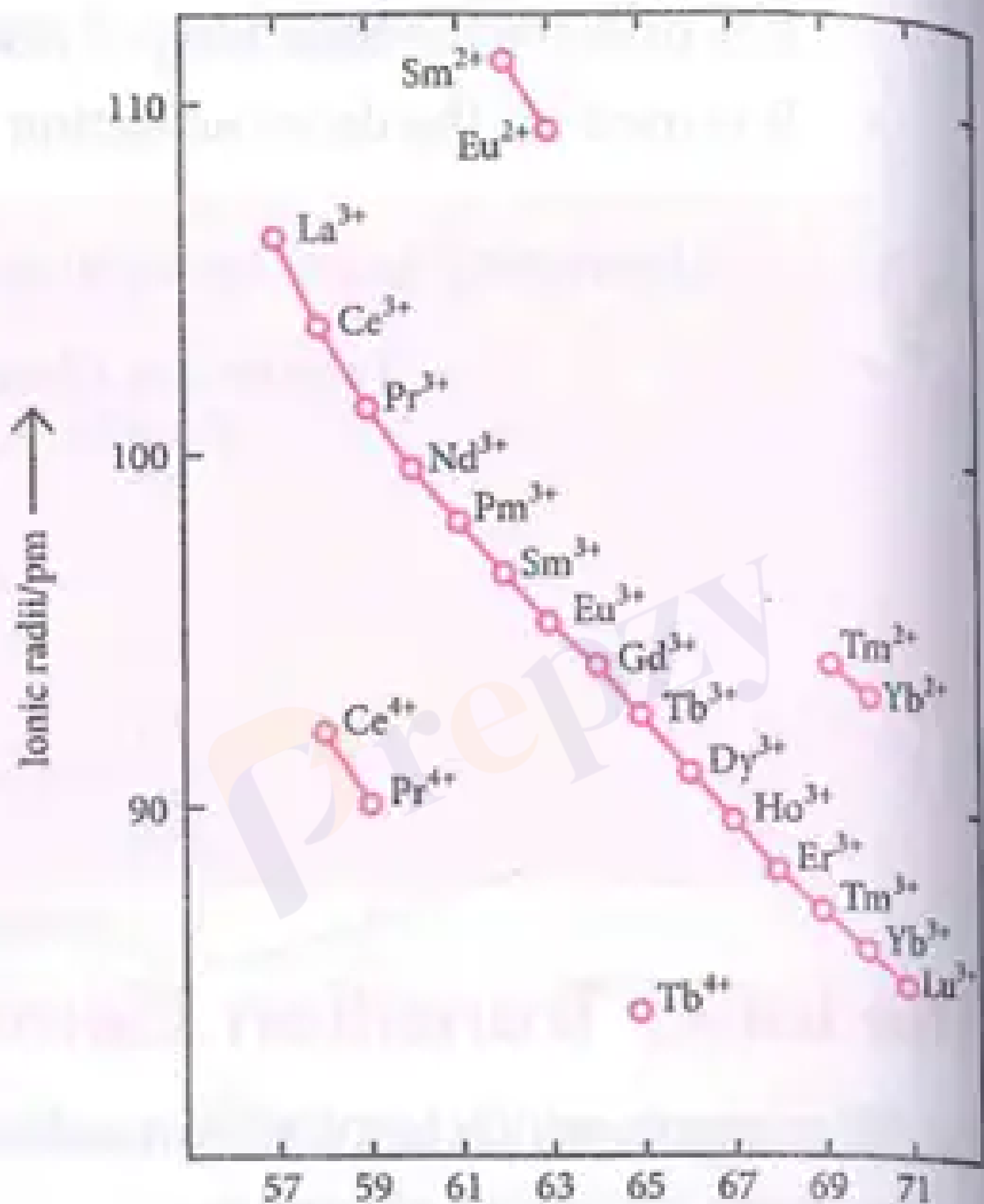
Electronic Configurations and Radii of Lanthanum and Lanthanoids

Atomic Number	Name	Symbol	Electronic Configurations*			Radii/pm		
			Ln	Ln ²⁺	Ln ³⁺	Ln ⁴⁺	Ln	Ln ³⁺
57	Lanthanum	La	$5d^1 6s^2$	$5d^1$	$4f^0$		187	106
58	Cerium	Ce	$4f^1 5d^1 6s^2$	$4f^2$	$4f^1$	$4f^0$	183	103
59	Praseodymium	Pr	$4f^3 6s^2$	$4f^3$	$4f^2$	$4f^1$	182	101
60	Neodymium	Nd	$4f^4 6s^2$	$4f^4$	$4f^3$	$4f^2$	181	99
61	Promethium	Pm	$4f^5 6s^2$	$4f^5$	$4f^4$		181	98
62	Samarium	Sm	$4f^6 6s^2$	$4f^6$	$4f^5$		180	96
63	Europium	Eu	$4f^7 6s^2$	$4f^7$	$4f^6$		199	95
64	Gadolinium	Gd	$4f^7 5d^1 6s^2$	$4f^7 5d^1$	$4f^7$		180	94
65	Terbium	Tb	$4f^9 6s^2$	$4f^9$	$4f^8$	$4f^7$	178	92
66	Dysprosium	Dy	$4f^{10} 6s^2$	$4f^{10}$	$4f^9$	$4f^8$	177	91
67	Holmium	Ho	$4f^{11} 6s^2$	$4f^{11}$	$4f^{10}$		176	89
68	Erbium	Er	$4f^{12} 6s^2$	$4f^{12}$	$4f^{11}$		175	88
69	Thulium	Tm	$4f^{13} 6s^2$	$4f^{13}$	$4f^{12}$		174	87
70	Ytterbium	Yb	$4f^{14} 6s^2$	$4f^{14}$	$4f^{13}$		173	86
71	Lutetium	Lu	$4f^{14} 5d^1 6s^2$	$4f^{14} 5d^1$	$4f^{14}$	–	–	–

* Only electrons outside [Xe] core are indicated.

Atomic and Ionic Sizes

- Atomic and ionic radii decrease from La to Lu (lanthanoid contraction)
- 4f electrons poorly shield nuclear charge, increasing effective nuclear charge
- Atomic radii decrease irregularly; ionic radii decrease regularly



Atomic number →
Trends in ionic radii of lanthanoids

Oxidation States

- Predominant oxidation state: +3
- +2 and +4 states occur due to stable empty ($4f^0$), half-filled ($4f^7$), and fully-filled ($4f^{14}$) subshells
- Examples: Ce^{4+} ($4f^0$), Eu^{2+} ($4f^7$), Tb^{4+} ($4f^7$), Yb^{2+} ($4f^{14}$)
- Ce^{4+} is a strong oxidant, $E^\circ = 1.74 \text{ V}$, slow water oxidation
- Pr, Nd, Tb, Dy show +4 only in oxides (MO_2)
- Eu^{2+} and Yb^{2+} are strong reductants
- Samarium shows both +2 and +3 states

General Characteristics

- Silvery white, soft metals; tarnish in moist air
- Burn in oxygen to form Ln_2O_3 type oxides
- Hardness increases with atomic number; samarium is very hard
- Melting points mostly 1000-1200 K; samarium melts at 1623 K
- Good conductors of heat and electricity
- Density changes smoothly except for Eu, Yb, Sm, Tm
- Colored ions due to f-f transitions; La^{3+} and Lu^{3+} are colorless
- La^{3+} and Lu^{3+} are diamagnetic; others paramagnetic
- Ionisation enthalpies: 1st $\sim 600 \text{ kJ/mol}$, 2nd $\sim 1200 \text{ kJ/mol}$, 3rd irregular
- Standard electrode potentials: $E^\circ(\text{Ln}^{3+}/\text{Ln}) \sim -2.2 \text{ to } -2.4 \text{ V}$ (Eu exception: -2.0 V)

Chemical Behaviour

- React with H_2 on heating to form hydrides
- Form carbides (Ln_3C , LnC_2 , Ln_2C_3) with carbon on heating
- React with dilute acids to liberate H_2 : $2\text{Ln} + 6\text{H}^+ \rightarrow 2\text{Ln}^{3+} + 3\text{H}_2$
- Burn in halogens to form halides: $2\text{Ln} + 3\text{X}_2 \rightarrow 2\text{LnX}_3$
- Burn in oxygen to form oxides: $4\text{Ln} + 3\text{O}_2 \rightarrow 2\text{Ln}_2\text{O}_3$
- Form basic oxides and hydroxides: M_2O_3 and $\text{M}(\text{OH})_3$

Solved Examples

Ex 1: Explain why Ce^{4+} is a strong oxidant but reacts slowly with water.

- Ce^{4+} has noble gas configuration ($4f^0$), making it stable.
- Standard electrode potential $E^\circ = 1.74 \text{ V}$ indicates strong oxidizing power.
- Slow reaction with water due to kinetic factors despite thermodynamic favorability.

Practice Set

- **Q1:** Which lanthanoid ion is colorless due to fully filled 4f orbitals?
A. Eu^{3+}
B. La^{3+}
C. Gd^{3+}
D. Tb^{3+}
- **Q2:** What causes the lanthanoid contraction?
A. Poor shielding by 4f electrons
B. Increase in atomic mass
C. Increase in 5d electron count
D. Decrease in nuclear charge
- **Q3:** Which lanthanoid shows both +2 and +3 oxidation states?
A. Samarium
B. Cerium
C. Ytterbium
D. Terbium

Answer Key

- **Q1:** B. La^{3+} - Has empty $4f^0$ orbitals, colorless ion.
- **Q2:** A. Poor shielding by 4f electrons - Leads to increased effective nuclear charge and contraction.
- **Q3:** A. Samarium - Exhibits both +2 and +3 oxidation states.

Memory Aids

- Lanthanoid contraction: Poor 4f shielding → radius decreases
- Stable oxidation states: Empty ($4f^0$), half-filled ($4f^7$), full ($4f^{14}$)
- Colorless ions: La^{3+} ($4f^0$), Lu^{3+} ($4f^{14}$)
- Samarium: Only lanthanoid with +2 and +3 states

Actinoids Overview

General Information

- Actinoids include 14 elements from Thorium (Th) to Lawrencium (Lr).
- They are radioactive elements.
- General electronic configuration: $5f^{0-14} 6d^{0-2} 7s^2$.
- Electrons fill 5f orbitals except Thorium ($Z=90$), with irregularities due to extra stability at f^0 , f^7 , and f^{14} configurations.

Electronic Configuration and Properties

- 5f orbitals extend beyond 6s and 6p orbitals, unlike 4f orbitals which are buried deep.
- Actinoid contraction is greater than lanthanoids due to poor shielding by 5f electrons.
- Ionic radii decrease regularly across the series.
- Most common oxidation state is +3; others include +4, +5, +6, +7 (e.g., Th, Pa, U, Np).
- Small energy gap between 5f, 6d, and 7s subshells allows multiple oxidation states.

Some Properties of Actinium and Actinoids

Atomic Number	Name	Symbol	Electronic Configurations*			Radii/pm	
			M	M^{3+}	M^{4+}	M^{3+}	M^{4+}
89	Actinium	Ac	$6d^1 7s^2$	$5f^0$		111	
90	Thorium	Th	$6d^2 7s^2$	$5f^1$	$5f^0$		99
91	Protactinium	Pa	$5f^2 6d^1 7s^2$	$5f^2$	$5f^1$		96
92	Uranium	U	$5f^3 6d^1 7s^2$	$5f^3$	$5f^2$	103	93
93	Neptunium	Np	$5f^4 6d^1 7s^2$	$5f^4$	$5f^3$	101	92
94	Plutonium	Pu	$5f^6 7s^2$	$5f^5$	$5f^4$	100	90
95	Americium	Am	$5f^7 7s^2$	$5f^6$	$5f^5$	99	89
96	Curium	Cm	$5f^7 6d^1 7s^2$	$5f^7$	$5f^6$	99	88
97	Berkelium	Bk	$5f^9 7s^2$	$5f^8$	$5f^7$	98	87
98	Californium	Cf	$5f^{10} 7s^2$	$5f^9$	$5f^8$	98	86
99	Einsteinium	Es	$5f^{11} 7s^2$	$5f^{10}$	$5f^9$	–	–
100	Fermium	Fm	$5f^{12} 7s^2$	$5f^{11}$	$5f^{10}$	–	–
101	Mendelevium	Md	$5f^{13} 7s^2$	$5f^{12}$	$5f^{11}$	–	–
102	Nobelium	No	$5f^{14} 7s^2$	$5f^{13}$	$5f^{12}$	–	–
103	Lawrencium	Lr	$5f^{14} 6d^1 7s^2$	$5f^{14}$	$5f^{13}$	–	–

* Only electrons outside [Rn] core are indicated.

Solved Examples

- Ex 1:** Write the general electronic configuration of actinoids.

Answer: $5f^{0-14} 6d^{0-2} 7s^2$.

- Ex 2:** Why do actinoids show multiple oxidation states?

Answer: Due to small energy differences between 5f, 6d, and 7s subshells.

Practice Set

- Q1: Which element starts the actinoid series?
 - Actinium
 - Thorium
 - Uranium
 - Lawrencium
- Q2: What is the most common oxidation state of actinoids?
 - +2
 - +3
 - +4
 - +5

Solved Examples

- **Ex 1:** Identify the highest oxidation state of Neptunium.
Answer: +7.
- **Ex 2:** Which oxidation state is common to all actinoids?
Answer: +3.

Practice Set

- Q1: Which actinoid shows +7 oxidation state?
A. Thorium
B. Protactinium
C. Uranium
D. Neptunium
- Q2: What is the common oxidation state for all actinoids?
A. +2
B. +3
C. +4
D. +5
- Q3: Why do actinoids show multiple oxidation states?
A. Large energy gap between subshells
B. Small energy gap between 5f, 6d, 7s
C. Only 5f electrons involved
D. Due to radioactive nature

Answer Key

- Q1: D - Neptunium shows +7 oxidation state.
- Q2: B - +3 is common to all actinoids.
- Q3: B - Small energy gap between 5f, 6d, and 7s subshells allows multiple states.

Memory Aids

- +3 oxidation state is universal in actinoids.
- Higher states (+4 to +7) appear in early actinoids (Th, Pa, U, Np).

- Small subshell energy gaps enable variable oxidation states.

General Characteristics

Physical and Chemical Properties

- Silvery white metals, tarnish rapidly in air forming oxide coating.
- Not attacked by alkalis; less reactive towards acids.
- Colored ions due to f-f transitions except Ac^{3+} ($5f^0$), Cm^{3+} ($5f^7$), Th^{4+} ($5f^0$) which are colorless.
- Strongly paramagnetic.
- High densities except Thorium and Americium.
- High melting and boiling points with no regular trend.
- Low ionization energies.
- Strong reducing agents.
- Highly electropositive metals.

Difference between lanthanoids and actinoids :

Lanthanoids	Actinoids
They show +2 and +4 oxidation states in few cases besides +3.	They show higher oxidation states of +4, +5, +6 and +7 besides +3.
Except promethium, they are non-radioactive.	All actinoids are radioactive.
They do not form oxo-cations.	They form oxo-cations like UO_2^{2+} , PuO_2^{2+} , UO_2^+ , etc.
The compounds of lanthanoids are less basic.	Actinoid compounds are more basic.
They have less tendency of complex formation.	They have greater tendency of complex formation.

Solved Examples

- **Ex 1:** Why are most actinoid ions colored?
Answer: Due to f-f electronic transitions.
- **Ex 2:** Which actinoid ions are colorless?
Answer: Ac^{3+} , Cm^{3+} , Th^{4+} .

Practice Set

- Q1: What happens to actinoids in air?
 - A. Remain shiny
 - B. Tarnish forming oxide coating
 - C. React violently
 - D. Dissolve
- Q2: Which actinoid ions are colorless?
 - A. Ac^{3+} , Cm^{3+} , Th^{4+}
 - B. All actinoid ions
 - C. Only Ac^{3+}
 - D. None
- Q3: What is the magnetic property of actinoids?
 - A. Diamagnetic
 - B. Paramagnetic
 - C. Ferromagnetic
 - D. Non-magnetic

Answer Key

- Q1: B - Actinoids tarnish rapidly forming oxide coating.
- Q2: A - Ac^{3+} , Cm^{3+} , Th^{4+} are colorless due to electronic configuration.
- Q3: B - Actinoids are strongly paramagnetic.

Memory Aids

- Actinoids tarnish in air forming oxide layers.
- Colorless ions: Ac^{3+} , Cm^{3+} , Th^{4+} .
- Strongly paramagnetic due to unpaired f electrons.

Applications of d- and f-Block Elements

Key Industrial Uses

- Iron and steel: Primary materials in construction.
- TiO_2 : Used as a white pigment in paints and coatings.
- MnO_2 , Zn, Ni, Cd: Essential components in battery manufacturing.
- Cu, Ag, Au: Used for coins and ornamental purposes due to their malleability and luster.
- V_2O_5 : Catalyst in the production of sulphuric acid.
- TiCl_4 with $\text{Al}(\text{CH}_3)_3$: Catalyst system for polythene synthesis.
- Iron catalyst: Used in Haber's process to synthesize ammonia (NH_3).
- Ni catalyst: Facilitates hydrogenation of fats to produce saturated fats.
- Ni complexes: Catalyze polymerization of alkynes and other organic compounds.
- PdCl_2 : Catalyst in Wacker's process converting ethyne (C_2H_2) to ethanal (CH_3CHO).
- AgBr: Light-sensitive compound used in photographic films.
- Neodymium and praseodymium oxides: Used in colored glasses for goggles, absorbing yellow sodium light, protecting glass blowers.

Solved Examples

- **Ex 1:** Write the catalyst used in the Haber process.
Answer: Iron catalyst (Fe).
- **Ex 2:** Identify the catalyst for hydrogenation of fats.
Answer: Nickel (Ni) catalyst.
- **Ex 3:** Name the catalyst used in Wacker's process.
Answer: Palladium chloride (PdCl_2).

Practice Set

- **Q1:** Which element is primarily used in the manufacture of steel?
A. Copper
B. Iron
C. Nickel
D. Zinc

- **Q2:** TiO_2 is mainly used in which industry?
A. Battery
B. Pigment
C. Photographic
D. Polymer
- **Q3:** Which catalyst is used in the oxidation of ethyne to ethanal?
A. Iron
B. Nickel
C. Palladium chloride
D. Vanadium pentoxide

Answer Key

- **Q1:** B. Iron - Iron is the main element in steel production.
- **Q2:** B. Pigment - TiO_2 is widely used as a white pigment.
- **Q3:** C. Palladium chloride - PdCl_2 catalyzes Wacker's process.

Memory Aids

- Iron = Steel (Construction)
- TiO_2 = White pigment
- MnO_2 , Zn, Ni, Cd = Batteries
- Cu, Ag, Au = Coins & Ornaments
- V_2O_5 = Sulphuric acid catalyst
- $\text{TiCl}_4 + \text{Al}(\text{CH}_3)_3$ = Polythene catalyst
- Fe = Haber's process (NH_3)
- Ni = Hydrogenation of fats
- PdCl_2 = Wacker's process
- AgBr = Photographic films
- Nd, Pr oxides = Colored goggles