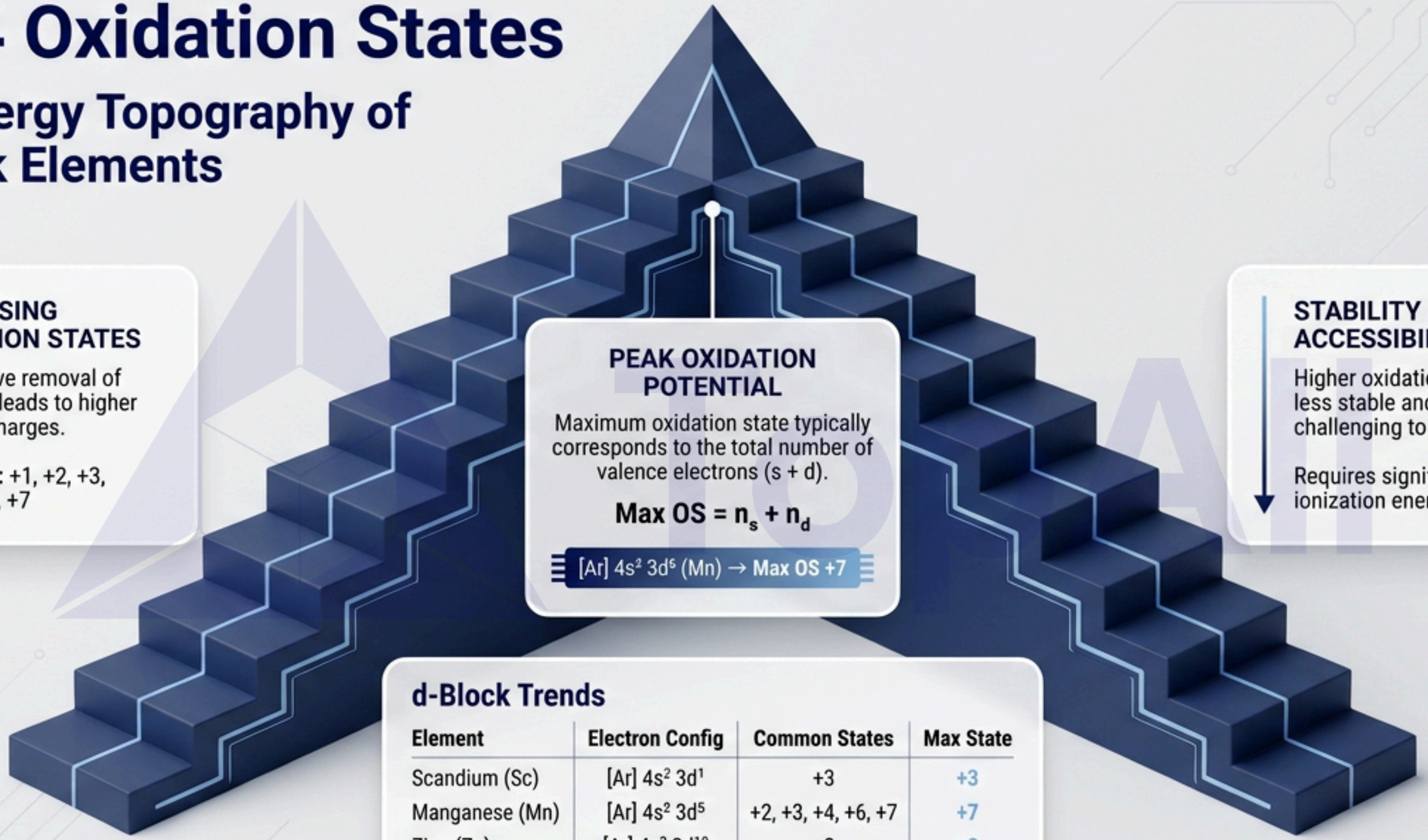
4.3.4 Oxidation States

The Energy Topography of d-Block Elements



INCREASING OXIDATION STATES

Progressive removal of electrons leads to higher positive charges.

Examples: +1, +2, +3, +4, +5, +6, +7

PEAK OXIDATION POTENTIAL

Maximum oxidation state typically corresponds to the total number of valence electrons (s + d).

$$\text{Max OS} = n_s + n_d$$

[Ar] $4s^2$ $3d^5$ (Mn) → **Max OS +7**

STABILITY & ACCESSIBILITY

Higher oxidation states are less stable and more challenging to achieve.

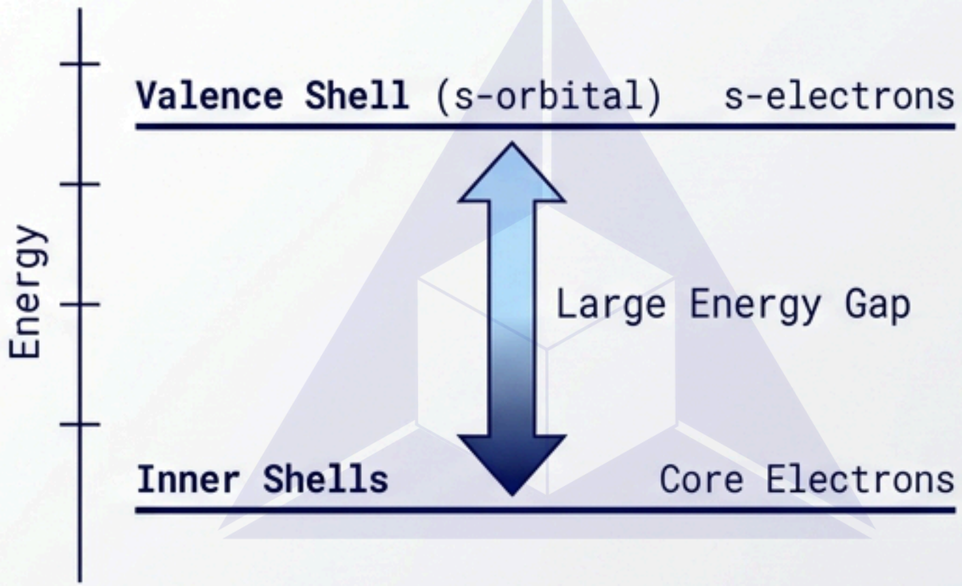
Requires significant ionization energy input.

d-Block Trends

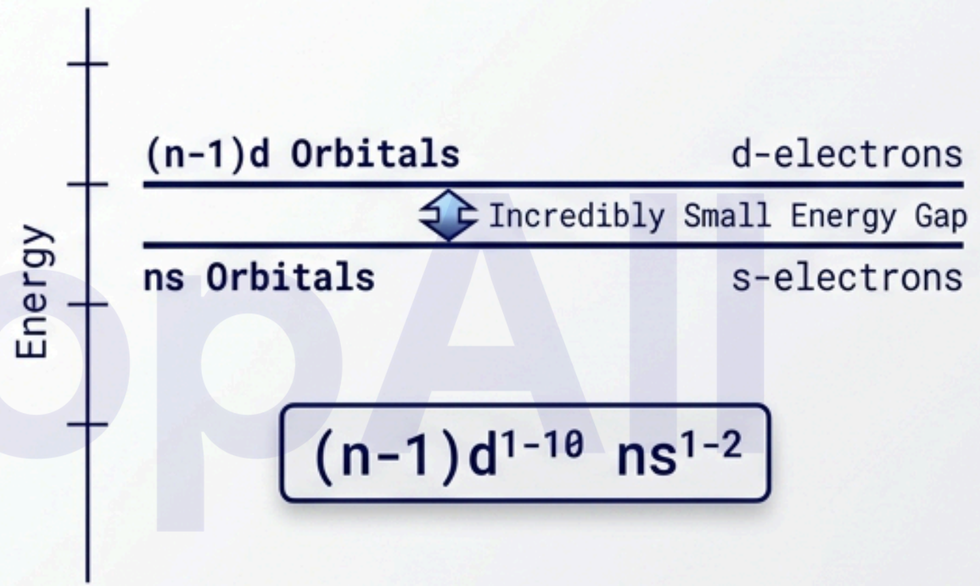
Element	Electron Config	Common States	Max State
Scandium (Sc)	[Ar] $4s^2$ $3d^1$	+3	+3
Manganese (Mn)	[Ar] $4s^2$ $3d^5$	+2, +3, +4, +6, +7	+7
Zinc (Zn)	[Ar] $4s^2$ $3d^{10}$	+2	+2

Note: Middle elements (e.g., Mn, Fe) exhibit the widest range of oxidation states.

The Mechanics of Variable States



Fixed States. Large energy gap prevents inner electron loss.



Variable oxidation states arise because the energy difference between (n-1)d and ns orbitals is exceptionally small.

Note: Both s and d electrons can be shared or lost during bond formation.

The Oxidation Matrix: 3d Series Trends



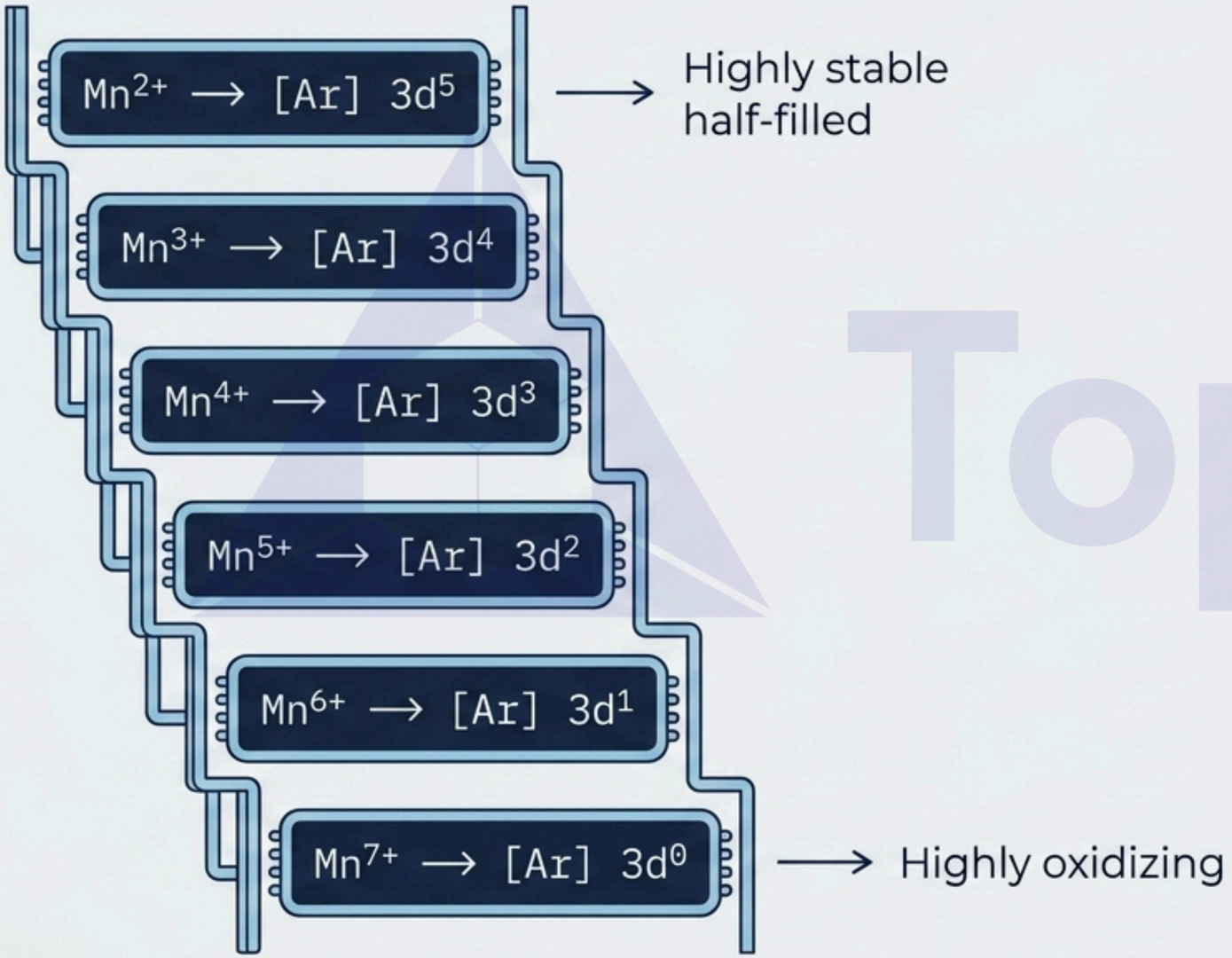
Calculating Maximum Oxidation States

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Element	Sum of (s + d) electrons	Max Oxidation State	Typical Species
Ti	4	+4	$Ti^{IV}O_2$
V	5	+5	$V^{V}O_2^{+}$
Cr	6	+6	$Cr^{VI}O_4^{2-}$
Mn	7	+7	$Mn^{VII}O_4^{-}$

The **maximum oxidation state** of reasonable stability corresponds exactly to the sum of the s and d electrons up to Manganese. After Mn, stability of higher states drops abruptly.

The Manganese Ladder



Key Insight

Manganese exhibits the greatest number of oxidation states in the 3d series because it has the maximum number of unpaired electrons to share/lose.

The Ligand Battle: Oxygen vs. Fluorine

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Fluorine

Max state achieved: MnF_4 (+4)

Mechanism: Stabilizes via high lattice energy or high single-bond enthalpy.



Strong Single Covalent Bond

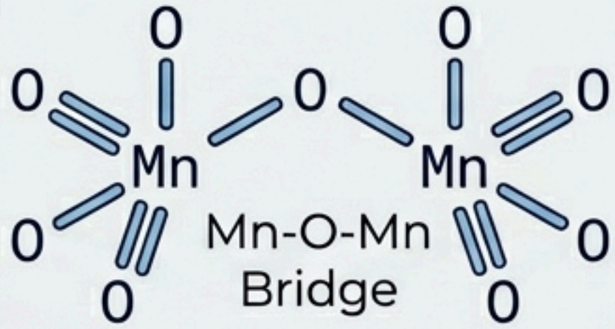
VS

Oxygen

Oxygen exceeds Fluorine in stabilizing the highest states due to multiple bond formation.

Max state achieved: Mn_2O_7 (+7)

Mechanism: Superior ability to form multiple bonds (pπ-dπ overlap).







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Thermodynamic Stability Markers

d^0 (Noble Gas Core)

Example: Sc^{3+}

Highly stable, unreactive.

E° value is deeply **negative**.

d^5 (Half-Filled)

Example: Mn^{2+} vs Fe^{2+}

Mn^{2+} is much more stable towards oxidation to +3 because the d^5 configuration is exceptionally stable.

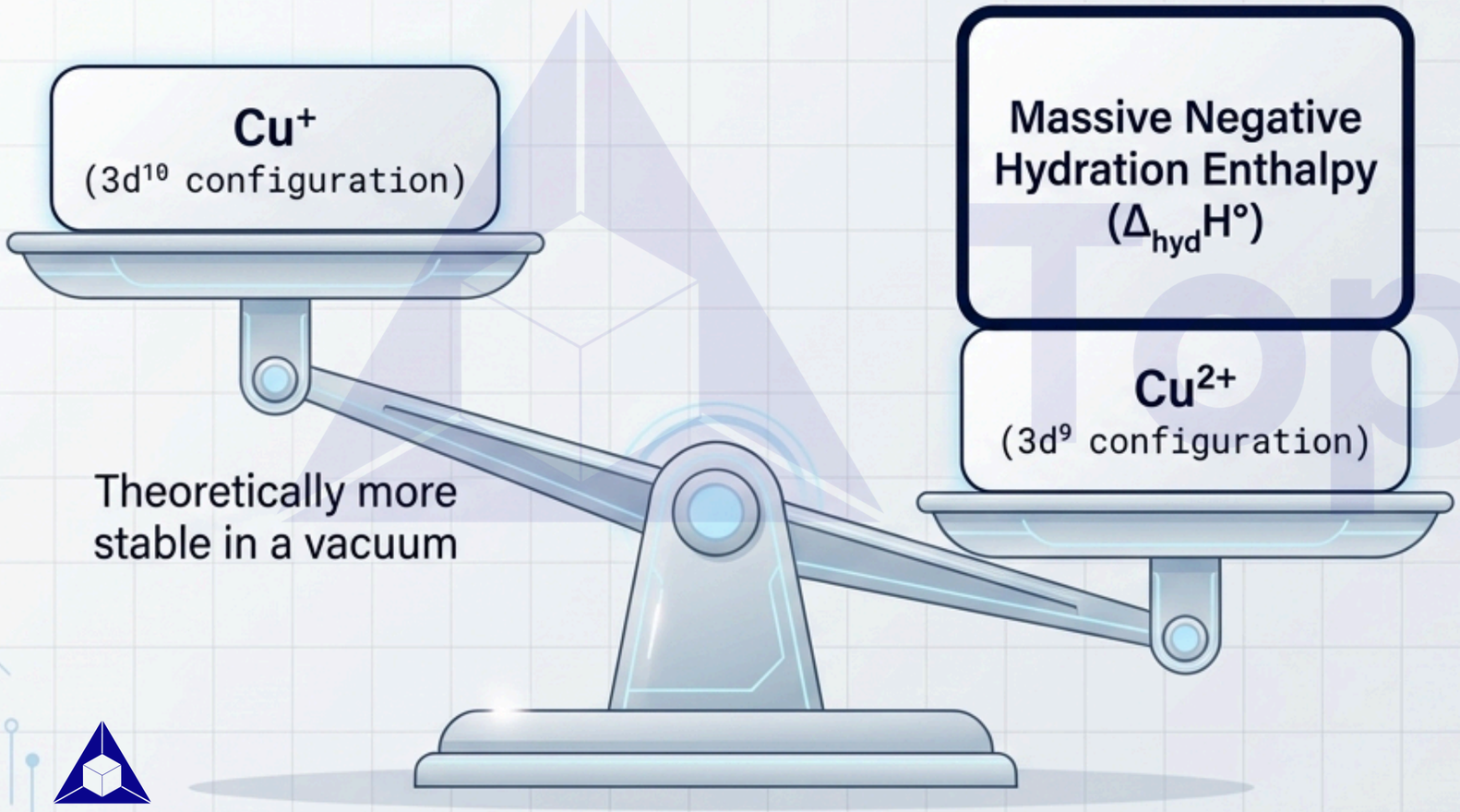
d^{10} (Fully Filled)

Example: Zn^{2+}

Exhibits the **highest E°** value due to the **extreme stability** of the **completely full subshell**.

Exam Alert: The relative stabilities of oxidation states are ultimately governed by electrode potentials (E°), which correlate heavily with these three subshell configurations.

The Copper Anomaly in Aqueous Solutions



Explanation

Why is Cu^+ unstable in aqueous solution?

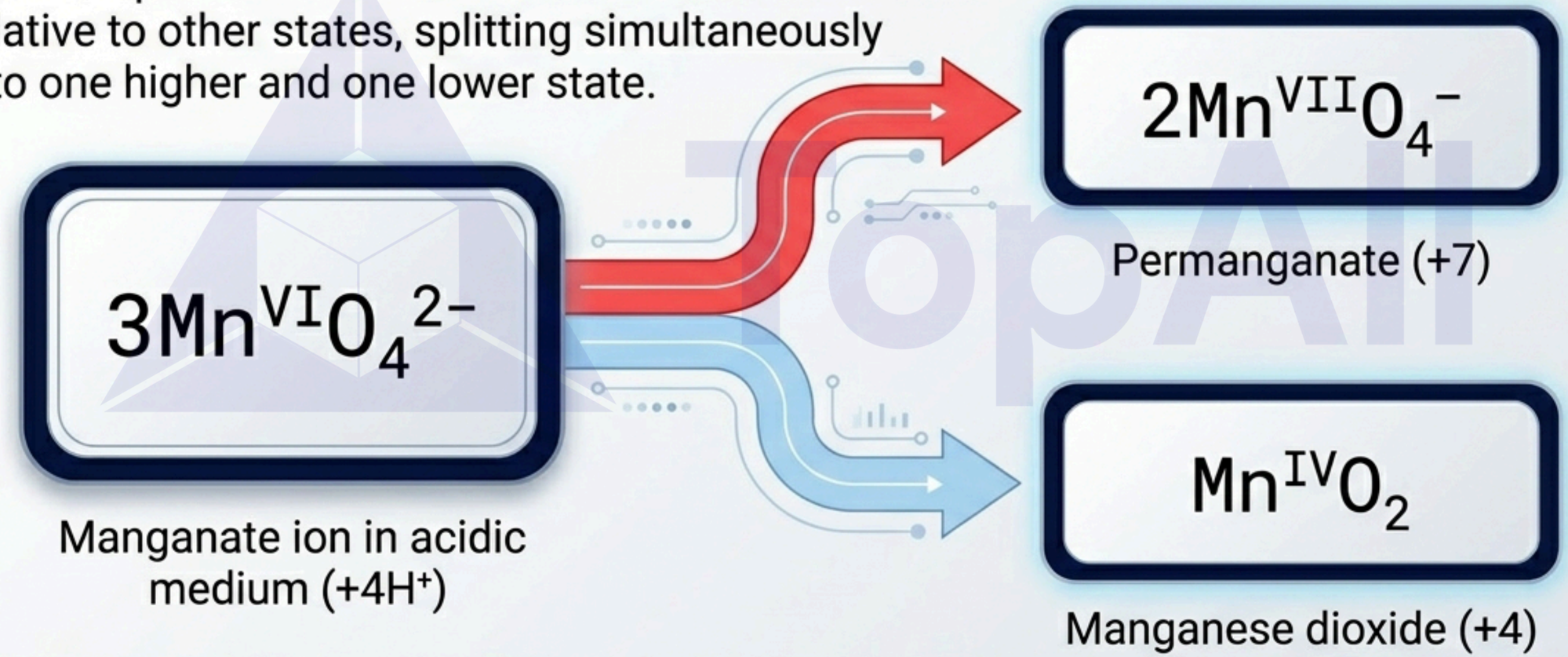
The much higher hydration enthalpy of Cu^{2+} more than compensates for the second ionization energy required to break the d^{10} configuration.

$$2Cu^+ (aq) \rightarrow Cu^{2+} (aq) + Cu (s)$$

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Disproportionation: When States Collapse

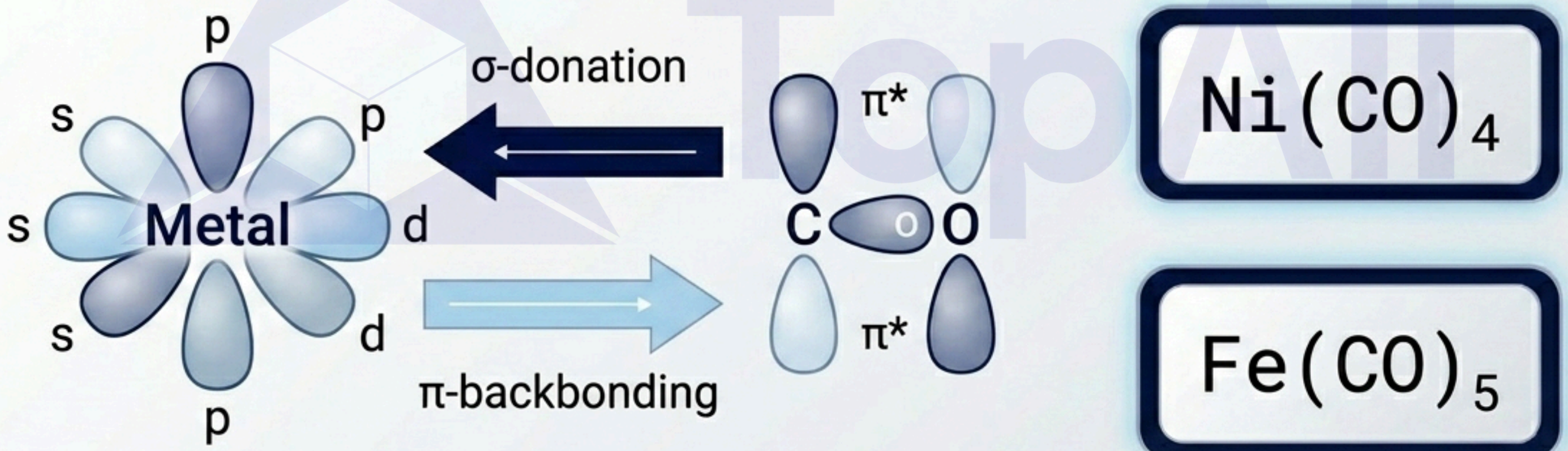
When a specific oxidation state becomes less stable relative to other states, splitting simultaneously into one higher and one lower state.



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Zero Oxidation States

Low or zero oxidation states are possible when complex compounds have ligands capable of **π-acceptor character** (in addition to σ-bonding).



$Ni(CO)_4$

$Fe(CO)_5$

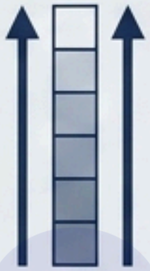
Vertical Trends: The Heavier Member Rule

p-block Trends

Lower oxidation states are favoured by heavier members (Inert Pair Effect).



d-block Trends (Group 6 Focus)



Higher oxidation states are favoured by heavier members.

Evidence Box

- **Chromium (Cr):** Cr(VI) in dichromate is highly unstable and acts as a strong oxidizing agent in acid.
- **Molybdenum & Tungsten (Mo, W):** Mo(VI) in MoO_3 and W(VI) in WO_3 are highly stable and are not oxidizing agents.

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Inner Transition Metals (f-block)

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Lanthanoids

- Exceptions: Ce(+4) due to f^0 core, Eu(+2) due to f^7 core.

Shared

- Overwhelmingly prefer the +3 oxidation state.

Actinoids

- Exhibit a much wider, uneven range of states (+4, +5, +6, +7).
- Reason: Comparable energies of 5f, 6d, and 7s orbitals allow more electrons to participate in bonding.

Key Distinction

Actinoids mirror the early d-block elements more than their lanthanoid counterparts.

The Titans of Oxidation

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Potassium Permanganate ($KMnO_4$)

Oxidation State: Mn^{VII} (d^0)
Structure: Tetrahedral MnO_4^-
Note: Diamagnetic. Intense color arises from oxygen p-orbital to metal d-orbital overlap.

Potassium Dichromate ($K_2Cr_2O_7$)

Oxidation State: Cr^{VI}
Note: Potent oxidizing agent in acidic medium; heavily used in volumetric analysis.



The Oxidation State Synthesis Map

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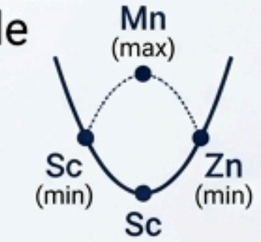
1. The Core Cause

Minimal energy gap between $(n-1)d$ and ns orbitals allows variable electron loss.



2. The Shape of the Series

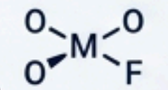
Parabolic trend. Middle elements (Mn) have max states; ends (Sc, Zn) have minimum.

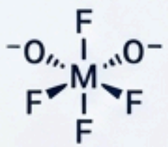


Oxidation State Synthesis

3. Stabilizing Factors

Max states stabilized by O/F ligands. Lower states stabilized by d^0, d^5, d^{10} configurations.





4. The Aqueous Exception

Hydration enthalpy can override orbital stability (e.g., $Cu^{2+} > Cu^{+}$ in water).



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Scandium (Z=21) does NOT exhibit variable oxidation states (only +3).

Zinc (Z=30) is ONLY +2 (no d-electrons involved in bonding).

Lower oxides = Basic. Higher oxides = Acidic/Amphoteric.

Mn^{2+} is more stable than Fe^{2+} towards oxidation due to d^5 half-filled stability.

Heavier d-block elements (Mo, W) form MORE stable high oxidation states than lighter ones (Cr).

Zero oxidation states require π-acceptor ligands (e.g., CO).

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