

4.3.2 Variation in Atomic and Ionic Sizes

A Dashboard View of d-Block Periodic Trends



[Z] Nuclear Charge

[σ] Shielding Effect

[r] Radius

The Core Mechanism: A Constant Tug-of-War

Nuclear Pull (Z)



Protons pull the outermost electrons inward, shrinking the radius.

Shielding Effect (σ)

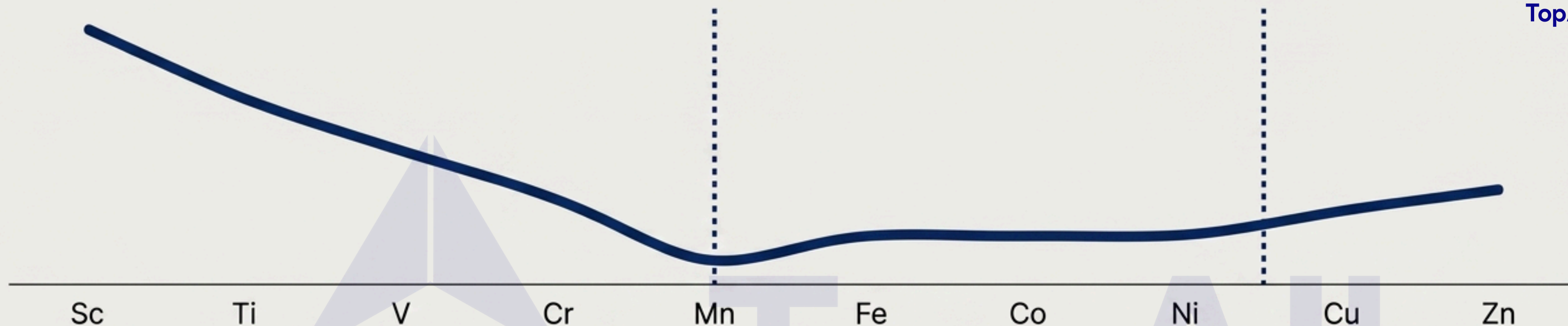


Inner d-electrons repel outer ns-electrons, expanding the radius.

$$Z_{\text{eff}} = Z - \sigma$$

Effective Nuclear Charge determines the final radius

Atomic Radius Trends (3d Series)



Zone 1: Decrease (Sc to Mn)



Nuclear Charge (Z) increases faster than Shielding (σ).

$$Z_{\text{eff}} > 0$$

Zone 2: Plateau (Fe, Co, Ni)



Increased nuclear charge is exactly balanced by increased d-electron shielding.

$$Z_{\text{eff}} \approx 0$$

Zone 3: Increase (Cu, Zn)

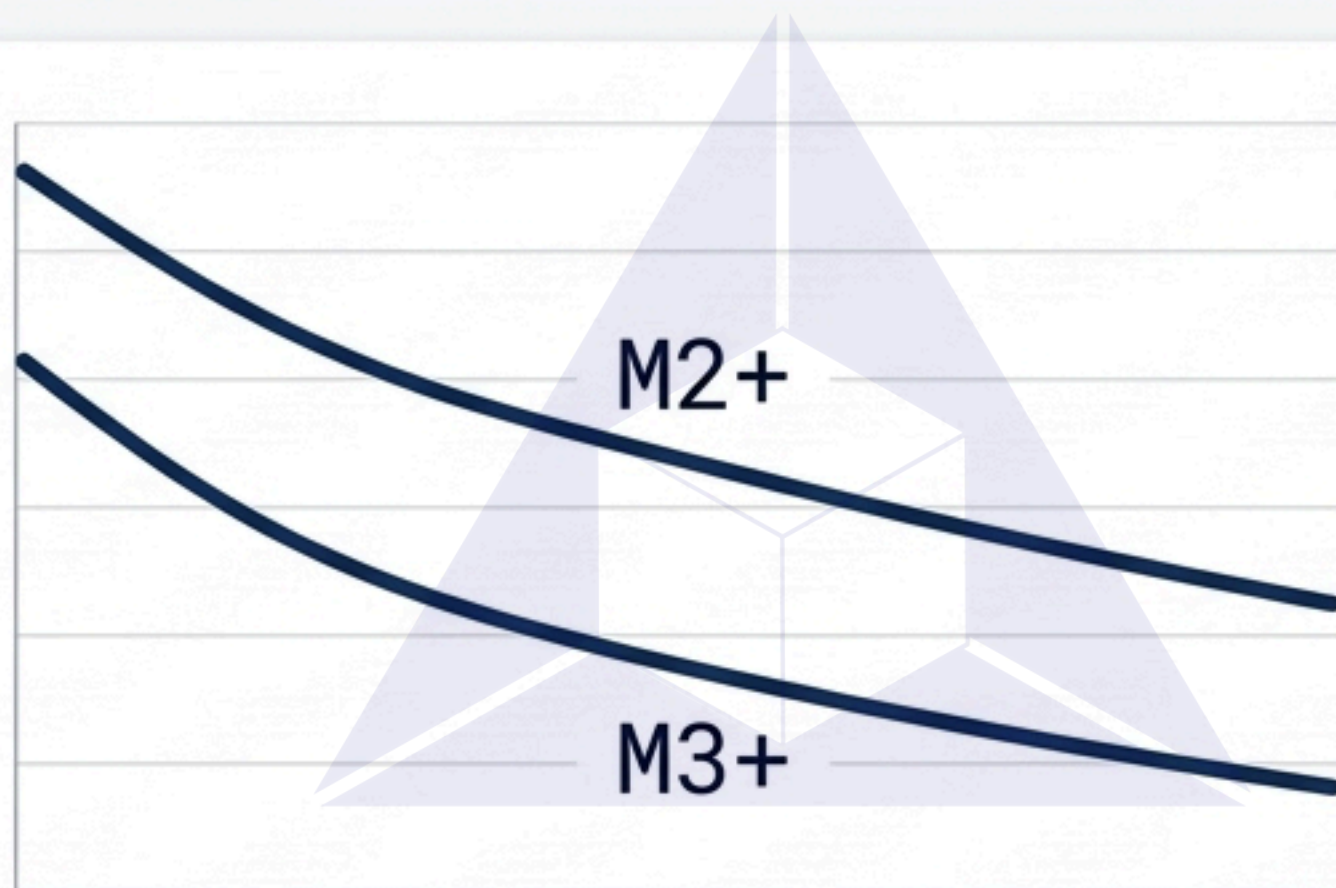


Fully/nearly filled d-orbitals cause strong electron-electron repulsion, overpowering the nucleus.

$$\text{Repulsion} > Z_{\text{eff}}$$

Ionic Radii: The Progressive Shrink

The Data



Unlike atomic radii, variation within a series is quite small and progressively decreases.

The Mechanic

1. Charge increases by +1.
2. New electron enters inner $(n-1)d$ orbital.
3. Shielding effect of d-electrons is exceedingly poor.

Result: Net electrostatic attraction increases → ionic radius shrinks.



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Key Highlights

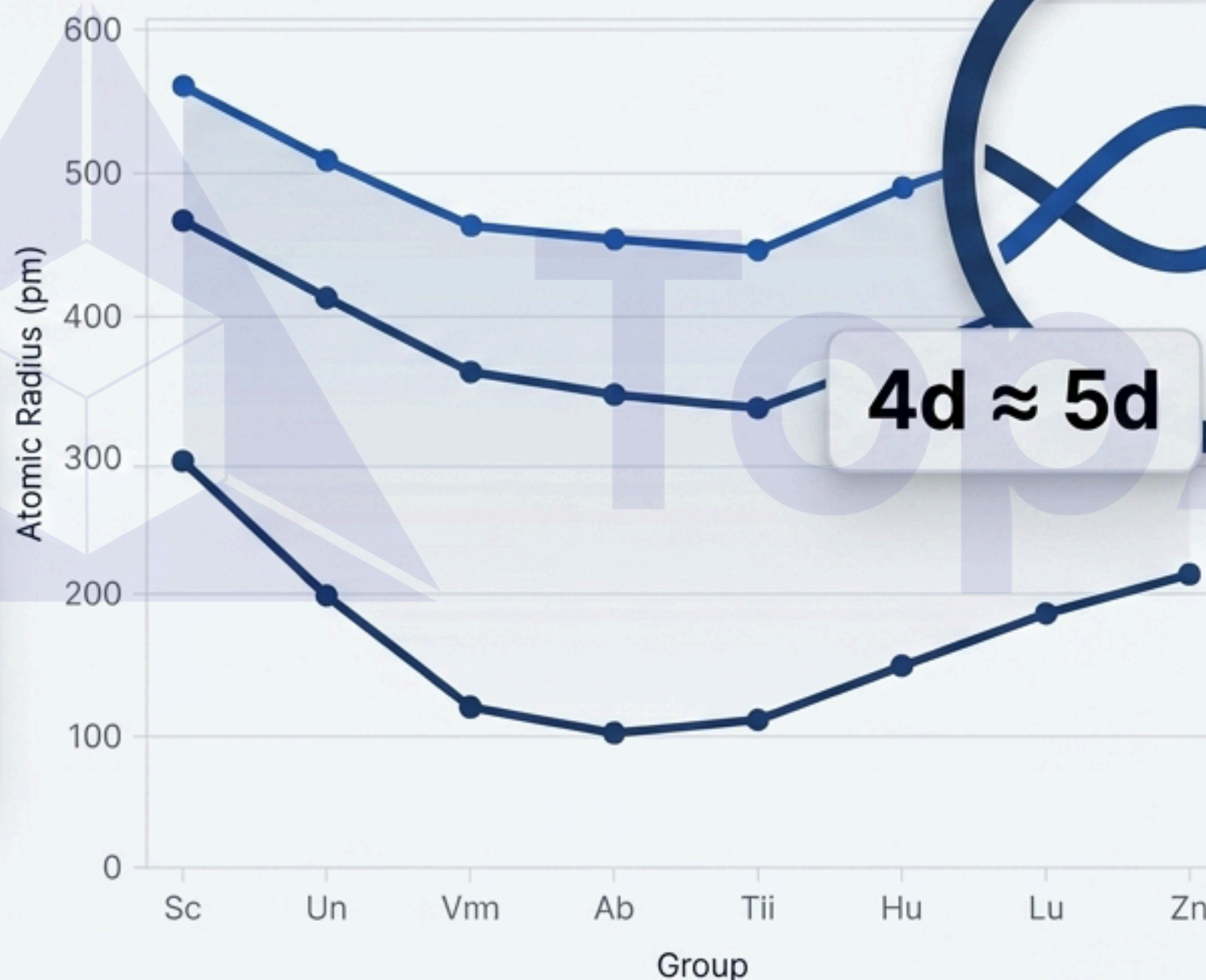
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The Vertical Anomaly: 4d vs. 5d Series

Expected Trend Box

Periodic Rule: Radius should increase down a group ($3d < 4d < 5d$).



Reality Box

Data shows: The radii of the 3rd (5d) series are virtually the same as the 2nd (4d) series.

The Culprit: Lanthanoid Contraction

1. Filling 4f Orbitals

Before the 5d series begins, 14 electrons must fill the deep 4f orbitals.

2. Poor Shielding

The shielding of one 4f electron by another is extremely weak (weaker than d-electrons).

3. Surging Nuclear Charge

As atomic number increases, the unshielded nuclear charge pulls the entire electron cloud inward.

4. Size Compensation

The expected size increase from adding a new shell is perfectly cancelled out.

$\text{Radius } 4d \approx \text{Radius } 5d$

The Chemical Twins: Zirconium (Zr) & Hafnium (Hf)

Zr

Series: 4d (2nd Transition Series)

Atomic Radius: 160 pm



Hf

Series: 5d (3rd Transition Series)

Atomic Radius: 159 pm

Consequence: Because their radii are nearly identical, Zr and Hf have indistinguishable physical and chemical properties. They occur together in nature and are exceptionally difficult to separate.

Secondary Consequence: The Density Spike

$$\text{Density (d)} = \frac{\text{Mass (m)}}{\text{Volume (v)}}$$

Mass (↑)

Atomic mass increases steadily across the period.

Dashboard Dial



Density spikes significantly from left to right.

Volume (↓)

Metallic radius decreases or stays constant, reducing overall atomic volume.

Titanium (Z=22) → 4.1 g/cm³

Copper (Z=29) → 8.9 g/cm³

NEET/JEE Trend Analysis Tricks



The Overlap Trap

Always pair 4d and 5d elements.

If asked to compare sizes (e.g., Nb vs Ta, Mo vs W), treat them as essentially equal due to Lanthanoid Contraction.



The 3d Tail End

Watch out for Cu and Zn.

Remember that the radius *increases* at the very end of the 3d series because electron repulsion finally beats the nuclear pull.



Ionic Smoothness

Ions don't plateau.

While atomic radii plateau in the middle, ions of the *same charge* (M^{2+} or M^{3+}) decrease progressively without flattening.

Quick Revision: The 4 Must-Know Facts



3d Trend

Decrease (Sc-Mn) → Constant (Fe-Ni) → Increase (Cu-Zn).

Z_{eff} vs Shielding

The atomic size is entirely controlled by the balance between Nuclear Pull and (n-1)d Shielding Repulsion.

Lanthanoid Contraction

Filling of 4f orbitals causes poor shielding, making 5d elements shrink to the exact size of 4d elements.

Zr & Hf

The ultimate proof of Lanthanoid Contraction.
Radii: Zr (160 pm) $\approx$ Hf (159 pm).
Identical chemical behavior.



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