

4.3.3 Ionisation Enthalpies

The Quantum Mechanics of the d-Block Series



The Quantum Equilibrium of the d-Block



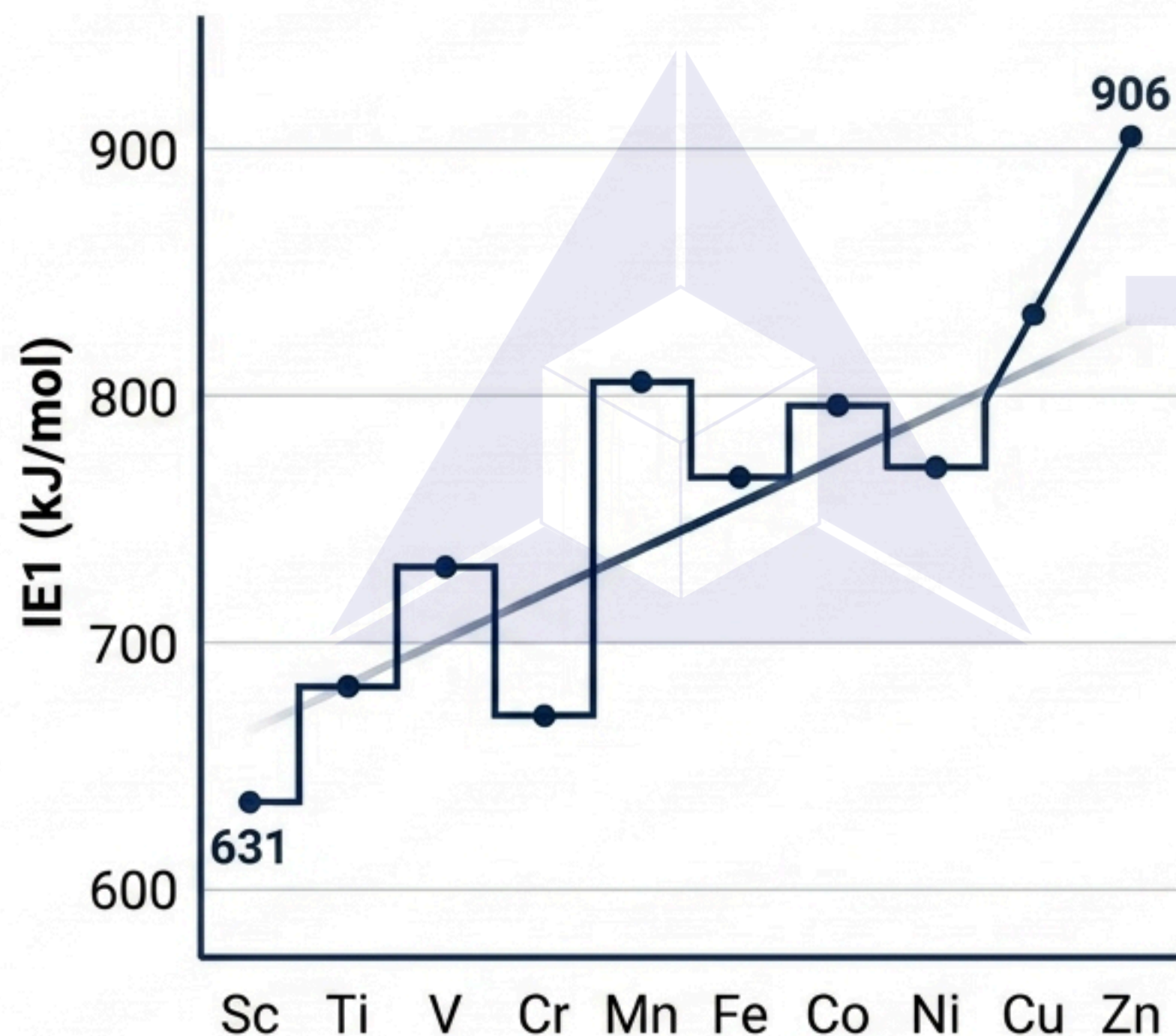
THE D-BLOCK PHENOMENON

In transition metals, electrons are added to inner 3d orbitals, effectively shielding the outer 4s electrons. These two opposing forces largely cancel each other out.

Result:

The variation in ionisation enthalpy along a transition series is much smaller compared to s- or p-block elements.

The First Ionisation Trend & The Golden Rule

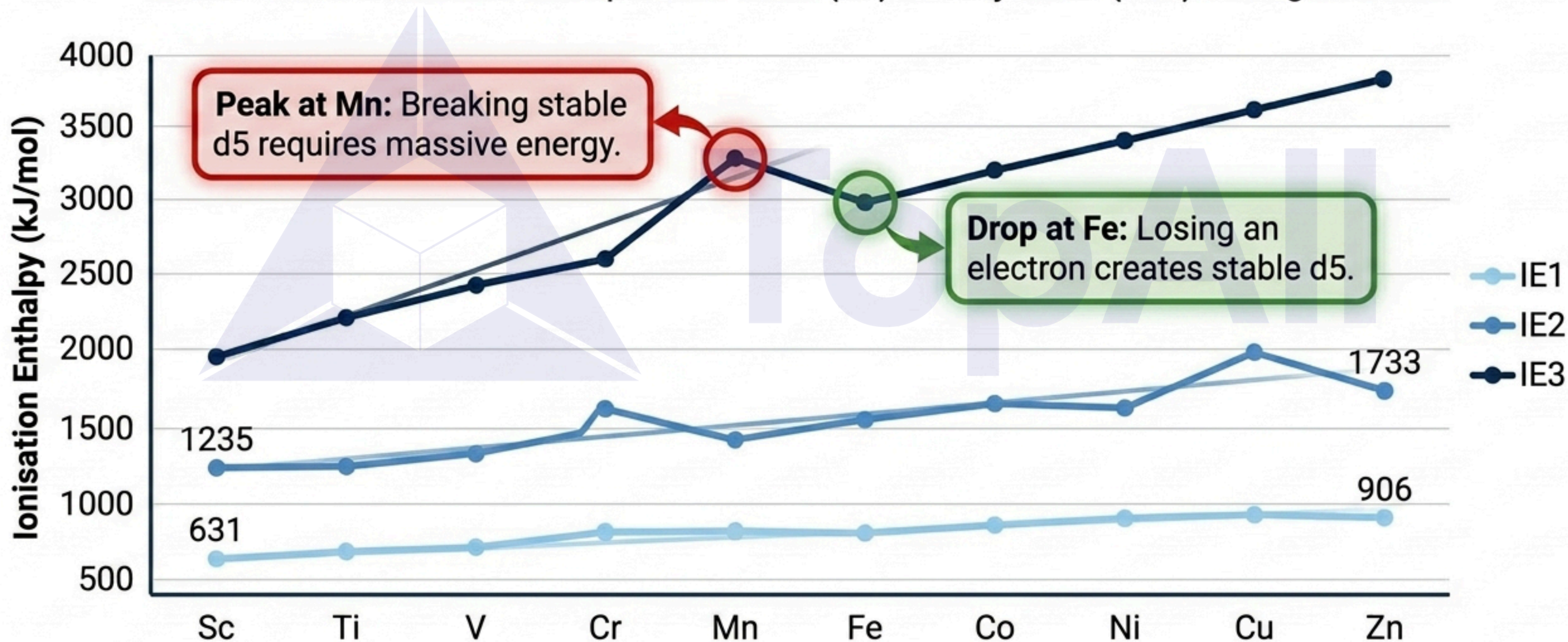


[RULE]
ns electrons are lost
BEFORE (n-1)d



Digging into the d-Orbitals: IE2 & IE3

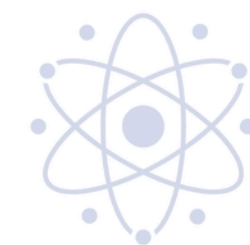
A steady increase is expected as effective nuclear charge rises. But this trend completely breaks when ionisation disrupts half-filled (d^5) or fully-filled (d^{10}) configurations.





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The Three Determinants of Ionisation Enthalpy



Nuclear Attraction

The electrostatic attraction of each electron towards the central positively charged nucleus.



Electron Repulsion

The outward repulsive force between electrons occupying the same subshell.



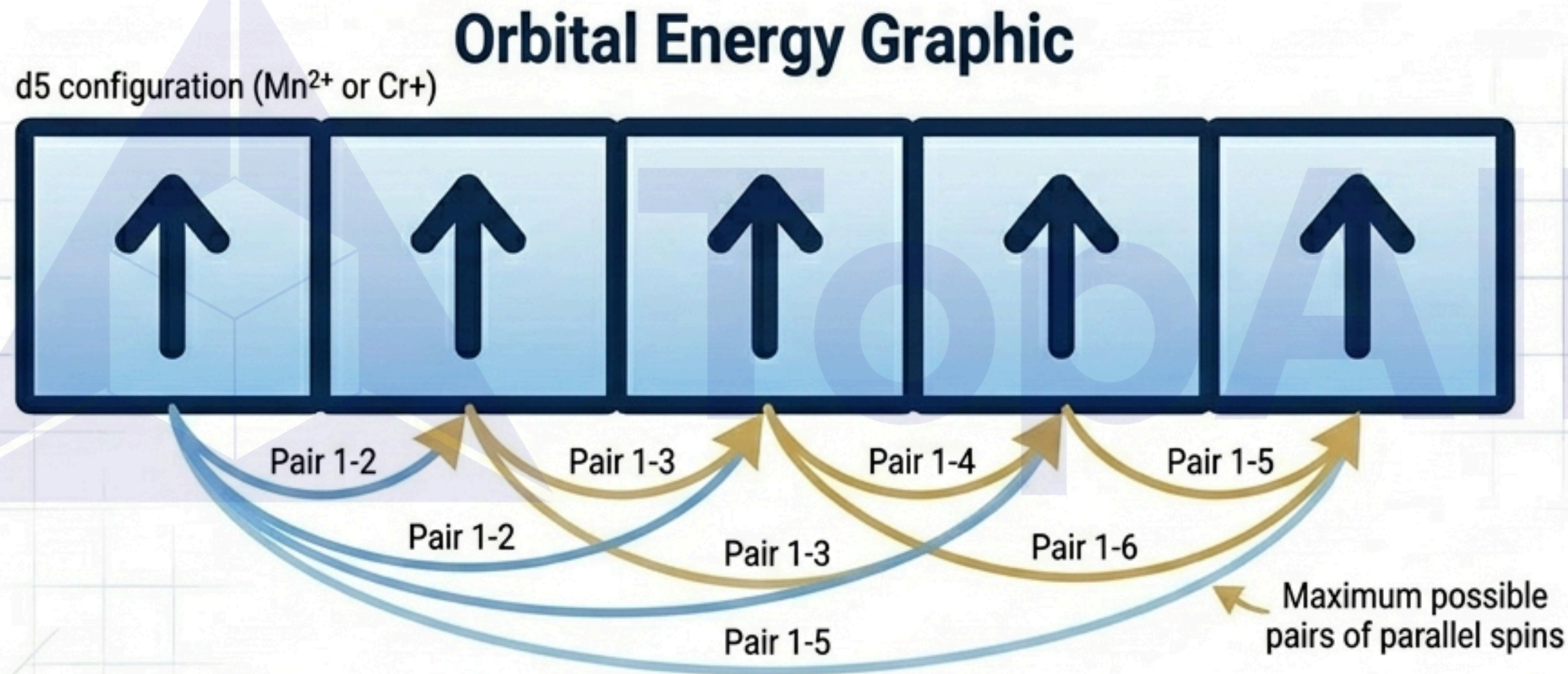
Exchange Energy

The stabilizing energy derived from parallel spins.

Exchange Energy is the primary driver of irregularities in the 3d series.

The Mechanics of Exchange Energy

According to Hund's Rule, the lowest energy state corresponds to the maximum extent of single occupation and parallel spins. Disrupting this state requires unusually high energy.



More parallel spins = Higher Exchange Energy = Greater Stability = Higher IE

Case Studies: Chromium, Copper, & Zinc

Chromium (Cr)

$3d^5 4s^1$



Removing the 1st electron ($4s^1$) is normal. Removing the 2nd electron breaks the highly stable half-filled d^5 core.

Result: Unusually high IE2 (1592 kJ/mol).

Copper (Cu)

$3d^{10} 4s^1$



Removing the 1st electron ($4s^1$) is normal. Removing the 2nd electron breaks the completely filled, highly stable d^{10} core.

Result: Unusually high IE2 (1958 kJ/mol).

Zinc (Zn)

$3d^{10} 4s^2$



Removing the 2nd electron actually creates a stable d^{10} configuration (low IE2: 1734 kJ/mol). But removing the 3rd breaks it.

Result: Massively high IE3 (3837 kJ/mol).

Quick Revision: Exam Traps vs. Truths

EXAM TRAP 1

Fe²⁺ has a higher IE₃ than Mn²⁺ because it has a higher nuclear charge (more protons).

THE TRUTH

FALSE. Mn²⁺ (d⁵ → d⁴) requires breaking a highly stable half-filled orbital. Fe²⁺ (d⁶ → d⁵) actually gains exchange energy stability. Therefore, IE₃: Mn > Fe.

EXAM TRAP 2

Transition metals show massive, predictable jumps in IE₁ across the period, exactly like s/p block elements.

THE TRUTH

FALSE. Inner 3d electrons effectively shield outer 4s electrons from the increasing nuclear charge. The IE₁ increase is very slight and highly irregular.



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