

UNIT 4 • d- AND f-BLOCK ELEMENTS

Trends in the M^{3+}/M^{2+} Standard Electrode Potentials

Why electronic configuration is the ultimate decider of reduction potential.

Core Concepts to Anchor On

Oxidising Agent

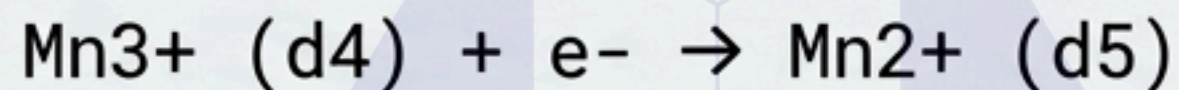
A species that gains electrons (gets reduced). A high positive E° value means the M^{3+} ion is a strong oxidising agent, eagerly rolling downhill to become M^{2+} .

d5 / d10 Stability

Half-filled (d5) and fully-filled (d10) subshells possess exceptional thermodynamic stability due to maximum exchange energy and perfect symmetry.

The d5 Paradox: Manganese vs. Iron

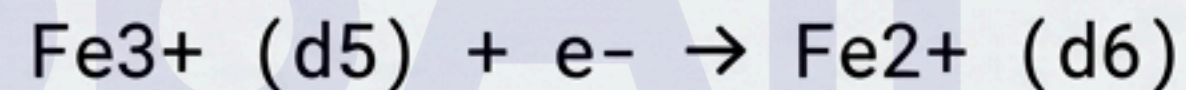
Mn³⁺ → Mn²⁺ (The Downhill Roll)



E° Value: +1.5 V (Comparatively High)

Highly favorable. The product side holds the ultra-stable d5 configuration. Mn³⁺ acts as a powerful oxidising agent to reach this stable valley.

Fe³⁺ → Fe²⁺ (The Uphill Climb)



E° Value: +0.8 V (Comparatively Low)

Less favorable. The reactant side already holds the stable d5 configuration. Forcing an electron onto stable Fe³⁺ disrupts its symmetry.



You've Learned the Theory. Let's Test Them Now.

$$E=mc^2$$



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Key Highlights

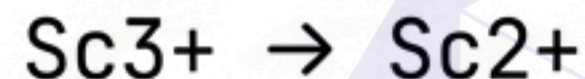
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Boundary Cases: Sc, Zn, and V

Low E°

Scandium (Sc)



Sc^{3+} has a stable noble gas configuration (d^0). It heavily resists gaining an electron to become Sc^{2+} , yielding a low potential.

Highest E°

Zinc (Zn)



Zn^{2+} holds a perfectly stable, fully-filled d^{10} configuration. Removing an electron to make Zn^{3+} is nearly impossible, driving the reduction potential massively high.

Low E°

Vanadium (V)



V^{2+} possesses a stable half-filled t_{2g} level (d^3 in an octahedral field). Moving away from V^{3+} toward this stable V^{2+} state influences the potential.

Watch for this: The d5 Reversal Trap

Don't just blindly associate 'd5' with 'High E° '.

The examiner's favorite trap is relying on your muscle memory of the d5 configuration without checking its placement.

The exact same concept (d5 stability) gives OPPOSITE outcomes depending entirely on where it sits in the redox couple.

IF stable config is on PRODUCT side (Mn^{2+}) = High E°

IF stable config is on REACTANT side (Fe^{3+}) = Low E°

Knowledge Check

Which of the following factors is primarily responsible for the comparatively high E° value of the $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple?

A. The large hydration enthalpy of the Mn^{3+} ion.

Watch out! Hydration enthalpy matters more for Ni^{2+} .

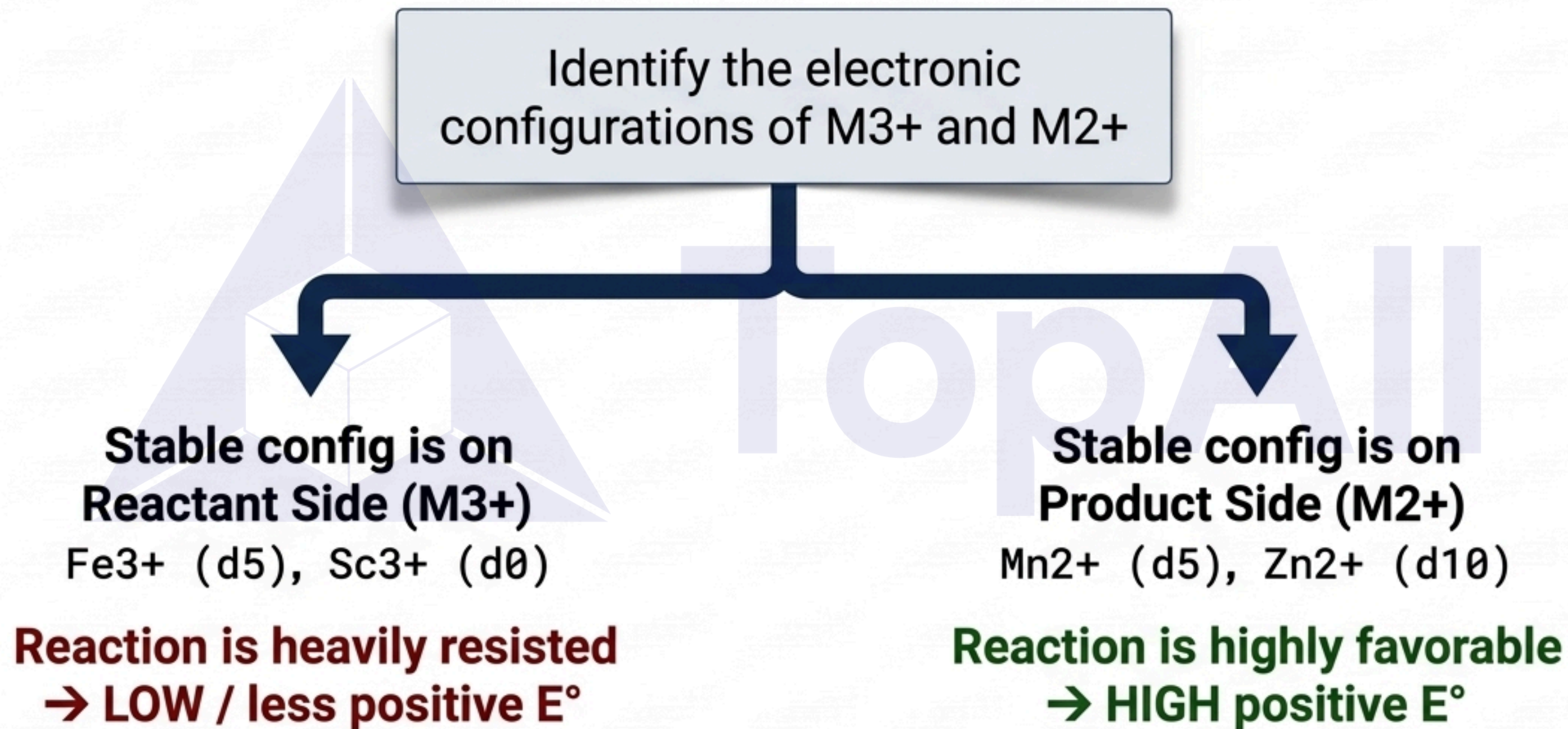
B. The stable d5 configuration of the Mn^{3+} ion.

C. The stable d5 configuration of the Mn^{2+} product ion.

Spot on! The stability sits on the product side, driving the reaction forward.

D. The noble gas configuration of Manganese.

The Electrode Potential Algorithm



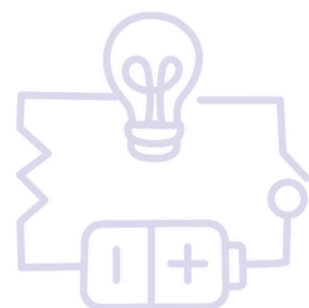
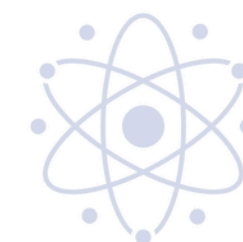
Key Takeaways

- **Stability dictates the gradient:** Unusually high or low M^{3+}/M^{2+} standard electrode potentials are almost always driven by the exceptional stability of d^0 , half-filled (d^5 , t_{2g}^3), or fully-filled (d^{10}) configurations.
- **Position is everything:** A highly stable product (like Mn^{2+}) results in a high positive E° (making the reactant a strong oxidising agent), while a highly stable reactant (like Fe^{3+}) yields a comparatively low E° .



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