



4.3.6 M^{3+}/M^{2+} Standard Electrode Potentials

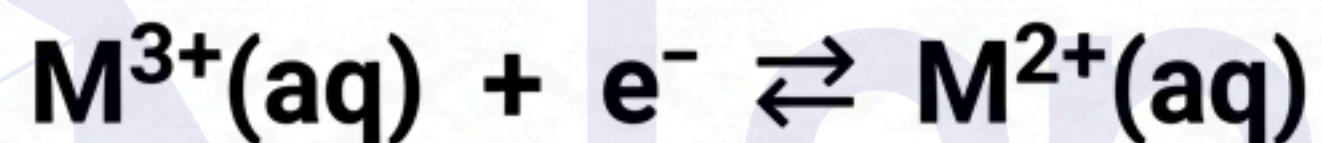
The Thermodynamic Battle of Stabilities in the 3d Series

The M^{3+} Champion

The M^{2+} Champion



**Negative /
Low E° Value**



**Highly Positive
 E° Value**



The equilibrium shifts LEFT.
The metal inherently prefers the +3 state.

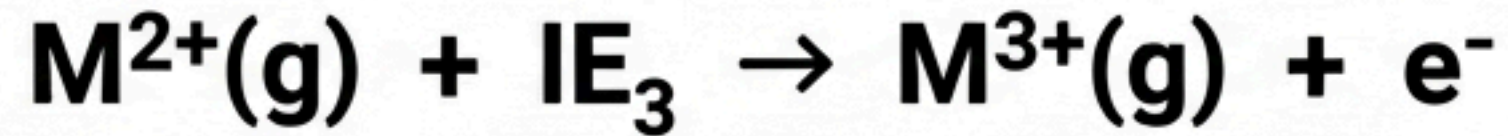
Outcome: Acts as a **Reducing Agent**
(eases its own oxidation).

The equilibrium shifts RIGHT.
The metal inherently prefers the +2 state.



Outcome: Acts as an **Oxidizing Agent**
(forces its own reduction).

The Driver of the Trend: 3rd Ionization Enthalpy (IE₃)



IE₃
(Energy required
to remove the
3rd electron)

M²⁺

M³⁺

The E° value is fundamentally tied to the difficulty of removing the third electron.

High IE₃ barrier = The metal strongly resists becoming M³⁺.

Result: High positive E° value (wants to stay M²⁺).

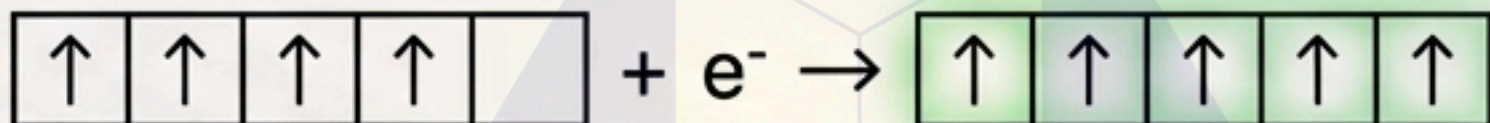
Low IE₃ barrier = The metal easily gives up the third electron.

Result: Low/Negative E° value (happy to become M³⁺).

The d^5 Stability Anchor: Mn vs. Fe

Manganese ($\text{Mn}^{3+} \rightarrow \text{Mn}^{2+}$)

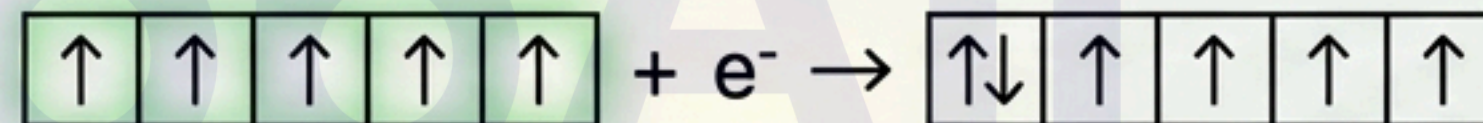
$$E^\circ = +1.57 \text{ V}$$



Gaining an electron creates the exceptionally stable, exactly half-filled d^5 configuration. Mn^{2+} is the anchor.

Iron ($\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$)

$$E^\circ = +0.77 \text{ V}$$



The +3 state already possesses the extra stability of the d^5 configuration. Fe^{3+} resists gaining an electron to become d^6 .



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$$E=mc^2$$



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Key Highlights

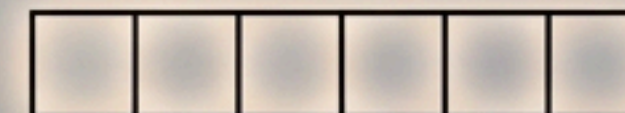
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The Boundary Walls: Scandium & Zinc

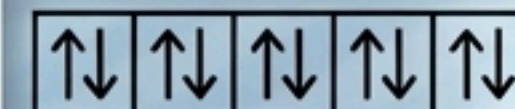
Scandium (The d⁰ Seeker)

The E° value is exceptionally low. Removing the 3rd electron achieves the ultimate stability of a noble gas core. It wants to be Sc³⁺.



Zinc (The d¹⁰ Wall)

Zinc has the highest hypothetical E° value. Removing a 3rd electron from the completely filled, highly stable d¹⁰ configuration of Zn²⁺ requires an insurmountable IE₃. **It absolutely refuses** to become Zn³⁺.



The t_{2g} Exception: The d^4 Dilemma

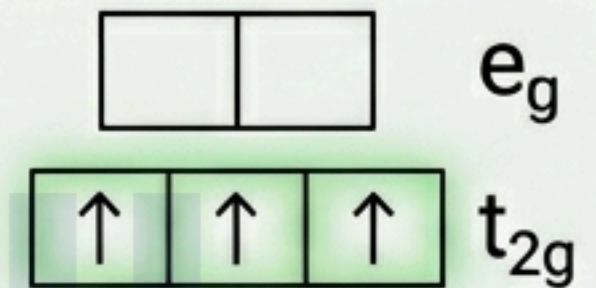
Why is Cr^{2+} reducing and Mn^{3+} oxidising when both are d^4 ?

Pathway 1: Cr^{2+} (Reducing Agent)

$\text{Cr}^{2+} (d^4)$

LOSES e^- (Oxidation)

$\text{Cr}^{3+} (d^3)$



Reason: Achieves the highly stable, half-filled t_{2g}^3 level (crystal field theory).

Pathway 2: Mn^{3+} (Oxidizing Agent)

$\text{Mn}^{2+} (d^5)$



GAINS e^- (Reduction)

$\text{Mn}^{3+} (d^4)$

Reason: Achieves the extra stability of the exactly half-filled d^5 configuration.

3d Series Stability Matrix (M^{3+}/M^{2+})

Element	E° Value (V)	Favorable Shift	Thermodynamic Driver
Titanium (Ti)	-0.37	$Ti^{3+} \leftarrow Ti^{2+}$	Ease of achieving $d^1 \rightarrow d^0$
Vanadium (V)	-0.26	$V^{3+} \leftarrow V^{2+}$	Stability of V^{2+} (t_{2g}^3) balances it
Chromium (Cr)	-0.41	$Cr^{3+} \leftarrow Cr^{2+}$	Strong drive to half-filled t_{2g}^3 (Cr^{3+})
Manganese (Mn)	+1.57	$Mn^{3+} \rightarrow Mn^{2+}$	Extra stability of d^5 (Mn^{2+})
Iron (Fe)	+0.77	$Fe^{3+} \leftarrow Fe^{2+}$	Extra stability of d^5 (Fe^{3+})
Cobalt (Co)	+1.97	$Co^{3+} \rightarrow Co^{2+}$	Exceptionally high IE_3 required

NEET/JEE Application Tip



Pro Tip: When comparing reducing power, always check the destination configuration!

Which is a stronger reducing agent in aqueous solution: Cr^{2+} or Fe^{2+} ?
(Example 4.7)

Answer: Cr^{2+}

The "Why": While Fe^{2+} (d^6) oxidation leads to a stable Fe^{3+} (d^5), Cr^{2+} (d^4) oxidation leads to Cr^{3+} (d^3). In aqueous medium, the d^3 configuration provides superior stability due to a half-filled t_{2g} level.

Quick Revision: The 4 Extremes

The Noble Goal Scandium (Sc)

Lowest E° value. Desperately sheds electrons to reach $[\text{Ar}] 3d^0$.

The d^5 Destination Manganese (Mn)

Highest standard value (+1.57V). Aggressively takes an electron to reach $\text{Mn}^{2+} (d^5)$.

The d^5 Defender Iron (Fe)

Comparatively low value (+0.77V). Resists taking an electron because Fe^{3+} is already d^5 .

The Unbreakable Wall Zinc (Zn)

Unattainable E° . Will not sacrifice its $\text{Zn}^{2+} (d^{10})$ core under standard conditions.

Master the **Configurations**, Master the Potentials.



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