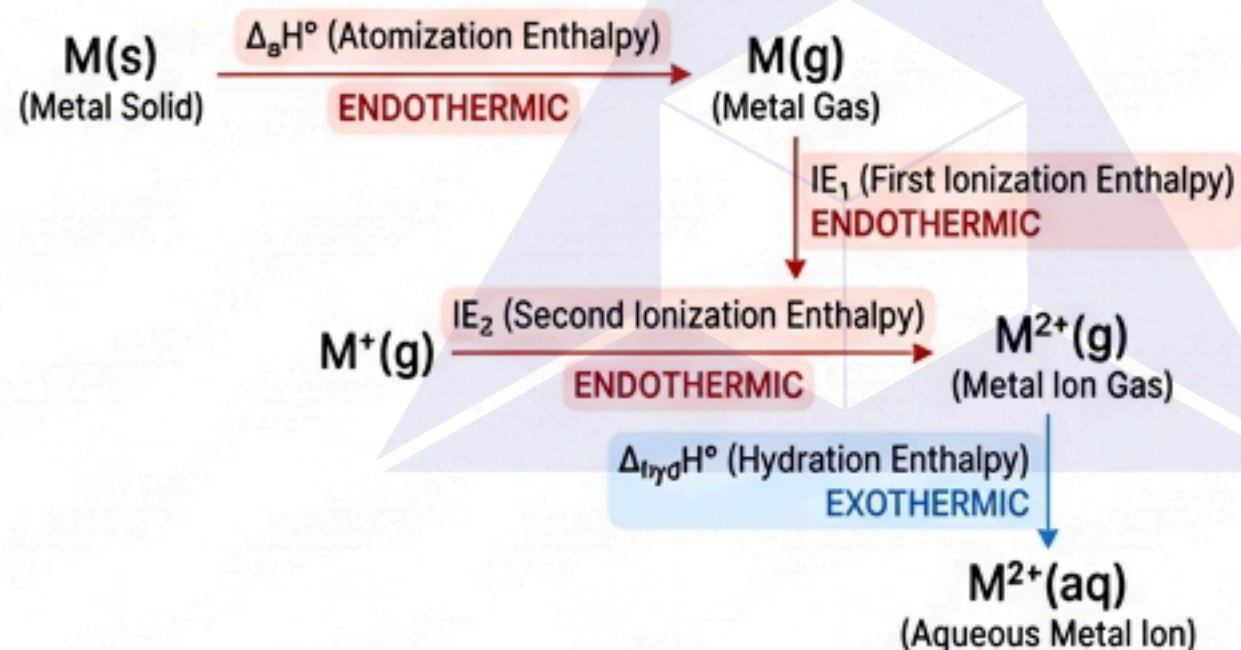


4.3.5 M^{2+}/M Standard Electrode Potentials

Decoding the Thermodynamic Trends, Enthalpy Cycles, and Anomalies of the 3d Transition Series.

THE BORN-HABER CYCLE: THERMODYNAMIC STEPS



$$\Delta_f H^\circ (M^{2+}(aq)) = \Delta_a H^\circ + IE_1 + IE_2 - \Delta_{hyd} H^\circ$$

Net Energy Change drives E° Value

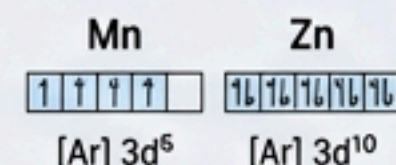
3d SERIES TRENDS & ANOMALIES: $E^\circ(M^{2+}/M)$ (Volts)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
-2.08 V	-1.63 V	-1.18 V	-0.90 V	-1.18 V	-0.44 V	-0.28 V	-0.25 V	+0.34 V	-0.76 V

General Trend: E° values become less negative (more positive) across the series.

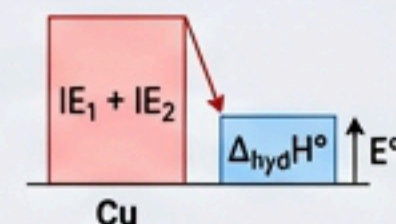
• ANOMALIES (Stable Configs)

- Mn (-1.18 V) & Zn (-0.76 V):** More negative E° than expected due to stable half-filled (d^5 for Mn^{2+}) and fully-filled (d^{10} for Zn^{2+}) configurations, making ion formation less favorable.



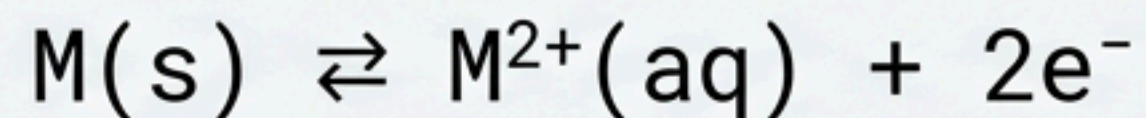
• UNIQUE CASE (Copper)

- Cu (+0.34 V):** Positive E° value. Indicates high $IE_1 + IE_2$ is not balanced by $\Delta_{hyd} H^\circ$, making $Cu(s) \rightarrow Cu^{2+}(aq)$ overall less favorable than $H_2(g) \rightarrow 2H^+(aq)$. Cu is unable to displace H_2 from acids.



What Does $E^\circ(M^{2+}/M)$ Actually Tell Us?

The standard electrode potential measures the tendency of a solid transition metal to oxidize into an aqueous ion. It dictates chemical reactivity and nobility.

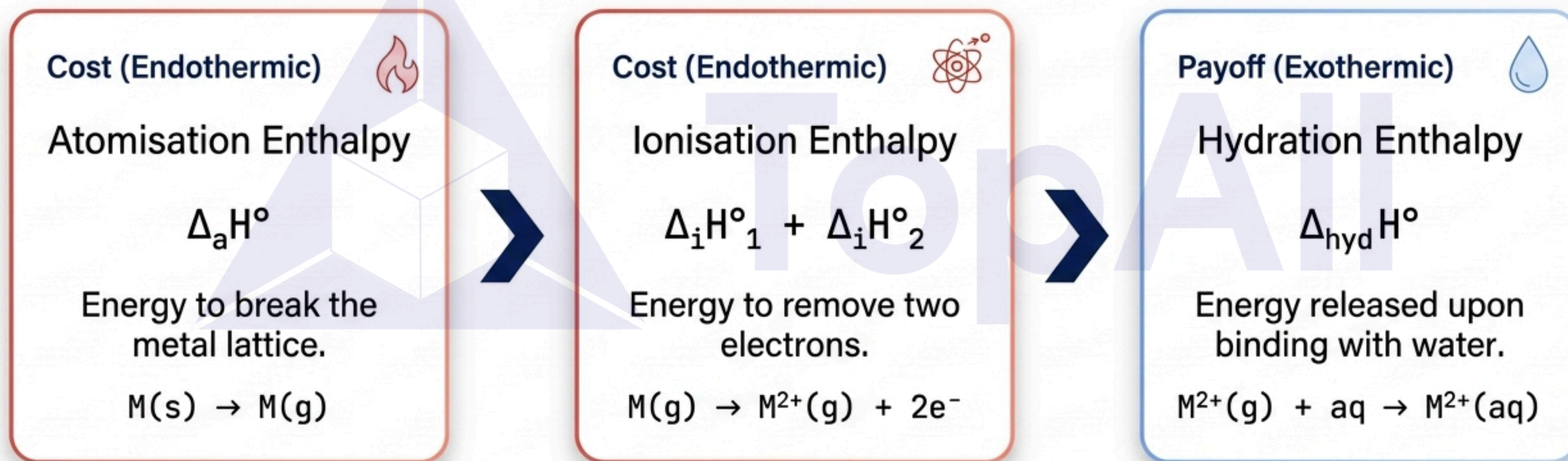


THE GOLDEN RULE OF E°

- **More Negative E°** → Metal easily loses electrons → Stronger reducing agent → More reactive
- **Less Negative / Positive E°** → Metal holds onto electrons → Tends to be noble → Less reactive

The Anatomy of Electrode Potential

E° is not a single value—it is the sum of three distinct thermochemical steps. The total energy balance determines the final potential.



$$\Delta_{Total} H = \Delta_a H^\circ + (\Delta_i H^\circ_1 + \Delta_i H^\circ_2) + \Delta_{hyd} H^\circ$$

The Energy Inputs: Atomisation & Ionisation



Why does the energy required to create gaseous ions vary across the 3d series?

Atomisation Enthalpy ($\Delta_a H^\circ$)

- ✓ **The Driver:** Number of unpaired d electrons.
- ✓ **The Trend:** Peaks in the middle of the series (d^5) due to maximum unpaired electrons causing strong interatomic metallic bonding.
- ✓ **Exception:** Mn and Zn have lower $\Delta_a H^\circ$ due to stable configurations preventing strong metallic bonding.

Ionisation Enthalpy ($\Delta_i H_1 + \Delta_i H_2$)

- ✓ **The Driver:** Increasing effective nuclear charge.
- ✓ **The Trend:** Gradually increases across the series from Sc to Zn.

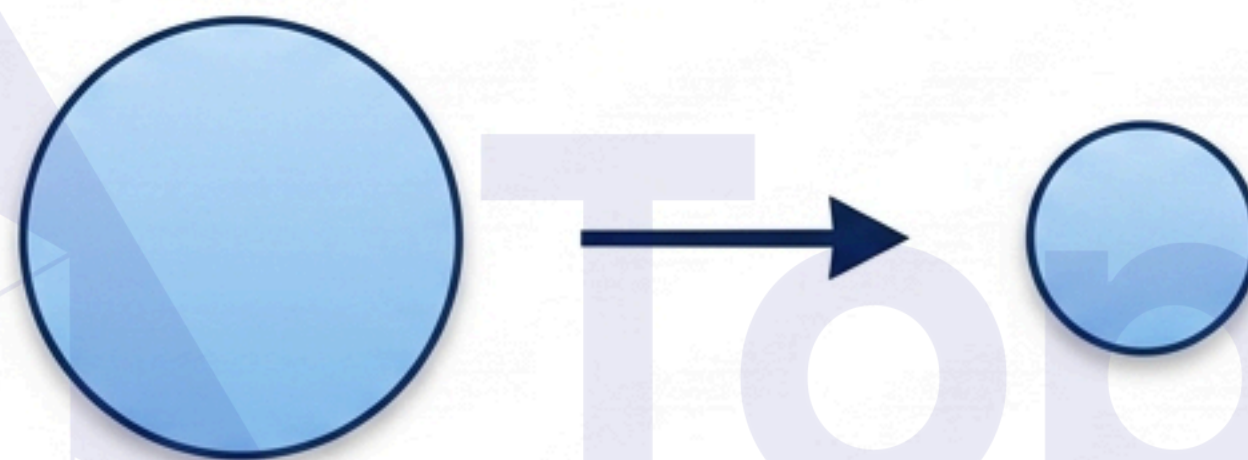
The d^5 and d^{10} Shield:

High second ionisation energy for Cr and Cu because removing a second electron disrupts highly stable d^5 and d^{10} configurations.

Hydration Enthalpy ($\Delta_{\text{hyd}} H^\circ$)

The energy released when water molecules surround the metal ion. This is the crucial counter-balance to the high ionization energies.

The Rule of Size



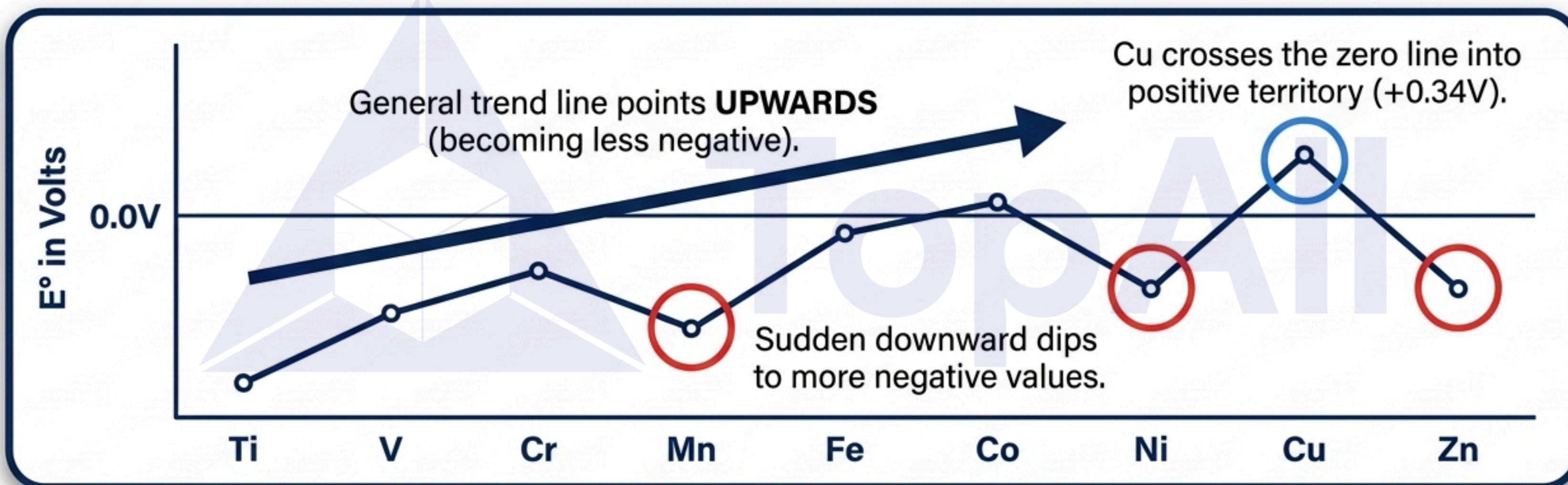
- Rule: As atomic number increases $\rightarrow$ Ionic radius of M^{2+} decreases $\rightarrow$ Charge density increases.
- Result: Hydration enthalpy becomes more negative (more energy released) across the series.

The Nickel Exception

Ni^{2+} possesses the highest negative $\Delta_{\text{hyd}} H^\circ$ (-2121 kJ/mol) in the entire 3d series. This massive energy release significantly boosts its E° value, making it more negative than the general trend predicts.

Trend Analysis of $E^\circ (M^{2+}/M)$

The general trend towards less negative values is driven by the steady increase in the sum of 1st and 2nd ionization enthalpies.

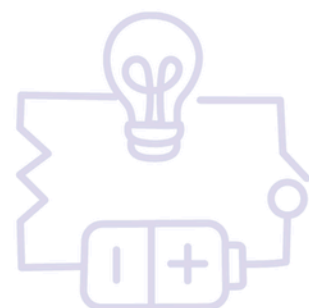
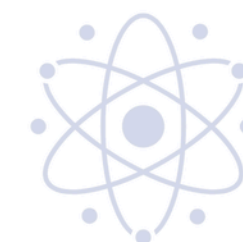


Unlike main block elements, transition metal E° values are highly irregular due to the delicate balance of competing enthalpies.



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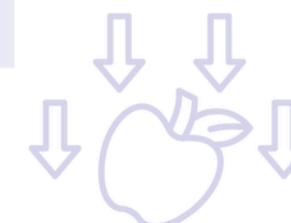
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- » Track Your Performance Smarter



Decoding the Negative Anomalies

Why are the E° values for Manganese, Nickel, and Zinc more negative than predicted?

Mn

Manganese

-1.18 V

The 'Why':

Stability of the half-filled d-subshell.

Mechanism:

Ionization easily forms Mn^{2+} ($3d^5$). This highly stable configuration makes the formation of the +2 state thermodynamically favorable.

Ni

Nickel

-0.25 V

The 'Why':

Exceptional hydration energy.

Mechanism:

Ni has the highest negative $\Delta_{\text{hyd}} H^\circ$. This massive energy release more than compensates for its high ionization enthalpy.

Zn

Zinc

-0.76 V

The 'Why':

Stability of the fully-filled d-subshell.

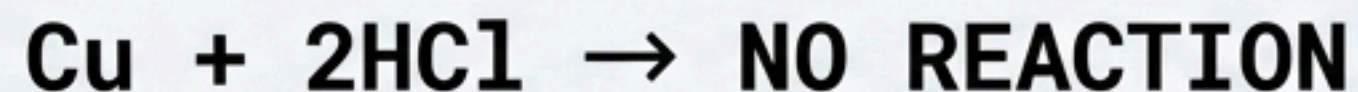
Mechanism:

Ionization easily removes 4s electrons to leave a perfectly stable Zn^{2+} ($3d^{10}$) core, driving the reaction forward.

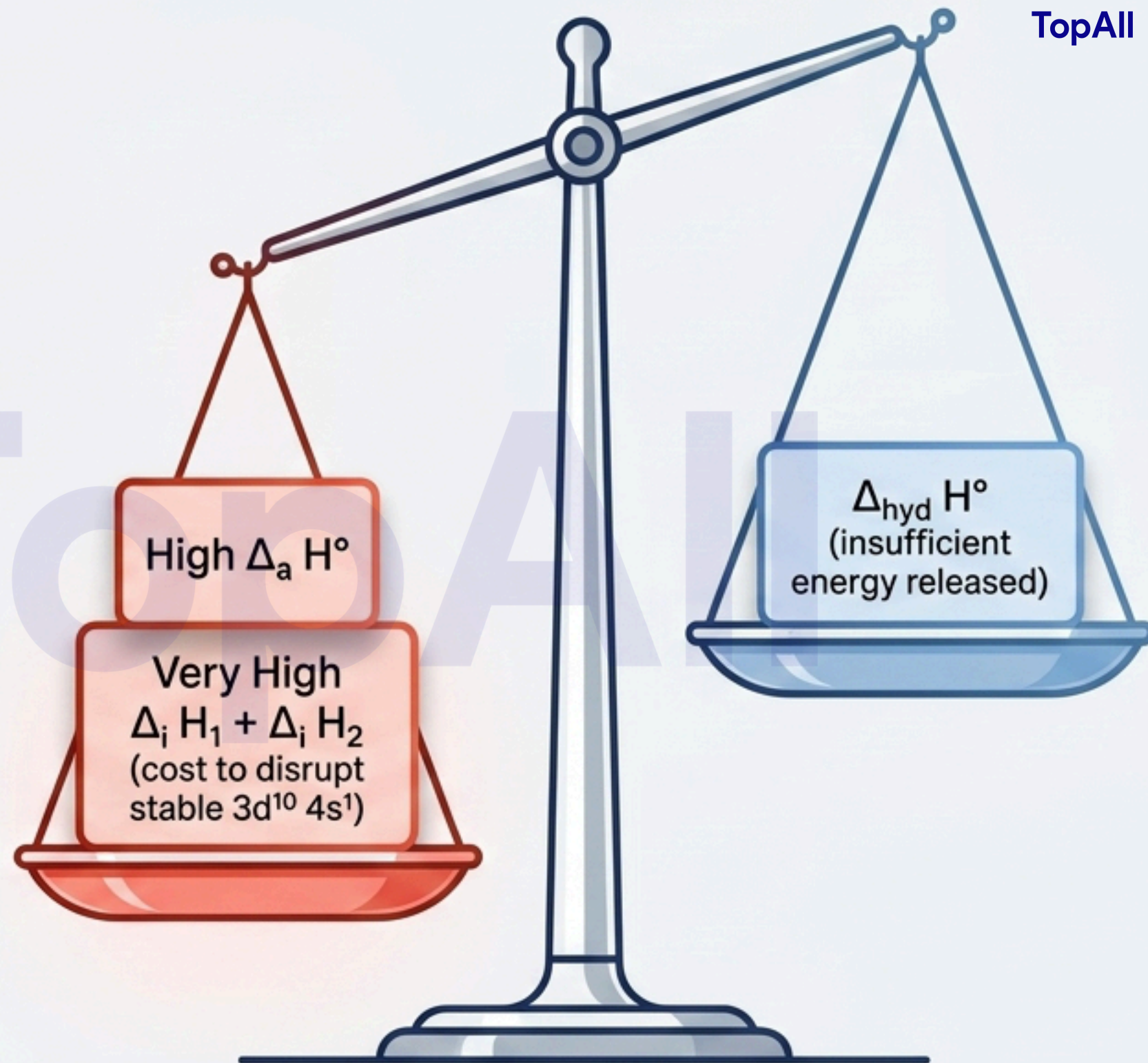
The Copper Exception (+0.34 V)

Copper is the only metal in the 3d series with a positive E° value. It is thermodynamically restricted from displacing hydrogen.

The high energy required to transform Cu(s) to $\text{Cu}^{2+}(\text{aq})$ is NOT balanced by its hydration enthalpy.



(Only oxidizing acids like HNO_3 or hot conc. H_2SO_4 can dissolve Cu).



Connecting E° to Chemical Reactivity

The E° value directly predicts how the metal will behave in chemical reactions, specifically with acids and as reducing agents.

Example of a highly negative metal reacting:



Top (Positive E°): Cu (+0.34V)

Noble behavior. Unaffected by standard non-oxidizing acids.

Middle (Weakly Negative E°): Fe (-0.44V), Co (-0.28V), Ni (-0.25V)

Moderate reactivity. Oxidized by 1M H^+ , but reaction rates can be slow/passive at room temp.

Bottom (Highly Negative E°): Ti (-1.63V), V (-1.18V), Mn (-1.18V)

Strong reducing agents. Easily liberate H_2 from dilute acids.

Higher Oxidation States: M^{3+}/M^{2+} Trends

The stability of the +3 state depends heavily on the orbital configuration resulting from the third ionization enthalpy.

Scandium (Sc)

Extremely Low E°

Reason: Extremely stable Sc^{3+} . Removing the 3rd electron leaves a noble gas core [Ar].

Zinc (Zn)

Highest E° Value

Reason: Removing a 3rd electron requires breaking the perfectly stable Zn^{2+} ($3d^{10}$) configuration. **Highly unfavorable.**

Manganese (Mn)

High Positive E° (+1.57V)

Reason: Mn^{3+} is **easily reduced** to Mn^{2+} because it desperately wants to achieve the stable **half-filled $3d^5$** state.
(Makes Mn^{3+} a strong oxidant).

Iron (Fe)

Comparatively Low E°

Reason: **Extra stability** of Fe^{3+} ($3d^5$) makes it easier to form than predicted.

The Anomaly Cheat Sheet



Quick-reference matrix for the most tested 3d electrode potential exceptions.

Metal	$E^\circ (M^{2+}/M)$	Key Thermodynamic Driver	Resulting Behavior
Cu	+0.34 V	High $\Delta_a H^\circ$ + High $\Delta_i H^\circ > \Delta_{hyd} H^\circ$	Noble; won't displace H_2 from acids.
Mn	-1.18 V	Extraordinary stability of half-filled 3d⁵ state.	Highly favorable +2 oxidation state.
Ni	-0.25 V	Highest negative Hydration Enthalpy ($\Delta_{hyd} H^\circ$).	Overcomes its high ionization energy.
Zn	-0.76 V	Extraordinary stability of fully-filled 3d¹⁰ state.	Only exhibits +2 oxidation state.

60-Second Summary

1 The Formula

E° is governed by a balance of Atomisation (+), Ionisation (+), and Hydration (-).

2 The Trend

Values generally become less negative across the 3d series due to steadily increasing ionization enthalpies.

3 The Copper Trap

Cu is +0.34V because its hydration energy cannot pay for its massive atomisation and ionisation costs.

4 The D-Orbital Rule

Dips in the trend graph at Mn and Zn are directly caused by the thermodynamic preference for d^5 and d^{10} states.

EXAM TIP: Whenever asked to explain an anomalous E° or oxidation state stability in the d-block, look first for d^0 , d^5 , or d^{10} configurations. If that fails, check Hydration Enthalpy!



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