▶ Video explanation (YouTube Short)

Trends in Standard Electrode Potentials of the 3d Metals

Drop zinc into dilute HCl and it fizzes (H_2); drop copper in and nothing happens. The reason is copper's **positive $E°(M^{2+}/M) = +0.34$ V**, the only positive value in the 3d series.

1. What $E°(M^{2+}/M)$ tells you

The more negative $E°(M^{2+}/M)$, the more easily the metal turns into $M^{2+}(aq)$. Metals with negative E° (below the hydrogen electrode, 0.00 V) reduce H^+ to H_2 in dilute acids. Copper (+0.34 V) cannot.

Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
−1.63	−1.18	−0.90	−1.18	−0.44	−0.28	−0.25	**+0.34**	−0.76

2. The energy bill: $M(s) \rightarrow M^{2+}(aq)$ (NCERT 4.3.5, Table 4.4)

Net enthalpy = ΔaH (atomisation, cost) + IE_1 + IE_2 (ionisation, cost) + ΔhydH (hydration, energy released).

	ΔaH	IE_1	IE_2	$\Delta hydH(M^{2+})$	Net (kJ mol^{-1})	E° / V
Zn	130	906	1734	−2059	**711**	−0.76
Cu	339	745	1958	−2121	**921**	+0.34

Copper's high atomisation enthalpy and high second ionisation enthalpy are not balanced by its hydration enthalpy, so its E° is positive. (Across the series the nets follow the E° order: Mn 643, Zn 711, Fe 743, Ni 798, Cu 921.) *These are enthalpies only; the real E° also includes the hydrogen half and entropy, but the trend is explained by these terms.*

3. Myth: "copper does not react with acids"

Copper gives no H_2 with dilute HCl or H_2SO_4, but **oxidising acids** (nitric acid, hot concentrated sulphuric acid) dissolve it: the acid itself is reduced (with concentrated HNO_3, brown NO_2; the solution turns blue with Cu^{2+}).

4. Stable d^5 and d^{10} bend the trend

- The general trend towards less negative E° follows the rising IE_1 + IE_2.
- **Mn and Zn** are more negative than the trend: Mn^{2+} (half-filled d^5) and Zn^{2+} (full d^{10}) are especially stable. (Ni is also more negative, because of its highest negative hydration enthalpy.)

5. $E°(M^{3+}/M^{2+})$ (NCERT 4.3.6)

Ti	V	Cr	Mn	Fe	Co
−0.37	−0.26	−0.41	**+1.57**	+0.77	**+1.97**

- Mn^{3+} (d^4) → Mn^{2+} (d^5) gains a stable half-filled set: high E°, so **Mn^{3+} is a strong oxidising agent**.

- Fe^{3+} is already d^5 (extra stable), so $E°(Fe^{3+}/Fe^{2+})$ is comparatively low.
- Co^{3+} (+1.97 V) is also strongly oxidising.

Solved example (NCERT Example 4.4)

Q. Why is Cr^{2+} reducing and Mn^{3+} oxidising when both have d^4?
A. $Cr^{2+} \rightarrow Cr^{3+}$ changes d^4 to d^3 (a half-filled t_2g level, more stable), so Cr^{2+} readily loses an electron: reducing. $Mn^{3+} \rightarrow Mn^{2+}$ changes d^4 to the half-filled d^5, so Mn^{3+} readily gains an electron: oxidising.

Key takeaways

- Cu is the only 3d metal with positive $E°(M^{2+}/M)$: no H_2 from dilute acids.
- E° reflects the energy bill: atomisation + ionisation − hydration.
- Stable d^5 / d^{10} explain the Mn and Zn dips, the high $E°(Mn^{3+}/Mn^{2+})$ and the low $E°(Fe^{3+}/Fe^{2+})$.

Practice questions

1. (MCQ) The only 3d metal with a positive $E°(M^{2+}/M)$ is: (a) Zn (b) Ni (c) Cu (d) Fe
2. (MCQ) Which acid dissolves copper? (a) dilute HCl (b) dilute H_2SO_4 (c) nitric acid (d) acetic acid
3. (MCQ) Mn^{3+} is a strong oxidising agent because Mn^{2+} is: (a) d^4 (b) d^5 (c) d^6 (d) d^{10}
4. (Very short) Write the three energy terms that decide $E°(M^{2+}/M)$.
5. (Very short) Why is $E°(Fe^{3+}/Fe^{2+})$ comparatively low?
6. (Short) Explain why copper does not liberate H_2 from dilute acids.
7. (Short) Why are the E° values of Mn and Zn more negative than expected from the trend?
8. (Numerical) Using Table 4.4, find the net enthalpy for $Fe(s) \rightarrow Fe^{2+}(aq)$: ΔaH 418, IE_1 762, IE_2 1561, $\Delta hydH$ −1998.

Answer key

1. (c) Cu.
2. (c) nitric acid (an oxidising acid).
3. (b) d^5.
4. Enthalpy of atomisation, the sum of the first two ionisation enthalpies, and the hydration enthalpy of M^{2+}.
5. Fe^{3+} is d^5 (half-filled), which is extra stable.
6. Its $E°(Cu^{2+}/Cu)$ is positive (+0.34 V): the high energy to form $Cu^{2+}(aq)$ (atomisation + ionisation) is not balanced by the hydration enthalpy, so Cu cannot reduce H^+.
7. Mn^{2+} (d^5) and Zn^{2+} (d^{10}) are especially stable, so forming them is easier than the trend predicts.
8. 418 + 762 + 1561 − 1998 = 743 kJ/mol.

▶ Watch the video explanation