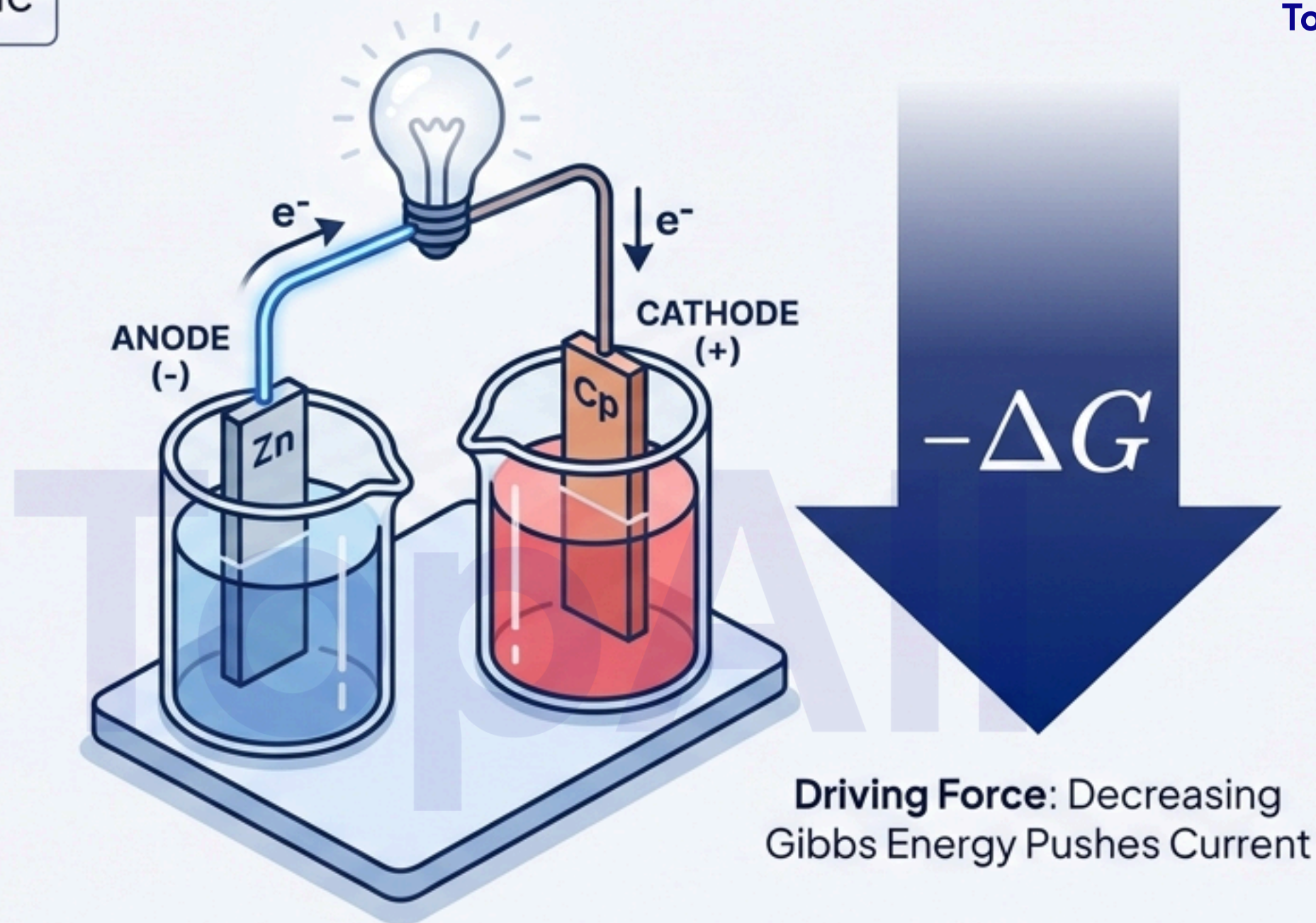


Cell Potential, Gibbs Energy & Spontaneity



Master the mathematical and conceptual bridge between electrical cell potential and thermodynamic spontaneity.

Defining Electrical Work

The Foundation of Electrochemistry

The reversible work done by a galvanic cell is strictly equal to the decrease in its Gibbs energy. To calculate this, we must first define maximum electrical work.

$$\text{Electrical Work} = \text{Potential} \times \text{Total Charge}$$



In an electrochemical cell, the total charge (Q) passed reversibly depends on the moles of electrons transferred.

$$Q = nF$$

- n = number of moles of electrons
- F = Faraday constant ($\approx 96487 \text{ C mol}^{-1}$)

The Key Relationship

General Conditions

The decrease in Gibbs energy equals the reversible electrical work done by the cell:

$$\Delta_r G = -nFE_{\text{cell}}$$

Standard Conditions

When the concentration of all reacting species is unity (1 M, 1 bar, 298 K):

$$\Delta_r G^\circ = -nFE_{\text{cell}}^\circ$$

Key Takeaways

- This equation is the fundamental bridge between Thermodynamics and Electrochemistry.
- By measuring the standard cell potential (E_{cell}°), we can accurately determine the standard Gibbs energy ($\Delta_r G^\circ$).



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

$$E=mc^2$$



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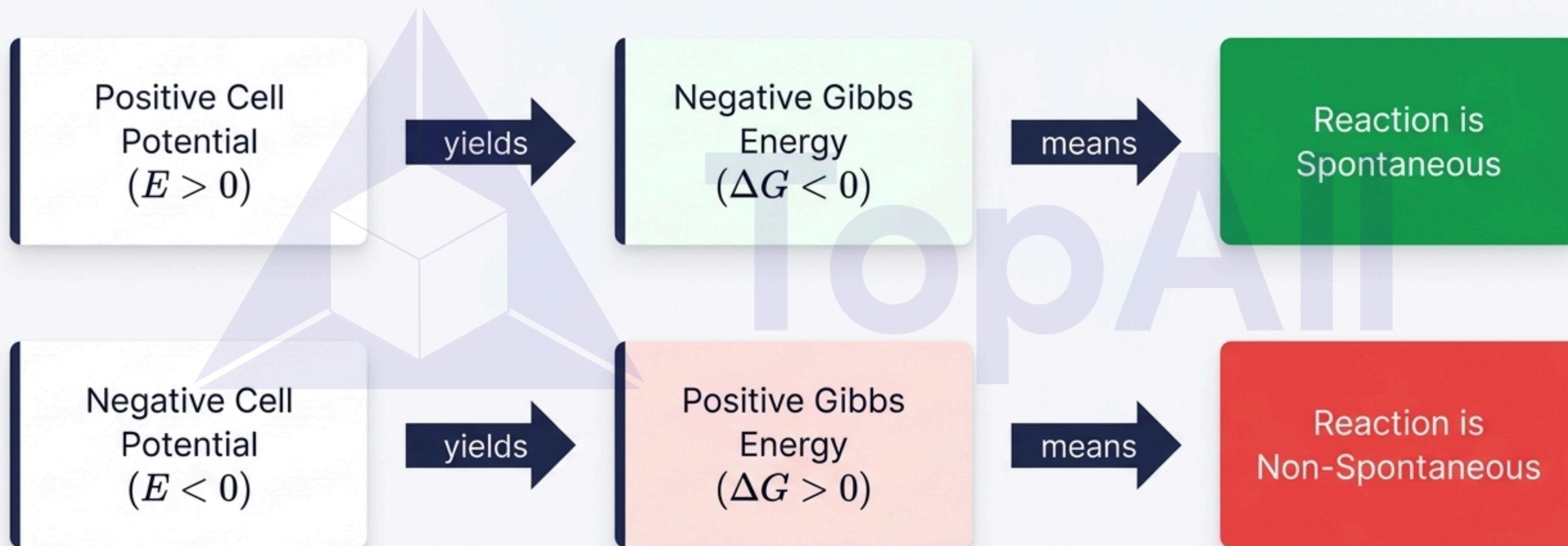
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Decoding the Signs: Spontaneity

For a Written Galvanic Reaction:



Note: A spontaneous redox reaction is the absolute requirement for a functioning Galvanic cell.

Intensive vs. Extensive Properties

$$E_{\text{cell}}$$

INTENSIVE PROPERTY

- **Definition:** A measure of the “push” or driving force per electron.
- **Scaling:** Does NOT scale with the reaction stoichiometry.
- **Analogy:** Like temperature or pressure; doubling the volume doesn't double the temperature.

$$\Delta_r G$$

EXTENSIVE PROPERTY

- **Definition:** A measure of the total usable energy released.
- **Scaling:** DOES scale proportionally with the reaction coefficients (n).
- **Analogy:** Like mass or volume; doubling the reactants doubles the total energy released.

Application: The Daniell Cell

Calculating standard Gibbs energy for the canonical Zn/Cu cell

The Reaction



Step 1. Identify Variables

- $n = 2$ (moles of electrons transferred)
- $E_{\text{cell}}^{\circ} = 1.10 \text{ V}$
- $F = 96487 \text{ C mol}^{-1}$



Step 2. Apply Formula

$$\begin{aligned}\Delta_r G^{\circ} &= -nFE_{\text{cell}}^{\circ} \\ \Delta_r G^{\circ} &= -(2) \times \\ &\quad (96487 \text{ C mol}^{-1}) \\ &\quad \times (1.10 \text{ V})\end{aligned}$$



Step 3. Final Result

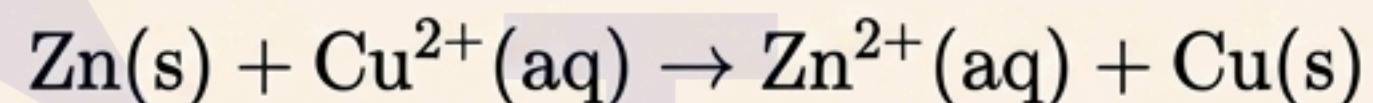
$$\begin{aligned}\Delta_r G^{\circ} &= -212,271 \text{ J mol}^{-1} \\ &\quad \mathbf{-212.27 \text{ kJ mol}^{-1}}\end{aligned}$$

The Stoichiometric Multiplier

JEE TRAP: MULTIPLYING THE REACTION.

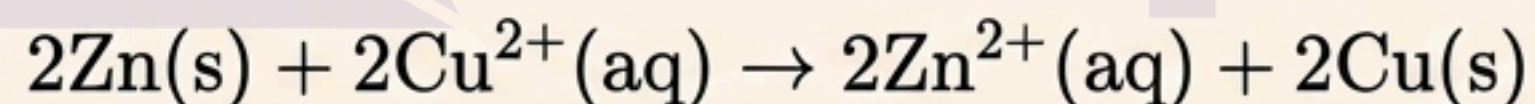
Examiners will frequently ask you to evaluate a reaction where the stoichiometric coefficients have been multiplied. Do not blindly multiply all values!

Original Reaction:



$$n = 2 \mid E^\circ = 1.1 \text{ V} \mid \Delta G^\circ = -212.27 \text{ kJ mol}^{-1}$$

Multiplied Reaction ($\times 2$):



Impact Grid

$$n \times 2 \text{ (Now } n = 4\text{)}$$

$\Delta G \times 2$ (Extensive: total energy doubles)

$E = \text{UNCHANGED}$ (Intensive: standard potential remains exactly 1.1 V)



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