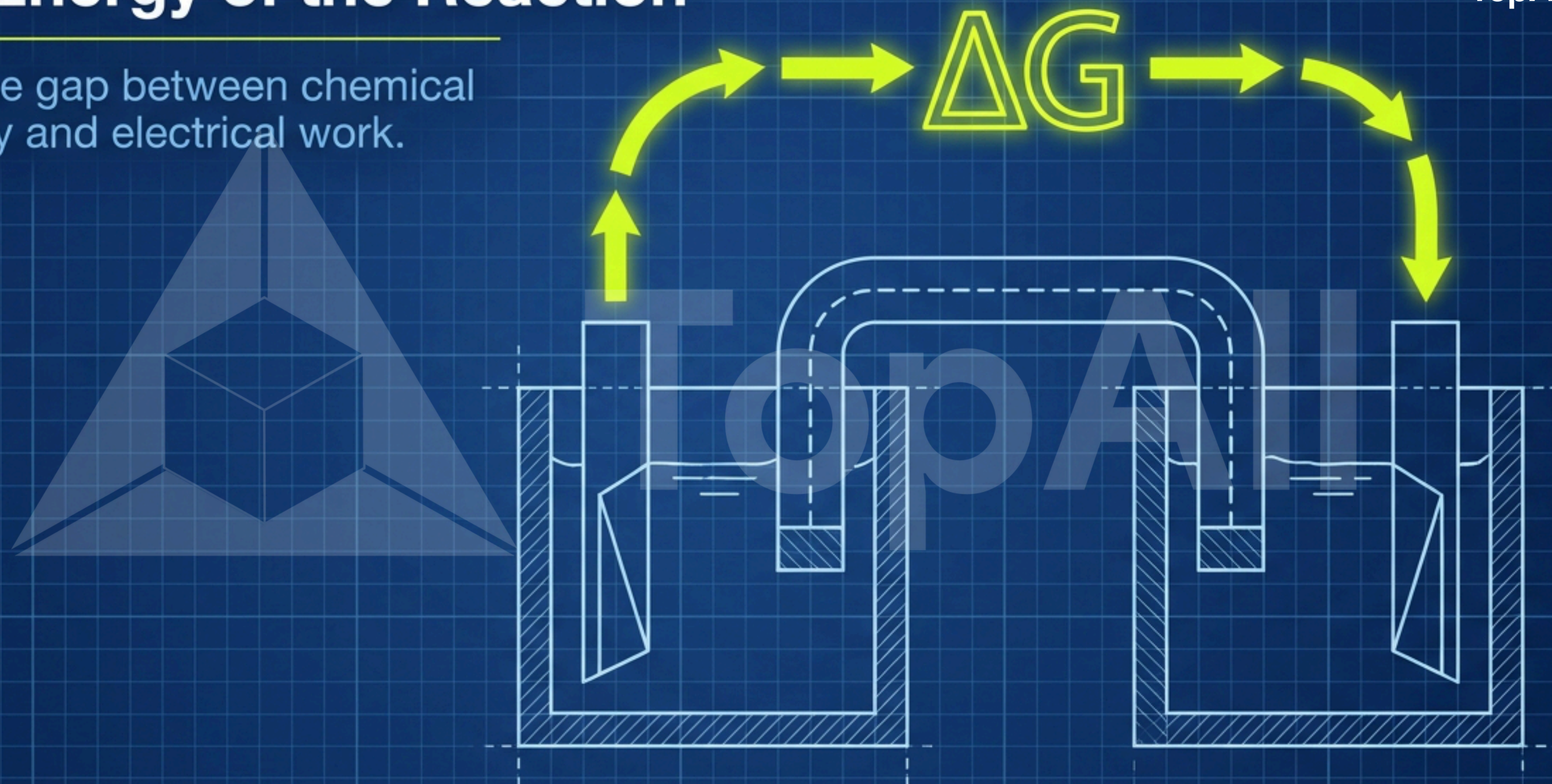


2.3.2 Electrochemical Cell and Gibbs Energy of the Reaction

Bridging the gap between chemical spontaneity and electrical work.



Extracting Electrical Work from a Galvanic Cell



Core Principle

Electrical Work = Electrical Potential $\times$ Total Charge Passed

The Maximum Work Condition

To extract the maximum possible work from a galvanic cell, charge must be passed reversibly.

Thermodynamic Equivalence

Under reversible conditions, the electrical work done by the cell is perfectly equal to the decrease in its Gibbs energy ($-\Delta_r G$).

[The Foundational Equation

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

Gibbs Energy (Joules).
The total chemical
driving force.

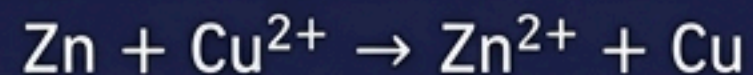
Moles of electrons
transferred in the
redox reaction.

Faraday constant
($\approx 96487 \text{ C mol}^{-1}$).
Total charge of 1
mole of electrons.

Cell Potential (Volts).
The 'pressure' of
the electron flow.

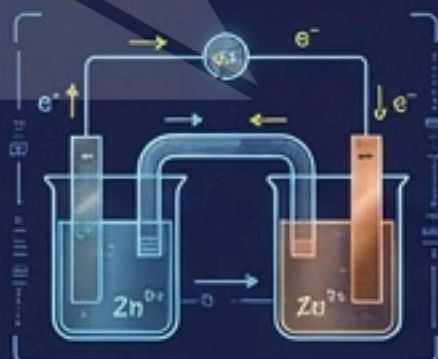
Scaling Insight Matrix

Reaction 1



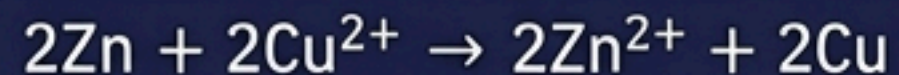
$$n = 2$$

$$\Delta_r G = -2FE_{cell}$$



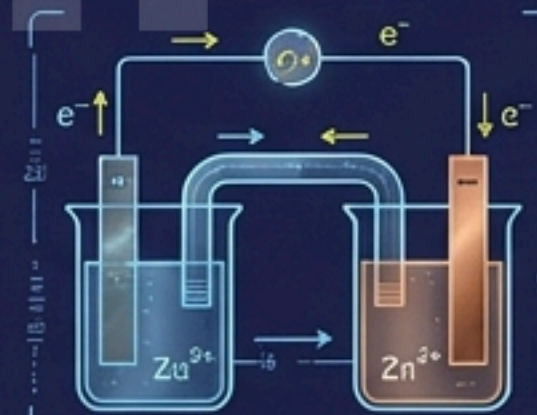
1x size Daniell Cell

Reaction 2



$$n = 4$$

$$\Delta_r G = -4FE_{cell}$$



2x size Daniell Cell

Key Takeaway:

Gibbs Energy is Extensive (doubles with stoichiometry).
Cell Potential is Intensive (remains 1.10 V regardless of amount).



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$$E=mc^2$$



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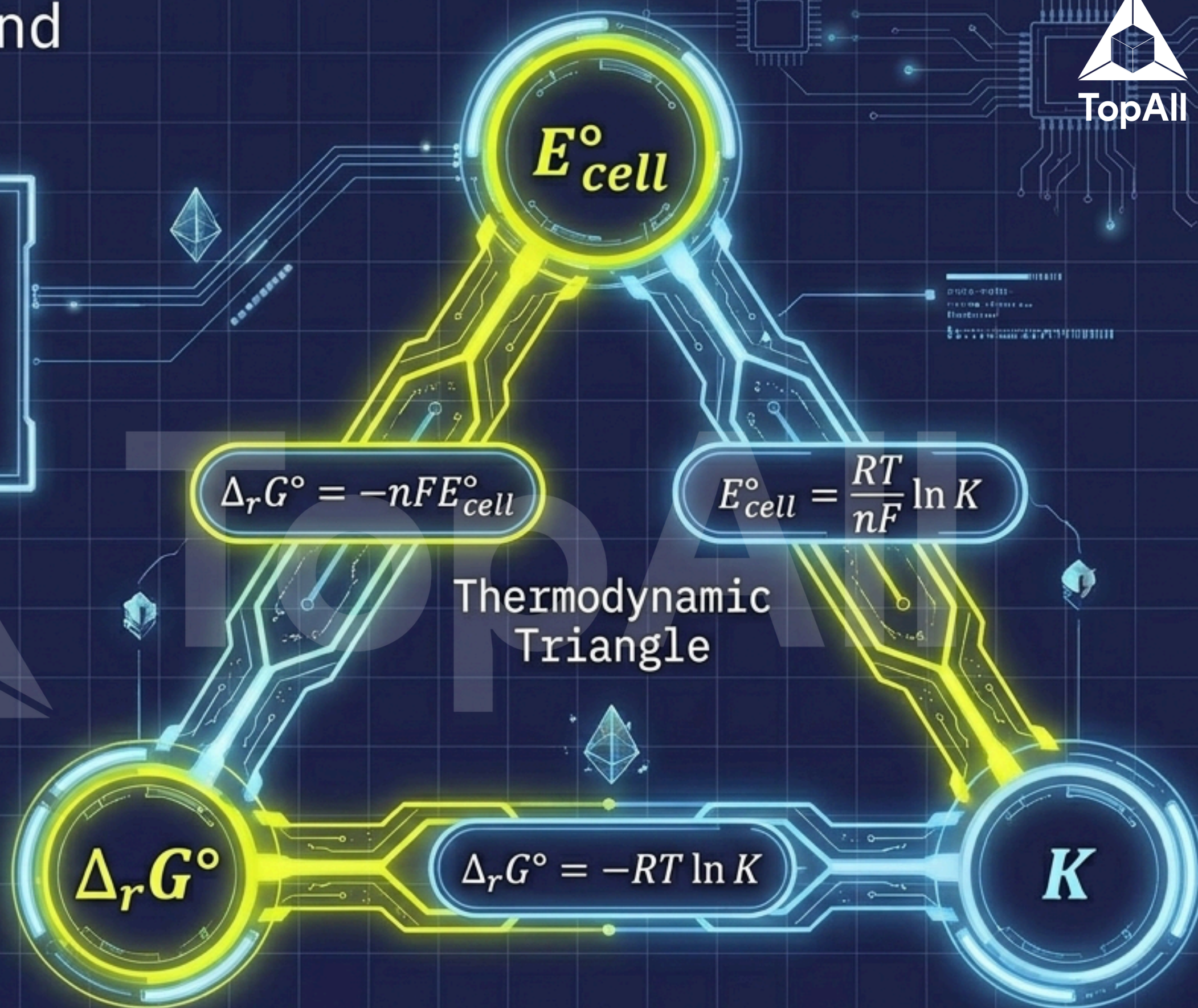
The Standard State and the Equilibrium Link

Standard Conditions Definition:

When all reacting species are at unity concentration (1 M solution, 1 bar gas), E_{cell} becomes the Standard Cell Potential (E°_{cell}).

Key Insight

Equilibrium constants (K) are notoriously difficult to measure directly. By simply measuring the standard voltage (E°_{cell}) of a cell with a voltmeter, we can calculate the exact equilibrium state of the chemical reaction.

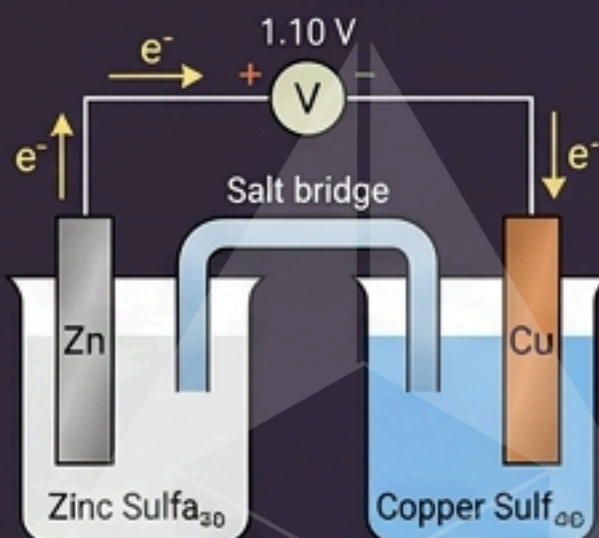


Decoding the Signs: Spontaneity vs. emf



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Galvanic Cell (Spontaneous)



$E_{\text{cell}} > 0$ (Positive)

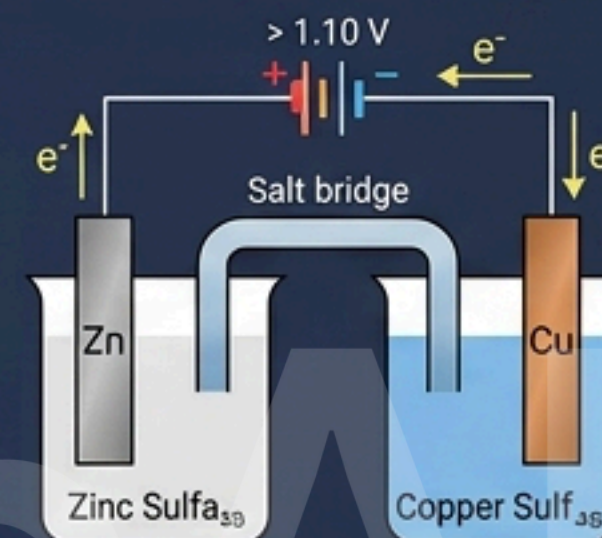


$\Delta_r G < 0$ (Negative / Decreasing)



System does electrical work on the surroundings.

Electrolytic Cell (Non-Spontaneous)



$E_{\text{cell}} < 0$ (Negative)



$\Delta_r G > 0$ (Positive / Increasing)



Surroundings must do electrical work on the system to force the reaction.

Final Recap: Thermodynamics of the Cell



- **Cell potential** (E_{cell}) quantifies the chemical driving force of a redox reaction.



- Maximum reversible **electrical work** is perfectly equivalent to the **drop in Gibbs energy** ($\Delta_r G$).



- **Standard potentials** (E°_{cell}) act as a direct bridge to calculate **equilibrium constants** (K).

Up Next: Transport, Resistivity, and Conductance in Solutions →



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