

Entropy & Spontaneity

The universal drive toward disorder and the hidden engine of chemical reactions.

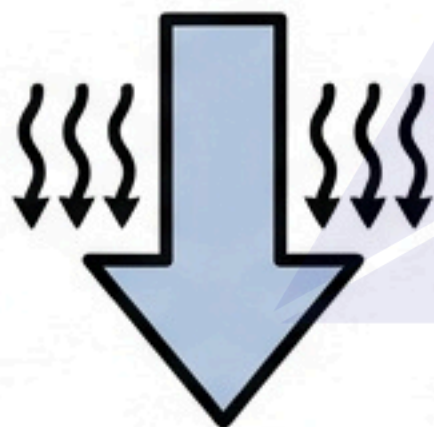


The Paradox of Spontaneity

A spontaneous process proceeds without external assistance. But is a **decrease in energy** (Enthalpy, ΔH) the only driving force? No.

The Enthalpy Rule

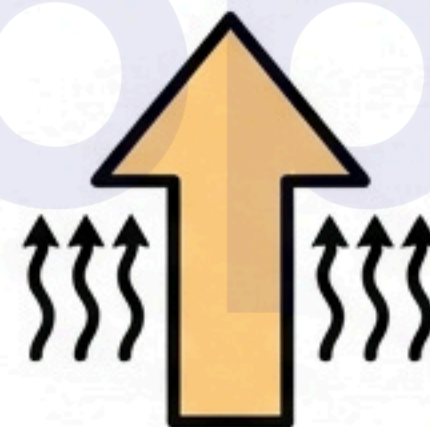
Exothermic



Water flowing downhill or a gas burning naturally loses energy ($\Delta H < 0$). This was historically thought to be the sole driving force of all natural processes.

The Paradox

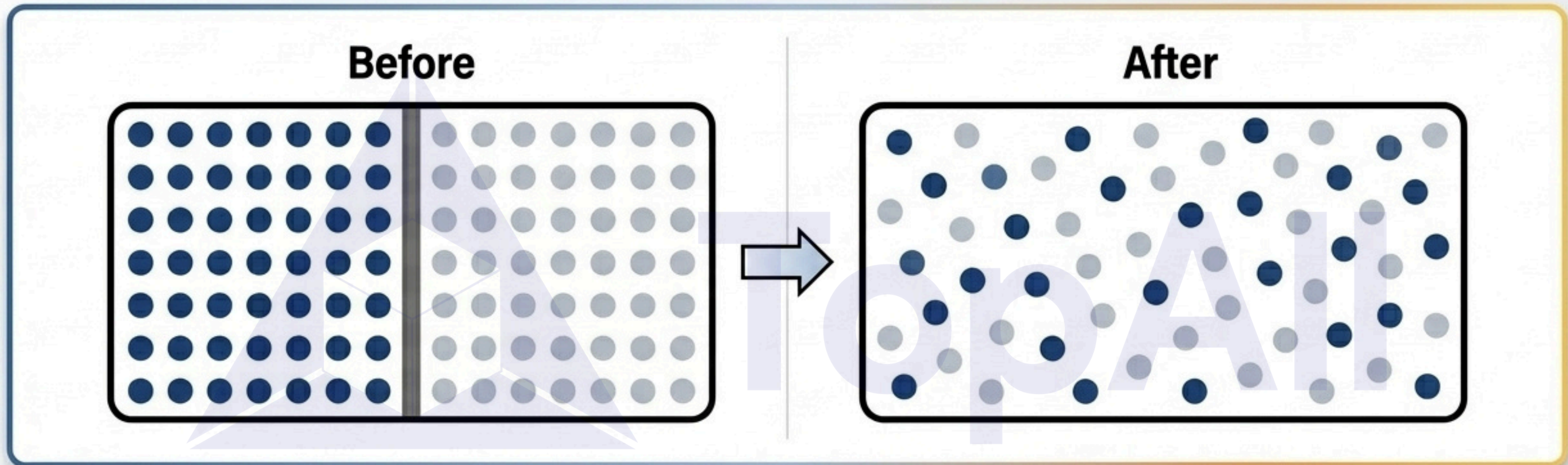
Endothermic



The dissolution of NaCl(s) or the reaction $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$ absorb heat ($\Delta H > 0$), yet they happen spontaneously. Why?

Entropy (S): A measure of the degree of randomness or disorder. The missing driver.

Gas Diffusion: A Drive Toward Chaos



Predictable

In State 1, picking a molecule from the left chamber guarantees it is Gas A. The system is ordered.

Chaotic

In State 2, picking a molecule anywhere yields a random result. The system is un-predictable.

Conclusion

Even with zero change in enthalpy ($\Delta H = 0$), the isolated system naturally progressed toward maximum disorder.



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$$E=mc^2$$



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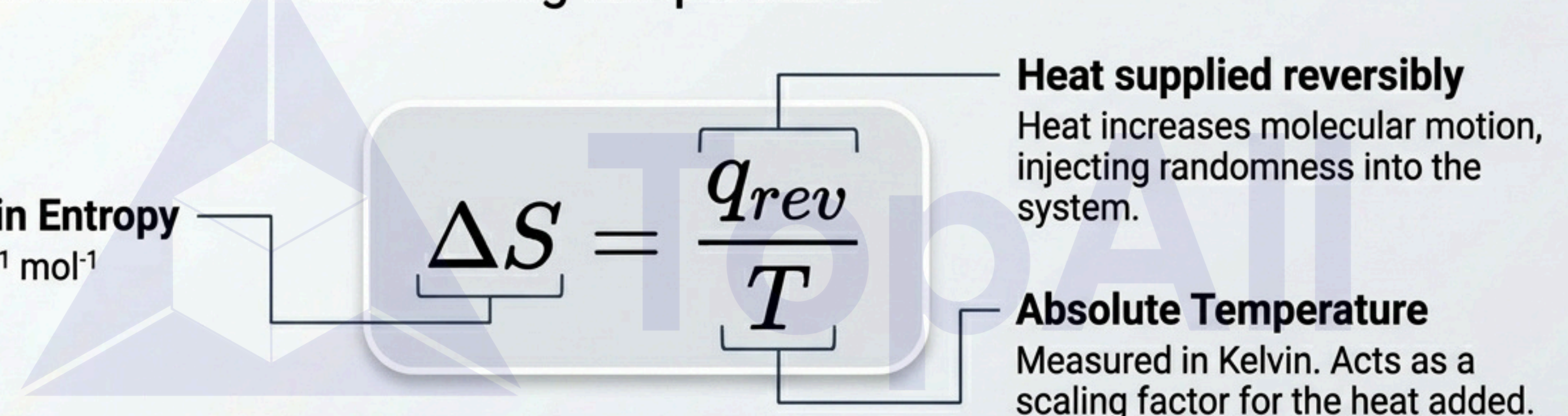


The Mathematics of Disorder

Entropy (S) is a state function. The change in entropy (ΔS) depends on the heat added and the starting temperature.

Change in Entropy

Units: $\text{J K}^{-1} \text{mol}^{-1}$


$$\Delta S = \frac{q_{rev}}{T}$$

The diagram shows the equation $\Delta S = \frac{q_{rev}}{T}$ with three callout lines. One line points from the text 'Change in Entropy' to the ΔS term. Another line points from the text 'Heat supplied reversibly' to the q_{rev} term. A third line points from the text 'Absolute Temperature' to the T term.

Heat supplied reversibly

Heat increases molecular motion, injecting randomness into the system.

Absolute Temperature

Measured in Kelvin. Acts as a scaling factor for the heat added.

Temperature scales the chaos: Adding heat to a cold system (low T) causes a massive spike in randomness. Adding the same heat to a hot, already-chaotic system (high T) has a much smaller effect.

The Universal Rule of Spontaneity

The Second Law of Thermodynamics states that for any spontaneous process, the total entropy of the universe must increase.

$$[\Delta S_{\text{system}}] + [\Delta S_{\text{surroundings}}] = [\Delta S_{\text{total}}]$$

$$\Delta S_{\text{total}} > 0$$

Spontaneous

The process is irreversible. The universe becomes more disordered.

$$\Delta S_{\text{total}} = 0$$

Equilibrium

Entropy has reached its maximum; macroscopic change stops.

$$\Delta S_{\text{total}} < 0$$

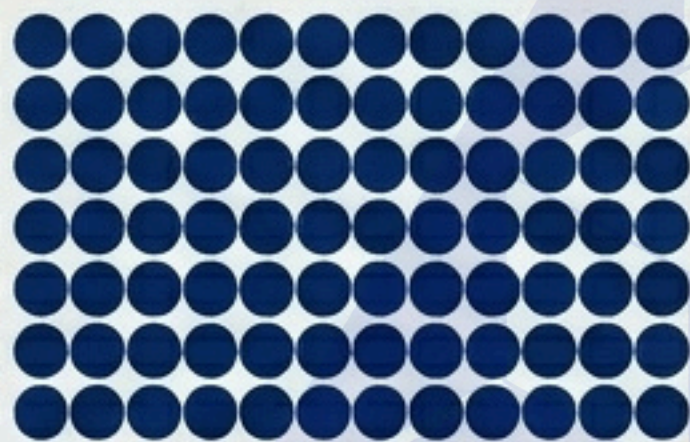
Non-spontaneous

The process will not happen under these conditions.

Entropy Across States of Matter

Solid

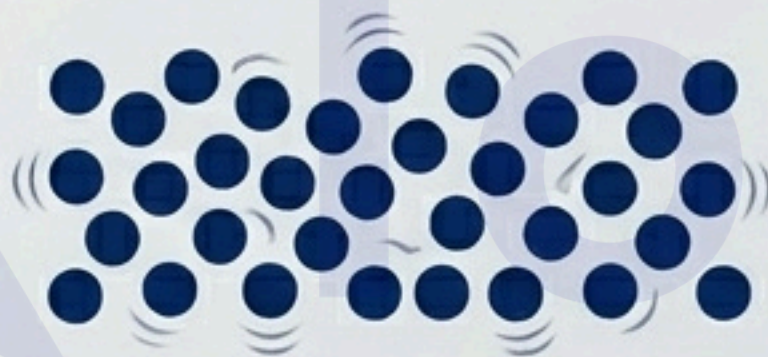
Lowest Entropy



Particles are restricted to oscillating about fixed positions.
High structural regularity.

Liquid

Moderate Entropy



Particles have translational and rotational freedom, but remain close together.

Gas

Highest Entropy



Maximum chaotic motion; molecules distribute freely to fill all available volume.

The Third Law of Thermodynamics: The entropy of a pure crystalline substance approaches zero as the temperature approaches absolute zero (0 K). At 0 K, there is perfect order.

Summary: The Two Engines of Spontaneity

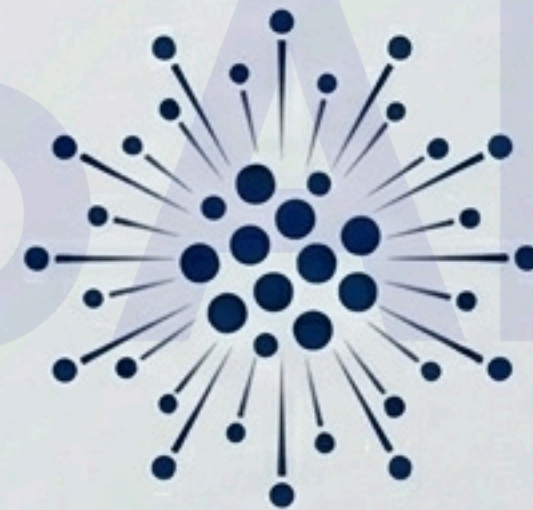
Whether a chemical reaction will happen naturally depends on a cosmic tug-of-war between two fundamental forces.

Engine 1: Enthalpy (ΔH)



The tendency of a system to seek the lowest possible energy state, typically by releasing heat to the surroundings.

Engine 2: Entropy (ΔS)



The tendency of an isolated system to seek maximum disorder, chaos, and unpredictability.

Aha! Spontaneity isn't just about losing heat—it's about the net balance of energy and chaos. This balance is calculated using the ultimate thermodynamic formula: **Gibbs Free Energy ($G = H - TS$)**.



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