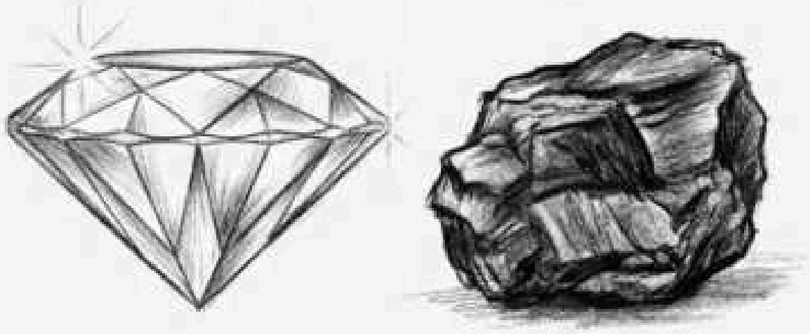
Entropy and Free Energy

¶ 5.1

CHEM 102 B Lecture 5

Spontaneity



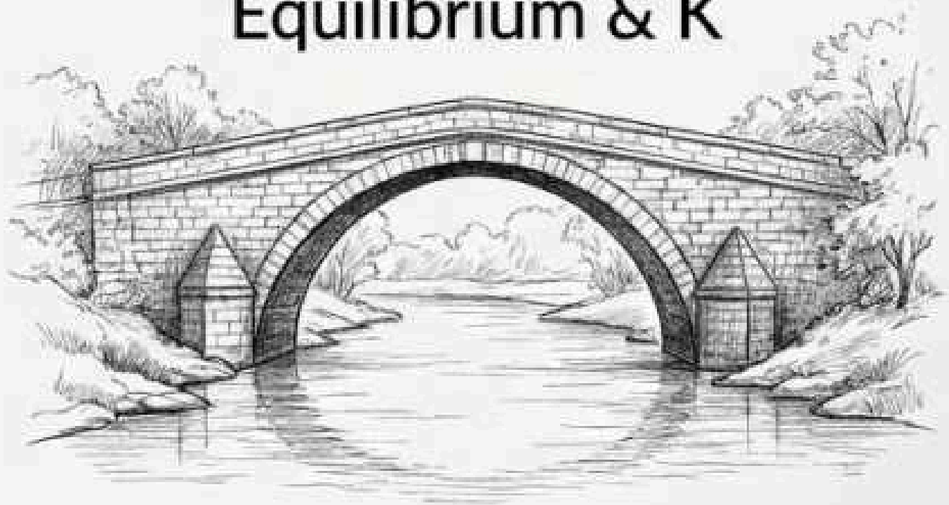
Laws of Thermodynamics

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

Gibbs Free Energy

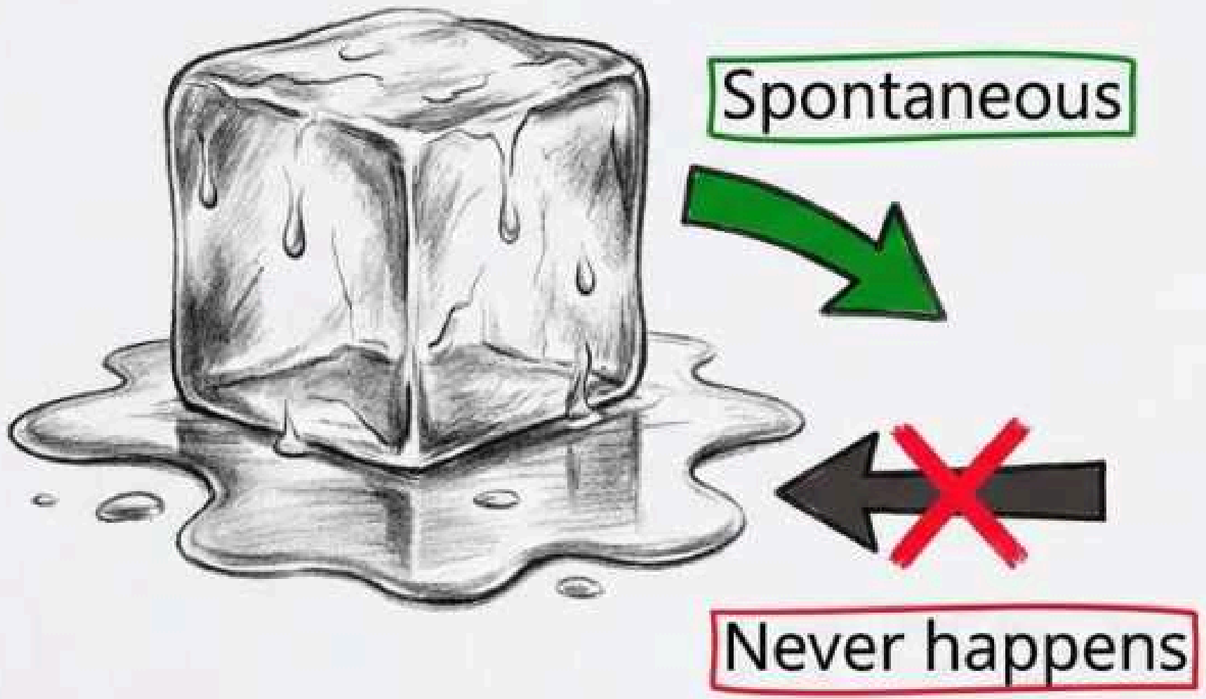
✓ → Spontaneous	← ✗ Non-spontaneous
✓ Forward Progress	✗ Reverse / No Progress

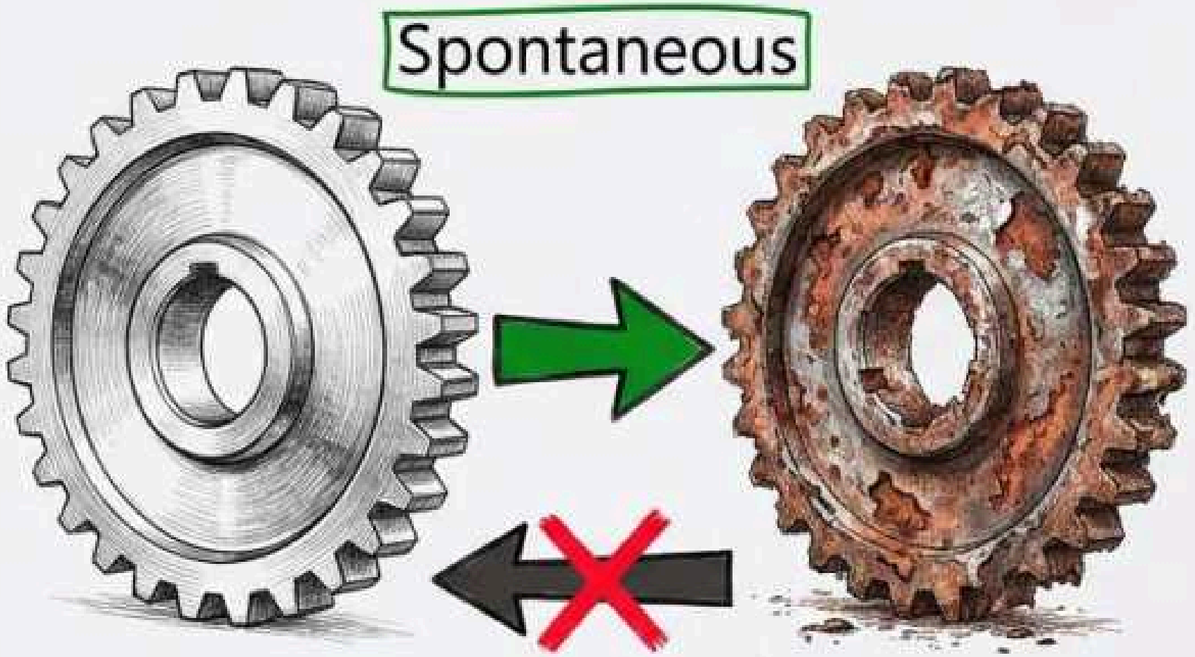
Equilibrium & K



The Direction of Nature: Why do some changes happen by themselves?

¶ 5.2

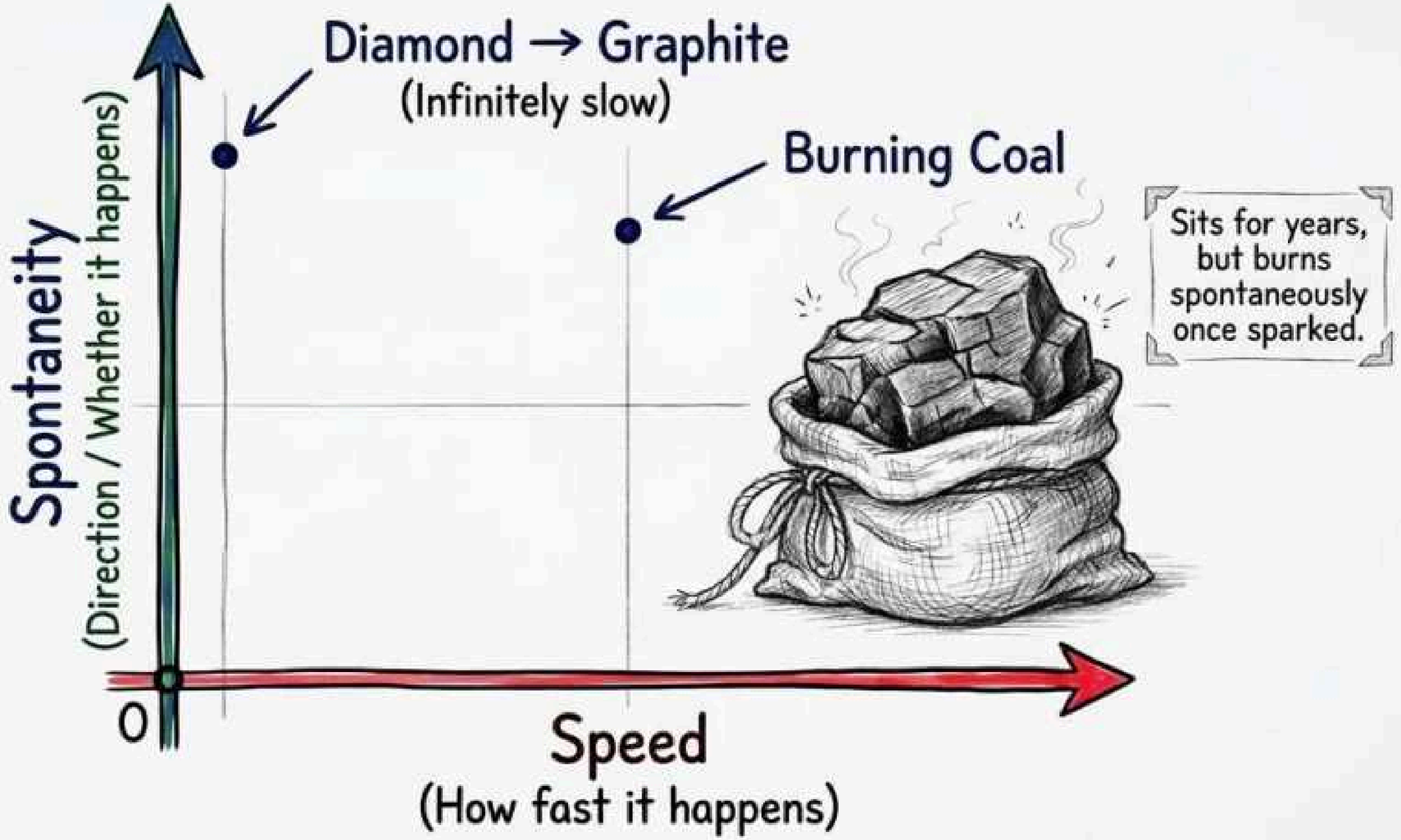




This lecture defines the underlying rule that governs this one-way direction, tying energy directly to equilibrium.

Spontaneous ≠ Fast: Direction vs. Speed

¶ 5.3



Kinetics tells you how fast. Thermodynamics tells you whether.

The Enthalpy Anomaly: Energy Alone is Not Enough

¶ 5.4

~~Only downhill energy (exothermic) is spontaneous.~~



Ice melting above 0°C

Absorbs heat (Endothermic) + Spontaneous



Ammonium nitrate dissolving

Absorbs heat (Endothermic) + Spontaneous

Many exothermic reactions are spontaneous, but these endothermic exceptions prove something else is at work.

The Missing Link: Boltzmann's **Entropy (S)**

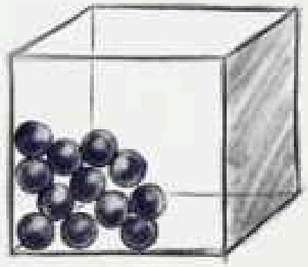
¶ 5.5

Entropy

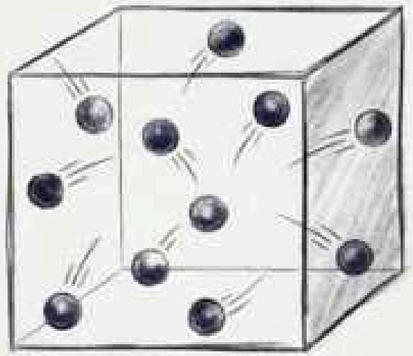
$$S = k \ln W$$

Boltzmann's constant

Number of microscopic arrangements (microstates)



Fewer arrangements
Low W / Low S

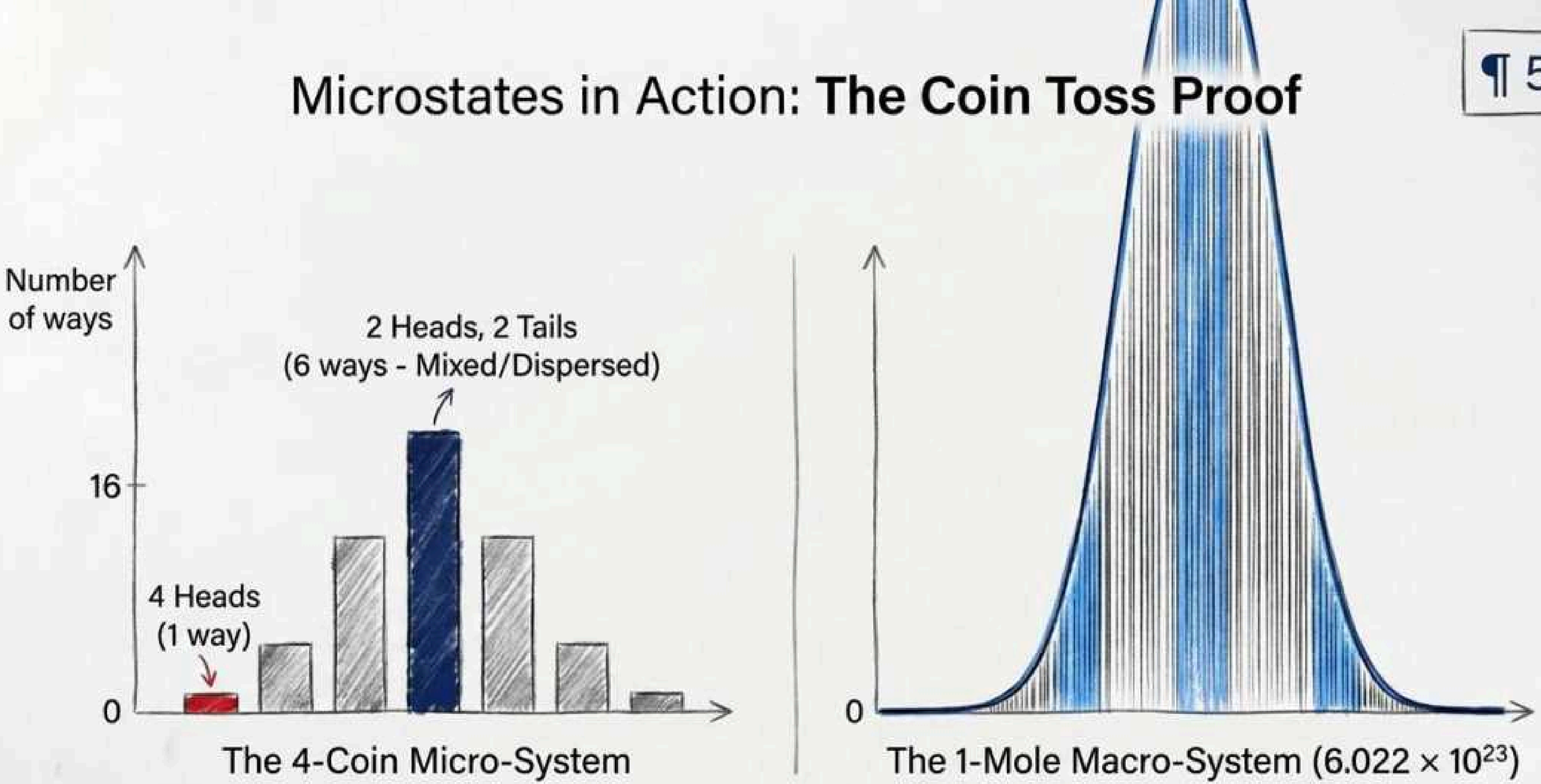


More arrangements
High W / High S

Entropy measures how widely energy and matter are dispersed among possible arrangements.

Microstates in Action: **The Coin Toss Proof**

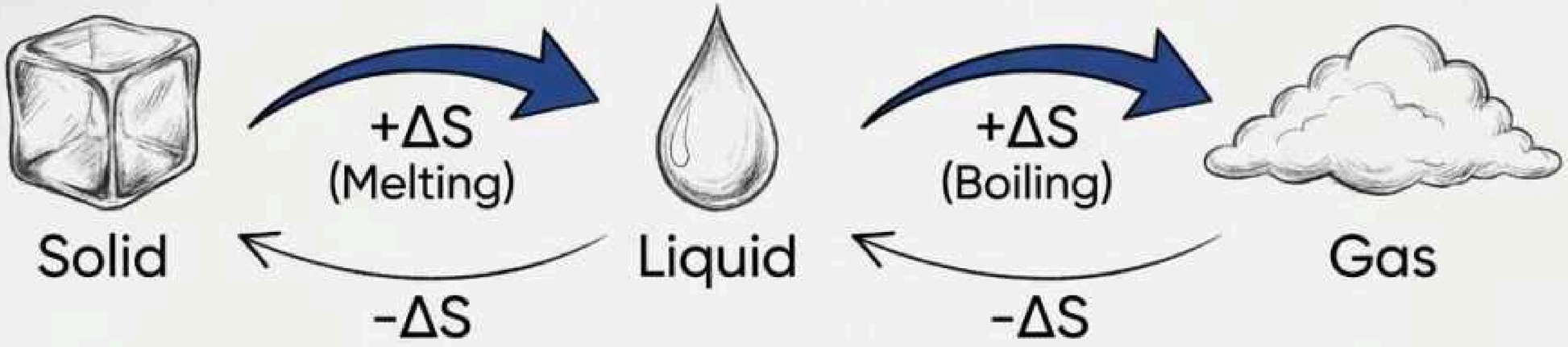
¶ 5.6



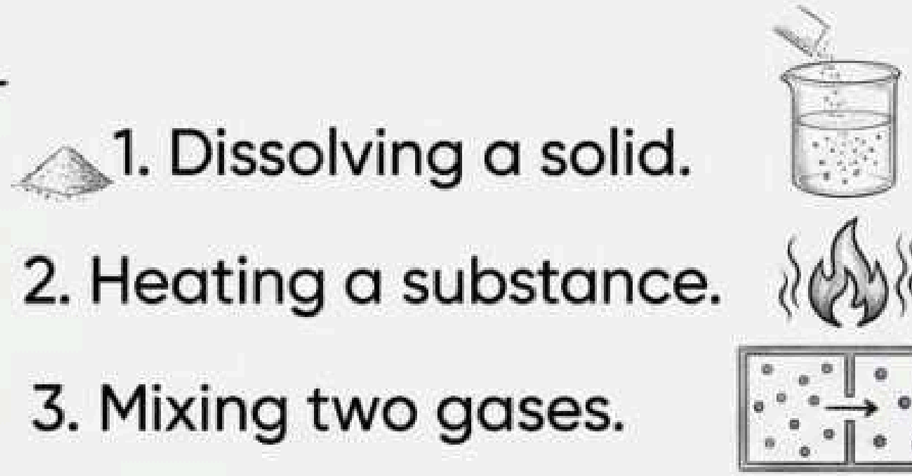
With a mole of particles, the odds against a perfectly ordered state are so astronomically huge that it never happens.

Predicting Entropy Changes (+ΔS)

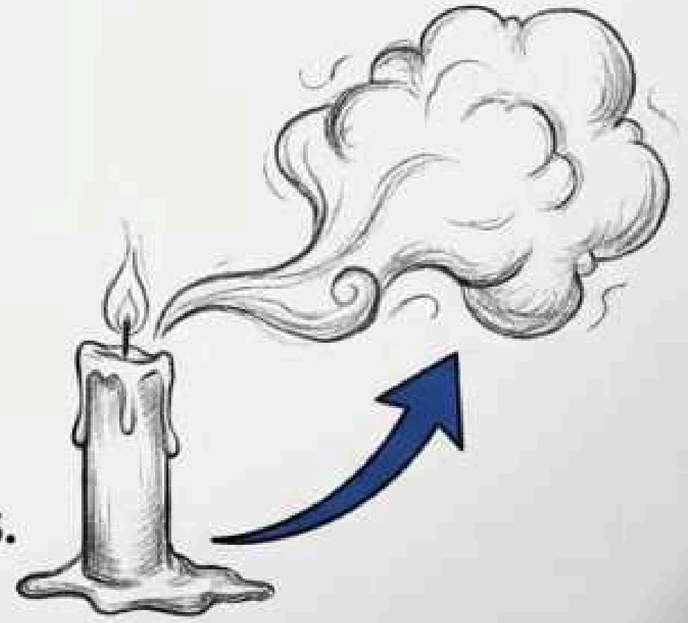
¶ 5.7



Actions that Increase Entropy:

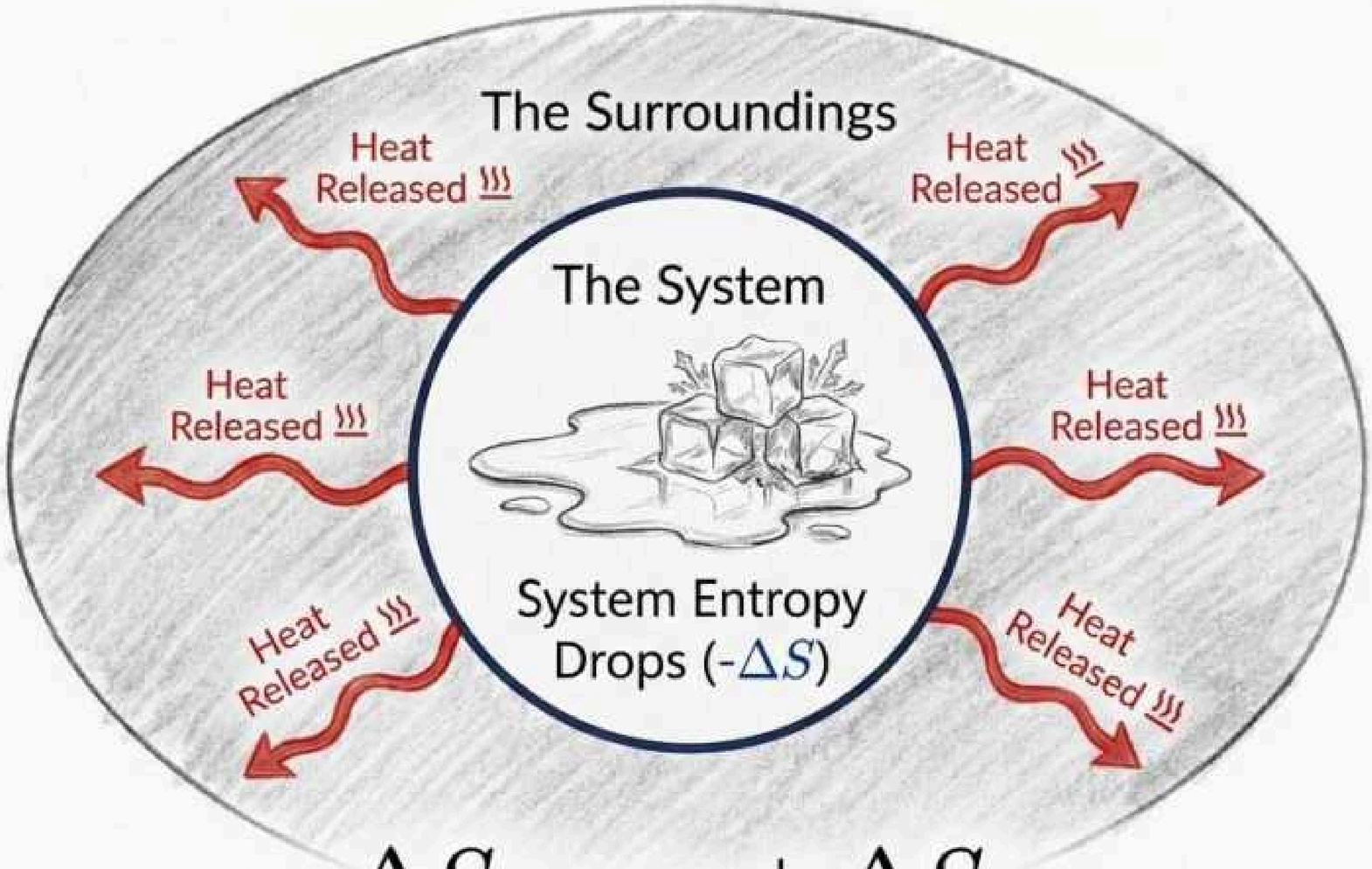


1. Dissolving a solid.
2. Heating a substance.
3. Mixing two gases.
4. Reaction producing more moles of gas.



The Second Law: The Universe Always Spreads Out

¶ 5.8

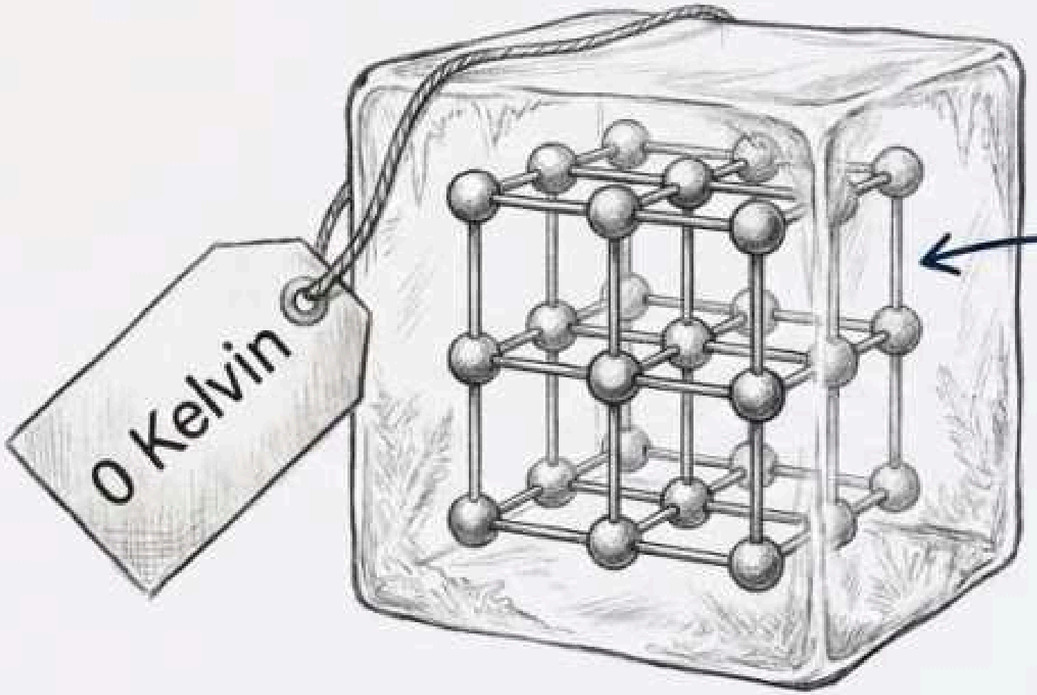


$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

A system can lower its own entropy (like water freezing) only if it dumps enough heat into the surroundings to raise their entropy by even more.

The Third Law: Establishing Absolute Zero

¶ 5.9



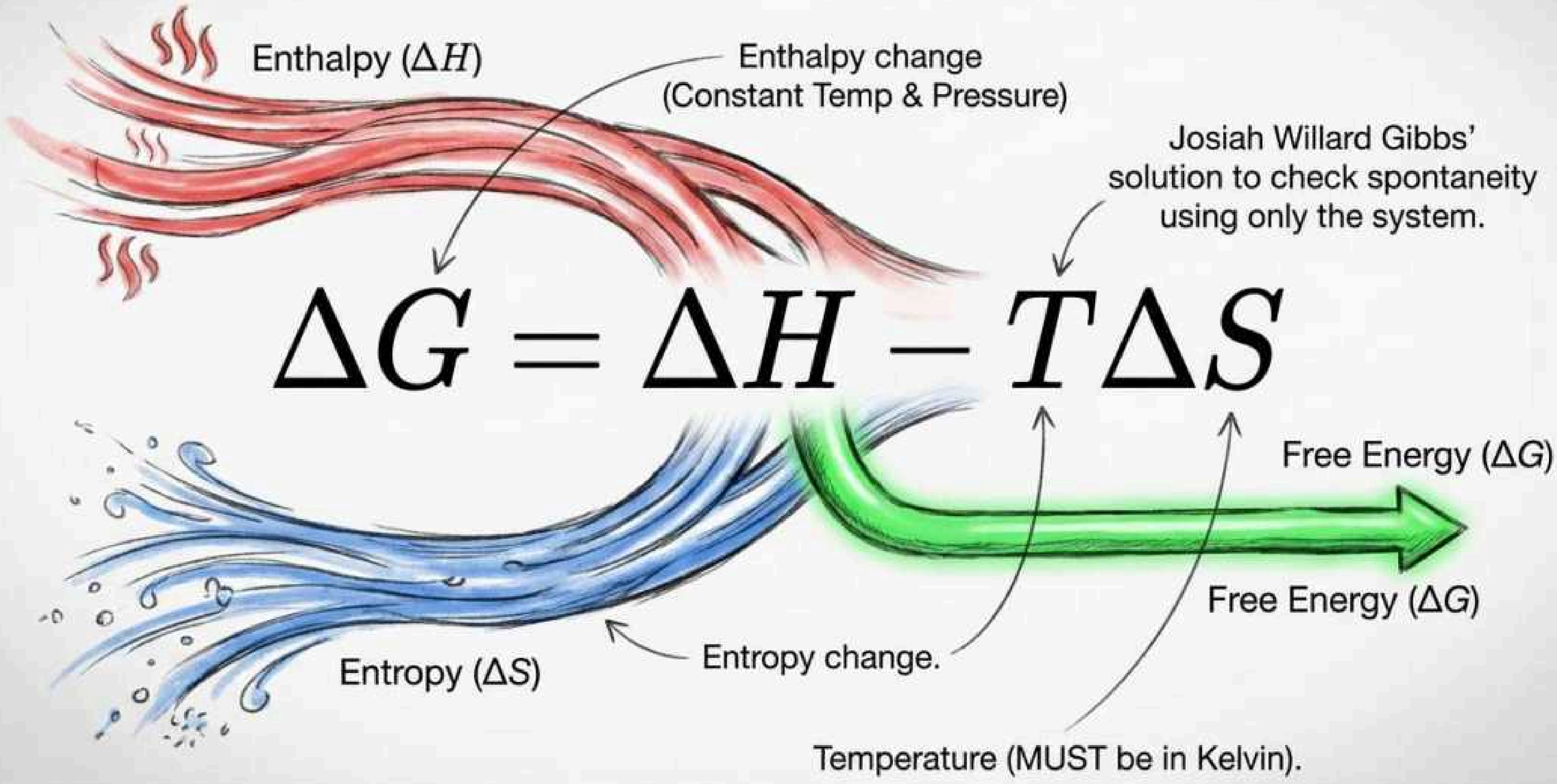
Only one possible arrangement. W = 1. Therefore, Entropy (S) = 0.

$$\Delta S_{reaction} = \sum(S_{products}) - \sum(S_{reactants})$$

Because we have a true zero point, we can tabulate absolute standard molar entropies for any substance.

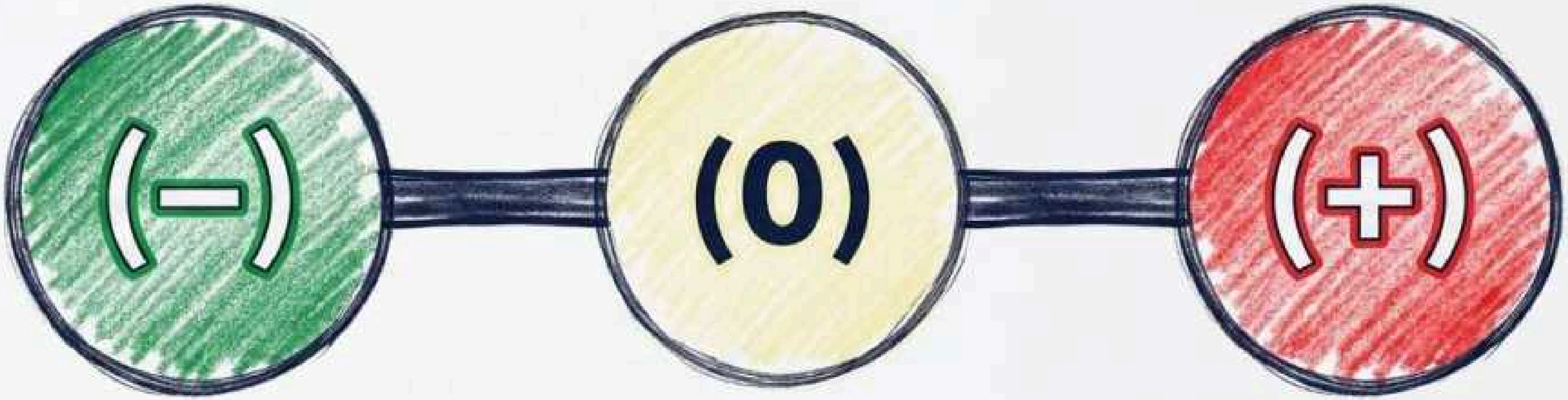
The Grand Unification: Gibbs Free Energy (G)

¶ 5.10



¶ 5.11

The Rule of ΔG: Reading the Output



ΔG is **NEGATIVE**.
Spontaneous as written.
(A drop in enthalpy or a rise in entropy helps).

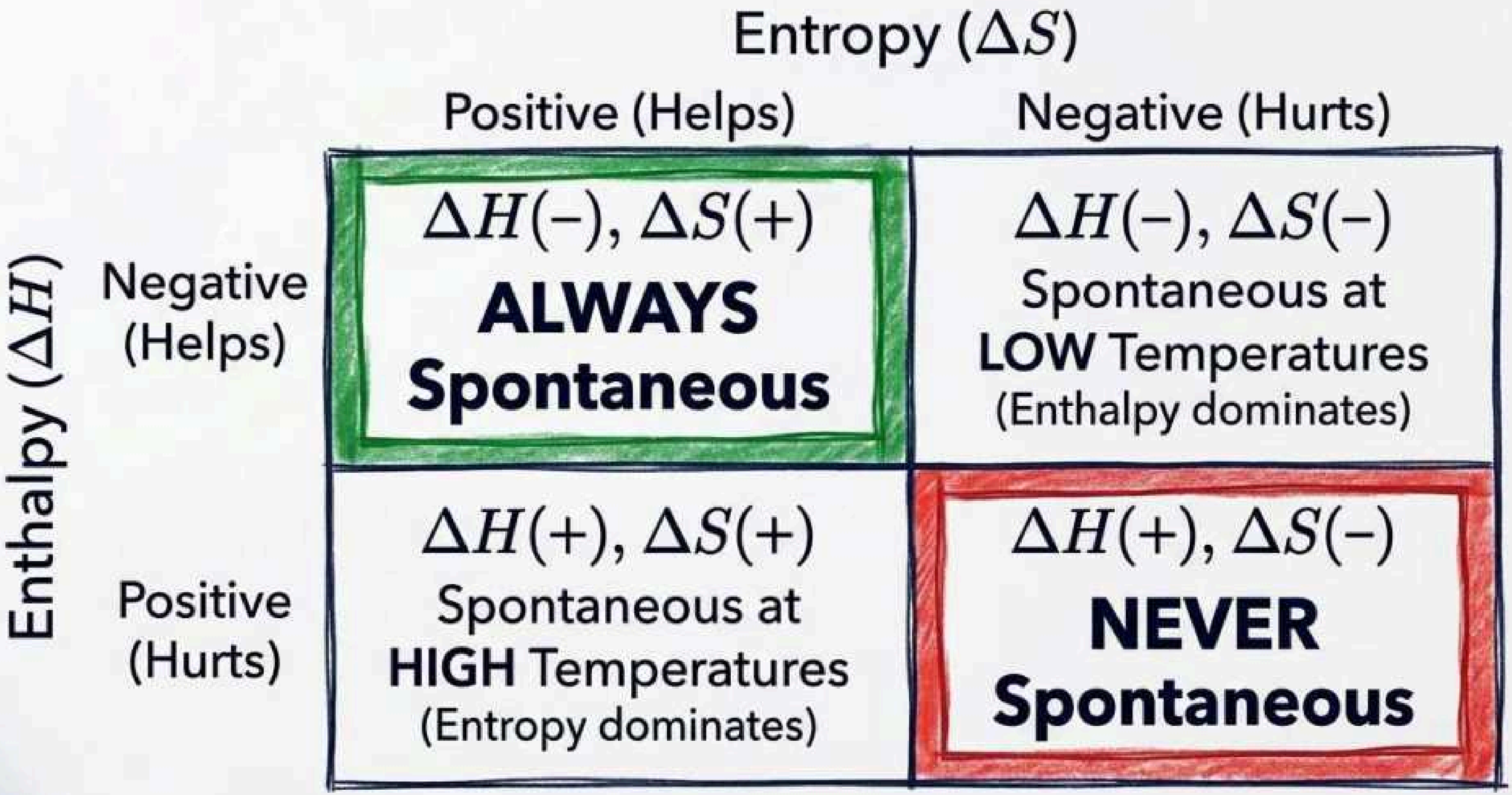
ΔG is **ZERO**.
System is at **Equilibrium**.

ΔG is **POSITIVE**.
Not spontaneous.
(But the reverse reaction is).

Temperature (T) sets the weight of the entropy effect in the equation.

The Four Cases of Free Energy

¶ 5.12



Equilibrium Math: Finding the Melting Point of Ice

¶ 5.13

Given Values: $\Delta H = +6.01$ kJ/mol (6010 J/mol)

$\Delta S = +22.0$ J/mol·K

Step 1: At equilibrium, $\Delta G = 0$

Step 2: Therefore, $0 = \Delta H - T\Delta S$, which rearranges to $T = \dfrac{\Delta H}{\Delta S}$

Step 3: $T = \dfrac{6010}{22.0}$

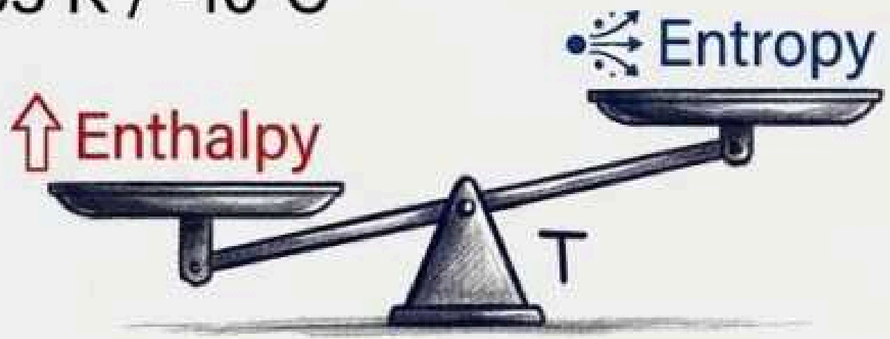
T = 273 K

Exactly the melting point of ice (0°C), perfectly predicted by the math.

Temperature as the Decider

¶ 5.14

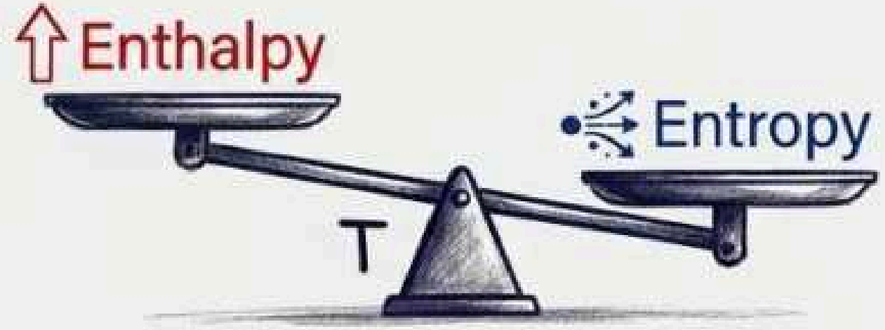
263 K / -10°C



$$6010 - (263 \times 22.0) = +224 \text{ J}$$

Positive $\Delta G \rightarrow$ Ice does not melt.

283 K / +10°C



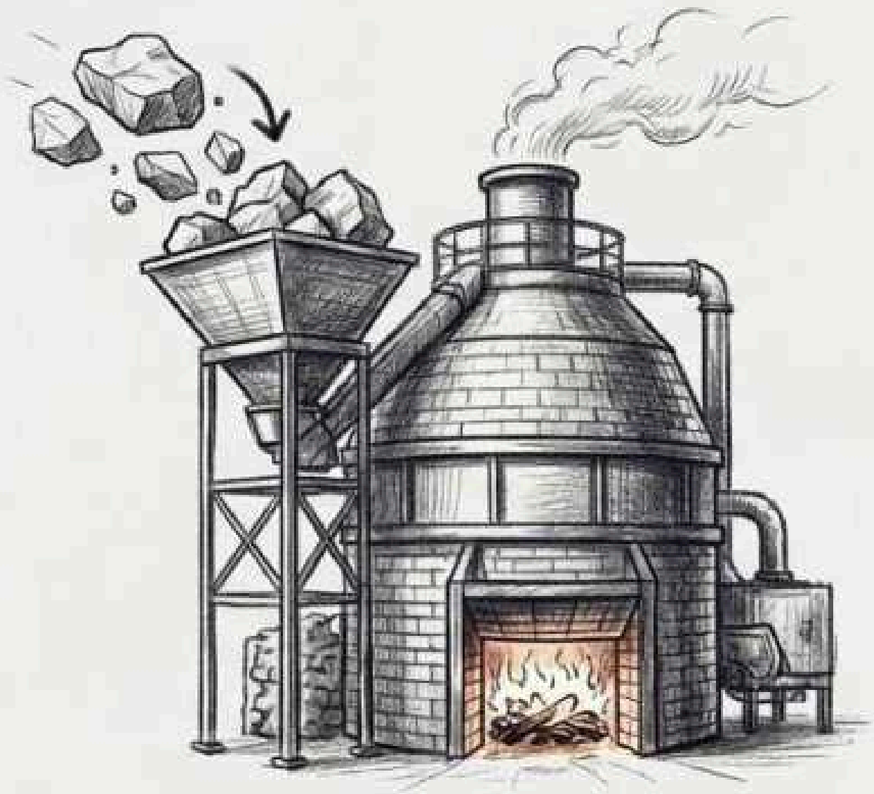
$$6010 - (283 \times 22.0) = -216 \text{ J}$$

Negative $\Delta G \rightarrow$ Ice melts.

Temperature shifts the balance of power between Enthalpy and Entropy.

The High-Temp Case: Unlocking Limestone

¶ 5.15



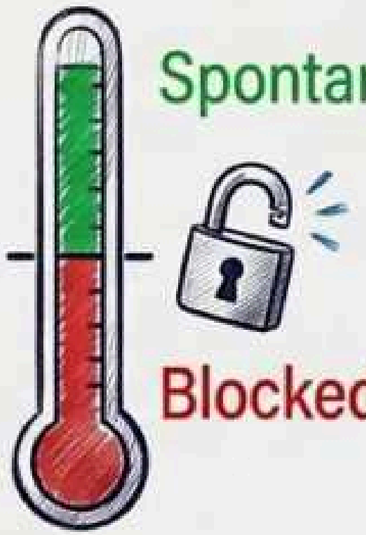
$$CaCO_3 \rightarrow CaO + CO_2$$

$\Delta H = +178$ kJ (Endothermic - hurts).

$\Delta S = +161$ J/K (Produces gas - helps).

Both are positive.

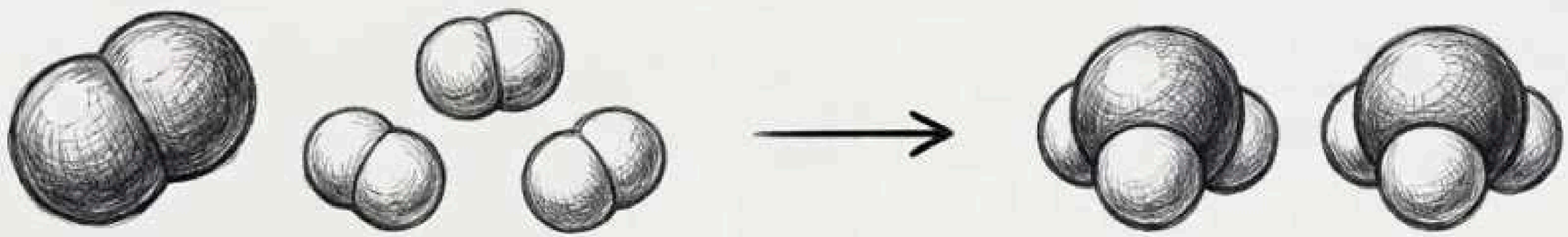
$$\frac{178{,}000}{161} \approx 1100 \text{ K}$$



This precise high-temperature threshold is how the world's lime is manufactured.

The Low-Temp Case: The Haber Process

¶ 5.16



$1\,N_2 + 3\,H_2$ $\longrightarrow$ $2\,NH_3$

4 moles of gas compress into 2 moles → Negative Entropy (−ΔS).

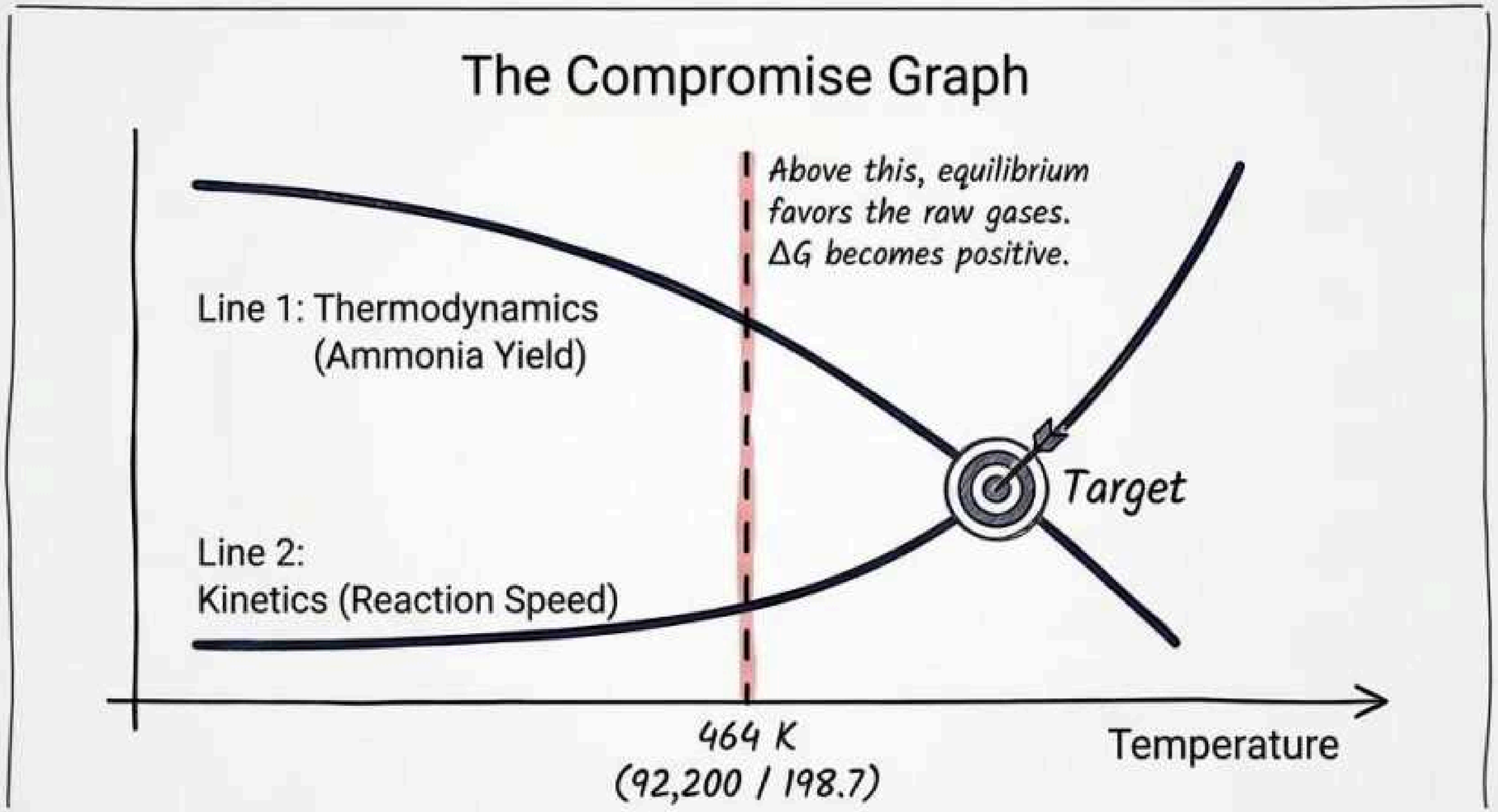
$\Delta H = -92.2\ \text{kJ}$ (Exothermic - helps).

$\Delta S = -198.7\ \text{J/K}$ (Decreases chaos - hurts).

Room Temp Check (298 K): $-92.2 + [298 \times (-0.1987)] = \boxed{-33\ \text{kJ}}$

It is spontaneous at low temperatures.

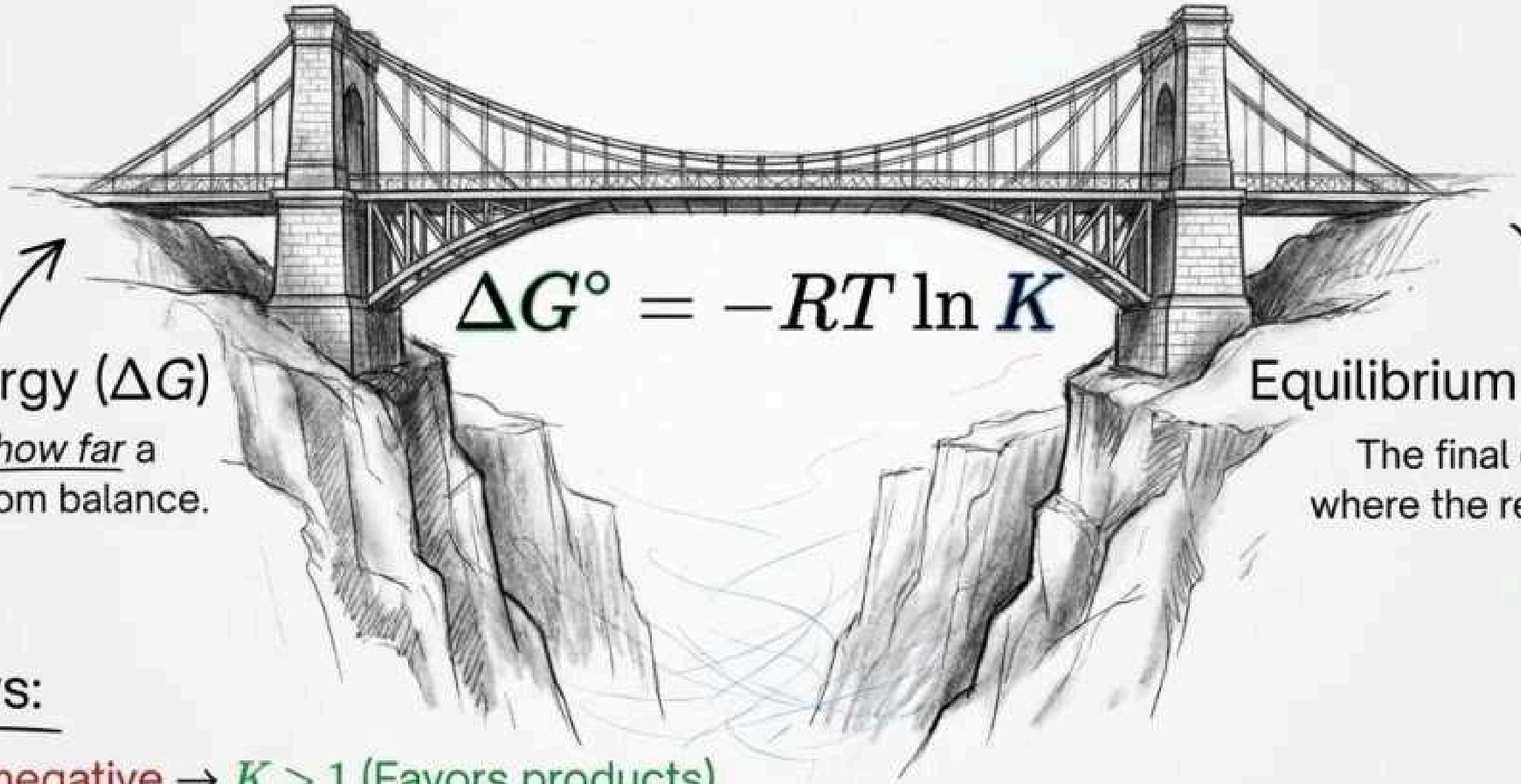
The Trade-Off: Thermodynamics vs. Kinetics



Takeaway: Low temp favors ammonia creation, but the reaction is too slow. Industry must operate at a compromise.

The Bridge to Equilibrium

¶ 5.18



$$\Delta G^\circ = -RT \ln K$$

Free Energy (ΔG)

Tells you *how far* a reaction is from balance.

Equilibrium Constant (K)

The final destination where the reaction stops.

Logic Keys:

- If ΔG° is negative $\rightarrow K > 1$ (Favors products)
- If $\Delta G^\circ = 0 \rightarrow K = 1$ (Perfect balance)
- If ΔG° is positive $\rightarrow K < 1$ (Favors reactants)

Calculating K: The Exponential Scale

¶ 5.19

At standard temperature (298 K), RT = 2478 J/mol

A Modest Reaction

$\Delta G°$ = -10 kJ (-10,000 J)

$$K = e^{\frac{10,000}{2478}}$$

$$K \approx 57$$

The Haber Process

$\Delta G°$ = -33 kJ (-33,000 J)

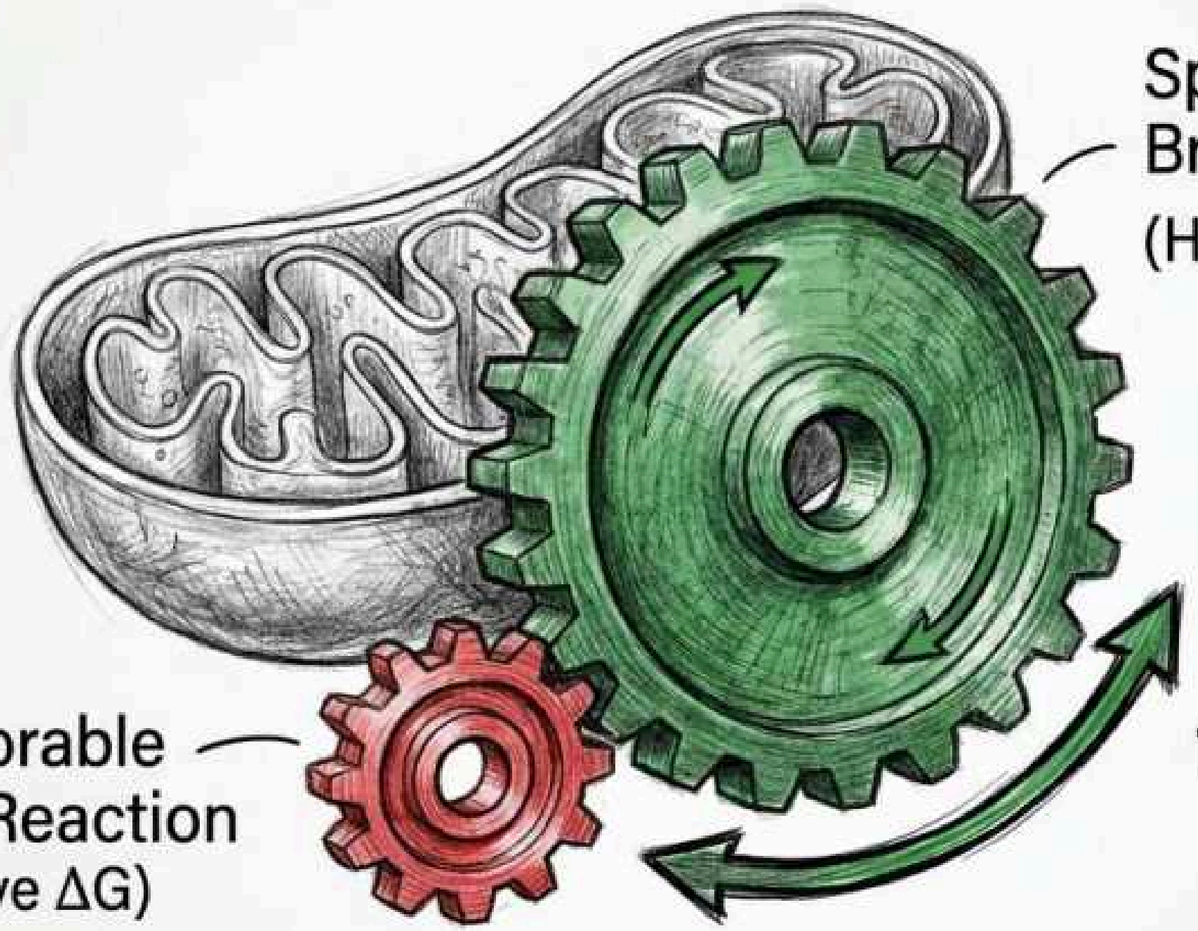
$$K = e^{\frac{33,000}{2478}}$$

$$K \approx 600,000$$

Because Free Energy and K are linked by a natural logarithm, even a modest increase in negative ΔG causes an explosive, exponential leap in the equilibrium constant.

Useful Work: How Life Hacks Thermodynamics

¶ 5.20



The sum of the coupled ΔG remains negative.

Free energy dictates the maximum useful work (or electrical voltage) a process can deliver. This is why living cells can build complex structures, and why heat strictly flows from hot to cold unless work is done.