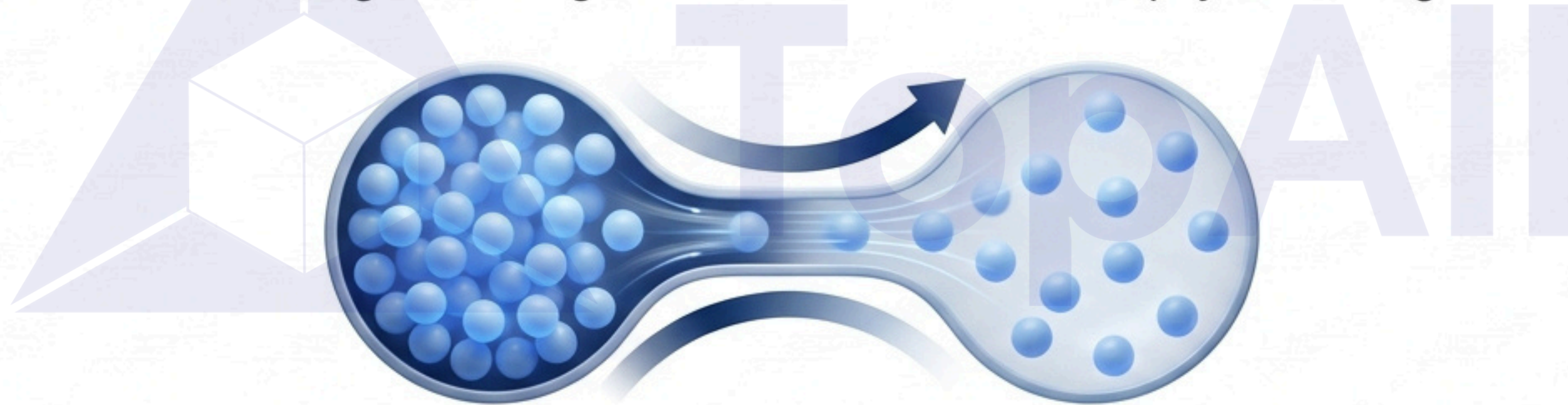


THERMODYNAMICS | SECTION 5.6

Spontaneity

Understanding the driving forces behind chemical and physical changes.



[Unidirectional Flow]

[Irreversibility]

[Driving Forces]

What Is a Spontaneous Process?

A process that has the potential to proceed without the assistance of an external agency.

It is a unidirectional, irreversible process.

“Spontaneous” does not mean fast—it simply means it can happen on its own (e.g., rusting is slow but naturally occurring).



Gas expanding to fill an available volume.



Heat flowing from a hotter body to a colder body.



Carbon burning in dioxygen to yield CO_2 .

Spontaneous $\neq$ Instantaneous. It strictly defines a natural tendency to occur.



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What Is a Non-Spontaneous Process?

 External Effort

A process that cannot occur on its own and requires continuous input of energy or work from an external agency.

If a process is spontaneous in one direction, it is strictly non-spontaneous in the **reverse** direction.

[Spontaneous]

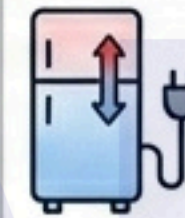


Heat flows from hot to cold (Happens naturally).

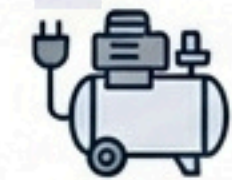


Gas expands to fill volume (Happens naturally).

[Non-Spontaneous]



Heat flows from cold to hot (Requires a refrigerator / external work).



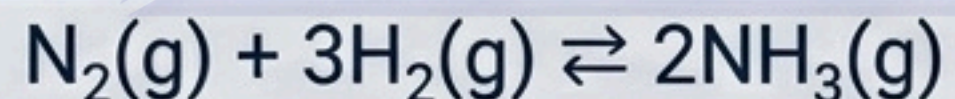
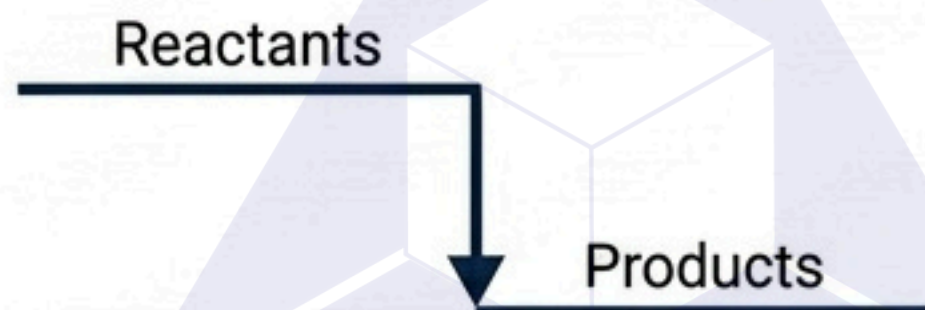
Gas contracts into one corner (Requires a compressor).

The reverse of any spontaneous process is always non-spontaneous.

Why Enthalpy Alone Is Not Enough

We might assume systems always seek the lowest energy state. But is a decrease in enthalpy the only rule?

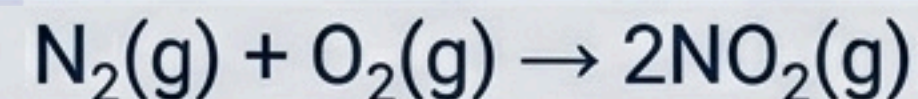
Many spontaneous reactions are **Exothermic** (release heat, decrease energy).



$$\Delta_r H = -46.1 \text{ kJ mol}^{-1}$$

[Supports Assumption]

However, some spontaneous reactions are **Endothermic** (absorb heat, increase energy).



$$\Delta_r H = +33.2 \text{ kJ mol}^{-1}$$

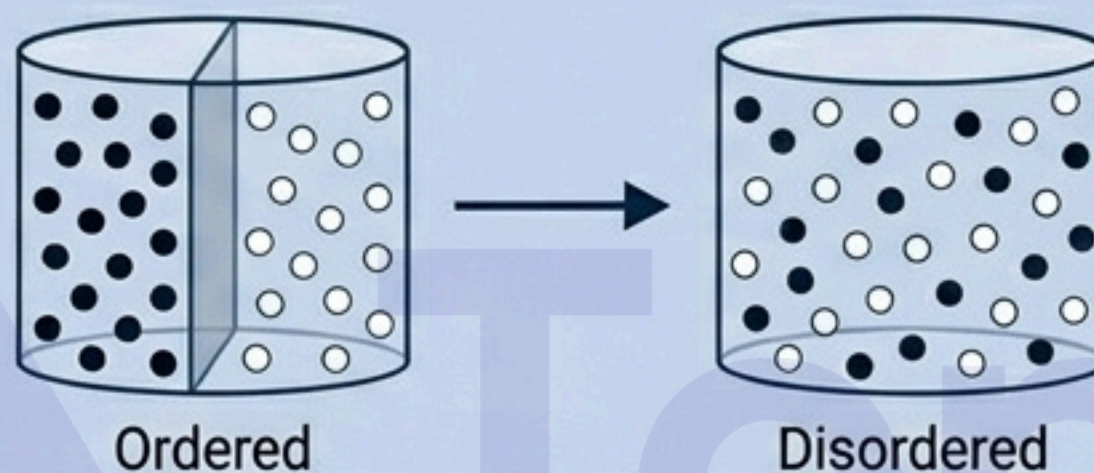
[Breaks Assumption]

The
Paradox

Conclusion: A decrease in enthalpy ($\Delta H < 0$) is a contributory factor for spontaneity, but it is not the sole criterion. Something else must be driving these reactions.

If Not Enthalpy, Then What?

Diffusion of two gases in an isolated closed container.



$$\Delta H = 0 \text{ (No energy change).}$$

Observation: The gases still mix spontaneously. **Why?** Because the system inherently moves from order to chaos.

In an isolated system, there is always a tendency for energy to become **more disordered or chaotic**. This drive toward randomness is the **true ultimate driver** of spontaneous change.

This degree of randomness introduces a new thermodynamic state function: **Entropy (S)**.

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0 \text{ (For a spontaneous process)}$$



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