Entropy and feasibility

Entropy as disorder, entropy changes of a system and its surroundings, total entropy and feasibility, the temperature at which a reaction becomes feasible, and thermodynamic versus kinetic stability.

Why enthalpy is not enough

Some **endothermic** reactions occur spontaneously at room temperature, for example dissolving ammonium nitrate in water or mixing solid barium hydroxide with ammonium chloride. So the enthalpy change alone does not decide whether a reaction happens.

Entropy

Entropy, S, is a measure of the **disorder** of a system: the number of ways in which the molecules and the energy quanta can be arranged. It has units J K^{-1} mol^{-1}.

- Entropy **increases with temperature**, because the energy is spread over more energy levels.
- S(solid) < S(liquid) < S(gas). A large jump occurs on boiling.
- A **perfect crystal at 0 K has zero entropy**.
- Reactions that produce **more moles of gas** have a positive entropy change.

Entropy changes occur:

- during **changes of state**: melting and boiling increase entropy,
- when an ionic lattice **dissolves** (usually an increase, as ions are dispersed, although hydration can order the water),
- when the number of **moles changes** in a reaction: more moles of products than reactants, particularly of gas, increases entropy.

The total entropy change

The natural direction of change is towards **greater total entropy**: gases spread out to fill the room and heat flows from hot to cold.

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

The system

$$\Delta S_{system} = \sum S(\text{products}) - \sum S(\text{reactants})$$

using standard entropy values (always positive for substances).

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The surroundings

An exothermic reaction transfers heat to the surroundings and increases their entropy.

$\Delta S_{surroundings} = -\frac{\Delta H}{T}$

with ΔH in **J mol^{-1}** (not kJ) and T in kelvin.

> **TRY IT**
>
> For $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$, $\Delta H = +178$ kJ mol^{-1} and $\Delta S_{system} = +161$ J K^{-1} mol^{-1}. Find ΔS_{total} at 298 K and the minimum temperature at which the reaction is feasible.

At 298 K: $\Delta S_{surr} = -178000/298 = -597$ J K^{-1} mol^{-1}. $\Delta S_{total} = 161 - 597 = -436$, which is negative, so the reaction is **not feasible** at 298 K.

The reaction becomes feasible when $\Delta S_{total} = 0$: $161 = 178000/T$, so $T = 1106$ K.

Feasibility

A reaction is **feasible** (thermodynamically able to occur) if $\Delta S_{total} > 0$. The sign and size of each contribution matter:

- If ΔH is negative and ΔS_{system} positive, ΔS_{total} is always positive.
- If ΔH is positive and ΔS_{system} positive, the reaction is feasible only at **high temperature**, because the term $-\Delta H/T$ gets smaller as T rises.
- A reaction can occur even when **one** of the entropy changes is negative, provided the total is positive.

> **NOTE**
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> You may use the equivalent $\Delta G = \Delta H - T\Delta S_{system}$. A reaction is feasible if $\Delta G < 0$. This is just $-T\Delta S_{total}$.

> **Remember to convert ΔH from kJ to J when you divide by T, because entropy is given in J K^{-1} mol^{-1}.**

Thermodynamic and kinetic stability

A reaction that is feasible ($\Delta S_{total} > 0$) may still not occur at a measurable rate, because of a high **activation energy**.

- **Thermodynamic stability**: the substance does not tend to react, because the reaction has a negative total entropy change.

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- **Kinetic stability**: the reaction is feasible but too slow, because E_a is high.

Diamond turning into graphite and a mixture of hydrogen and oxygen at room temperature are feasible but **kinetically stable**.

Some investigations: adding ammonium nitrate crystals to water (endothermic, spontaneous, entropy increases as the lattice dissolves), and reacting ethanoic acid with ammonium carbonate (endothermic, with gas produced).

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