23.3 ENTROPY CHANGE

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🎯 **Learning outcomes**

Candidates should be able to:

1. Define the term entropy, S, as the number of possible arrangements of the particles and their energy in a given system
2. Predict and explain the sign of the entropy changes that occur:
   (a) during a change in state, e.g., melting, boiling, and dissolving (and their reverse)
   (b) during a temperature change
   (c) during a reaction in which there is a change in the number of gaseous molecules
3. Calculate the entropy change for a reaction, ΔS, given the standard entropies, $S^{\ominus}$, of the reactants and products, $\Delta S^{\ominus} = \Sigma S^{\ominus}$ (products) – $\Sigma S^{\ominus}$ (reactants)
   (use of $\Delta S^{\ominus} = \Delta S_{surr} + \Delta S_{sys}$ is not required)

Introduction to entropy

What is Entropy?

Entropy (S) is a measure of the **number of possible arrangements** of particles and their energy within a system.

In simple terms, it measures how **disordered** or **spread out** a system is.

A **system** is the part under investigation. In chemistry, this is the chemical reaction itself, i.e., reactants being converted to products.

The system of magnesium reacting with sulfuric acid in a test tube to form magnesium sulfate and hydrogen releases energy to the surroundings.

Surroundings: anything other than the chemical reactants and products, e.g., the solvent and reaction vessel.

The **surroundings** include:

- the solvent (in this case, water)
- the air around the test tube
- the test-tube itself
- anything dipping into the test tube (e.g., a thermometer).

[Brian Cox explains why time travels in one direction - BBC]

✦ The Golden Rule of Entropy

The **more disordered** a system becomes, the **higher its entropy**, and the **more energetically stable** it is.

S(gas) > S(liquid) > S(solid)

Factors Affecting Entropy

Entropy is greater if:

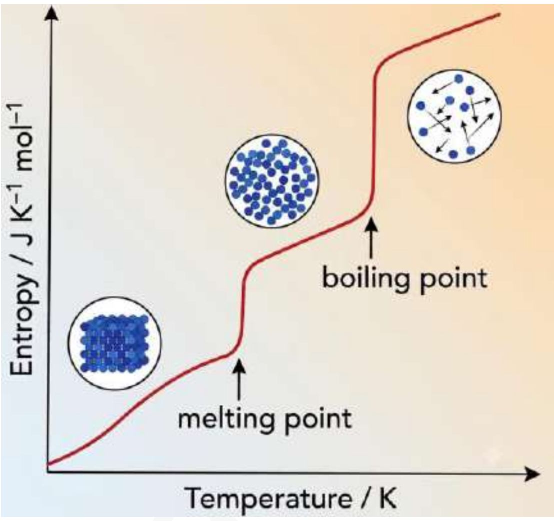
- ➢ there are more ways of arranging the energy in a molecule or atom
- ➢ There are more ways to arrange molecules or atoms in a given volume.

- **State of matter:** Gases have the highest entropy; solids have the lowest.
- **Temperature:** Higher temperature → more particle motion and more the number of possible energy arrancements→ higher entropy.
- **Number of particles:** More moles of gas molecules → more arrangements → higher entropy.
- For concentrated aqueous solutions of salts that have highly charged ions, there may be a considerable order in the solvent due to several hydration layers around these ions.

Changes that tend to continue to happen naturally are called *spontaneous changes*. Once started, a spontaneous change will carry on. When a spark is applied, methane gas reacts with oxygen in a spontaneous reaction to form carbon dioxide and water. The reaction is spontaneous because the methane continues to burn in the oxygen until either the methane or the oxygen is completely used up. For a reaction to be spontaneous, it does not need to happen rapidly. Many spontaneous reactions are slow or need an input of energy to start them.
Entropy can also be thought of as a dispersal of energy, either from the system to the surroundings or from the surroundings to the system. The system becomes energetically more stable when it becomes more disordered.

- All elements (and compounds) have positive standard molar entropy values.
- Larger, more complex molecules generally have higher entropy because they possess more ways of arranging energy. Example: $CH_4 < C_2H_6 < C_3H_8$

[What is entropy? - Jeff Phillips]



Signs of Entropy changes

Changes of State

Change	Effect on Entropy
Solid → Liquid (melting)	↑ Increases — regular lattice → irregular arrangement; particles can rotate & slide
Liquid → Gas (boiling)	↑ Increases significantly — particles now freely move, very disordered
Gas → Liquid (condensing)	↓ Decreases — particles brought together, more ordered
Liquid → Solid (freezing)	↓ Decreases — fixed lattice positions, least disorder
Dissolving a solid	↑ Increases — particles spread out in solvent; more arrangements of energy
Crystallisation	↓ Decreases — ions/molecules become locked in an ordered solid lattice

Entropy Changes in Reactions

The key driver is the **change in the number of gaseous molecules**:

- **More gas molecules in products → $\Delta S > 0$** (entropy increases)
- **Fewer gas molecules in products → $\Delta S < 0$** (entropy decreases)
- If no change in moles of gas, ΔS is small and determined by other factors.

Worked Examples — Qualitative

Worked Example 1: $CaCO_3$ decomposition

$CaCO_3$ (s) → CaO (s) + CO_2 (g)

Solid reactant produces a **gas**. CO_2 can move freely → system becomes more disordered.

Result: ΔS > 0 (entropy increases) ✓

Worked Example 2: Haber Process — ammonia formation

N_2 (g) + $3H_2$ (g) ⇋ $2NH_3$ (g)

4 moles of gas (reactants) → 2 moles of gas (products).

Fewer gas molecules → fewer ways of arranging energy → more ordered system.

Result: ΔS < 0 (entropy decreases) ✓

Calculating entropy changes

When selecting entropy and free energy values from data tables, make sure to look carefully at the state symbols.

The Formula

ΔS° system = ΣS° products – ΣS° reactants

Units: J K^{-1} mol^{-1} *(note: NOT kJ)*

Σ = 'sum of'. Multiply each S° value by the stoichiometric coefficient.

Step-by-Step Method

- Write the balanced equation with **state symbols**.
- List all S° values (given in data booklet or question).
- Multiply each S° value by its stoichiometric coefficient.
- $\Delta S° = \Sigma(S° \times \text{coefficient})_{\text{products}} - \Sigma(S° \times \text{coefficient})_{\text{reactants}}$
- Check sign: ΔS > 0 means more disorder; ΔS < 0 means more order.

Worked Example

Calculate ΔS° system for: 2Mg (s) + O_2 (g) → 2MgO (s)

Given:

S° [Mg (s)] = 32.60 J K^{-1} mol^{-1}

S° [O_2 (g)] = 205.0 J K^{-1} mol^{-1}

S° [MgO (s)] = 38.20 J K^{-1} mol^{-1}

Solution:

ΔS° = ΣS° products – ΣS° reactants

ΔS° = (2 × 38.20) – (2 × 32.60 + 1 × 205.0)

ΔS° = 76.40 – 270.20

ΔS° = −193.8 J K^{-1} mol^{-1}

Interpretation: ΔS < 0. Solid MgO is more ordered than Mg + O_2 gas. Entropy decreases. ✓

R1.4.1 Calculate the standard entropy change for a reaction [HL IB Chemistry]

✓ **DO remember:**

- Always use stoichiometric coefficients when calculating ΔS°.
- Include correct state symbols — entropy values differ significantly between states.
- Units for S° are J K^{-1} mol^{-1}, NOT kJ. Don't mix up with enthalpy (ΔH).
- $\Delta S > 0 \rightarrow$ products more disordered; $\Delta S < 0 \rightarrow$ products more ordered.

❌ **DO NOT confuse:**

- System vs. surroundings: The system = reacting molecules; surroundings = everything else.
- Entropy (S) with enthalpy (H) — they are different thermodynamic quantities.
- Forgetting to count moles of gas carefully in equations like the Haber process.
- Assuming that a positive ΔH always means entropy increases — these are independent.

Quick Summary

- Entropy = disorder/randomness gas > liquid > solid
- Higher temperature → higher entropy
- Producing gases usually increases entropy
- More gas molecules → larger entropy
- Dissolving usually increases entropy

Use: $\Delta S^\circ = \Sigma S^\circ(\text{products}) - \Sigma S^\circ(\text{reactants})$

***Use this guide alongside the prescribed textbooks for complete coverage & exam preparation. ***