Cambridge (CIE) A Level Chemistry

Your notes

Entropy Change, ΔS

Contents

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Defining Entropy

- The **entropy (S)** of a given system is the number of possible arrangements of the particles and their energy in a given system
    - In other words, it is a measure of how **disordered** a system is
- When a system becomes **more disordered**, its entropy will **increase**
- An increase in entropy means that the system becomes **energetically more stable**

Examples

- Thermal decomposition of calcium carbonate

$$CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)$$

- The entropy of the system increases
    - In this decomposition reaction, a **gas** molecule (CO_2) is formed
    - The CO_2 gas molecule is more disordered than the solid reactant ($CaCO_3$), as it is constantly moving around
    - The system has become more **disordered** and there is an **increase** in **entropy**
- Melting ice to form liquid water:

$$H_2O\,(s) \rightarrow H_2O\,(l)$$

- The water molecules in ice are in fixed positions and can only vibrate about those positions
- In the liquid state, the particles are still quite close together but are arranged more randomly, in that they can move around each other
- Water molecules in the liquid state are therefore more **disordered**
    - Thus, for a given substance, the **entropy increases** when its solid form melts into a liquid
- In both examples, the system with the **higher entropy** will be **energetically the most stable** (as the energy of the system is more spread out when it is in a disordered state)

Entropy between physical states

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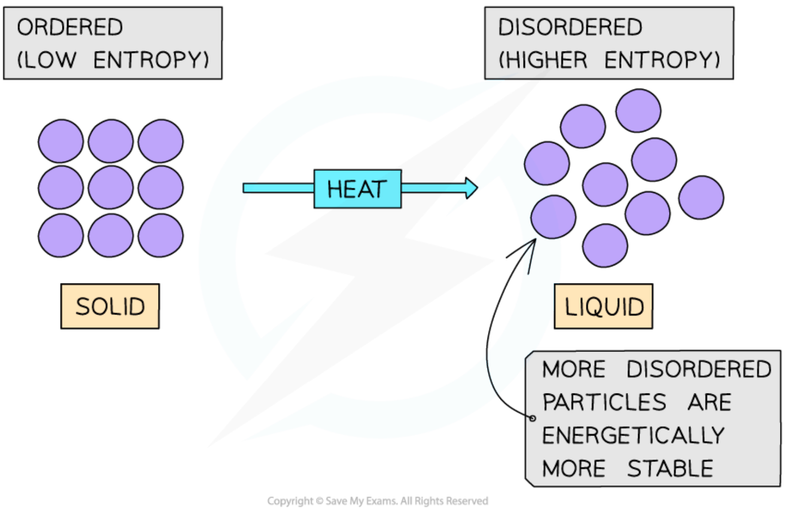

Melting a solid will cause the particles to become more disordered resulting in a more energetically stable system

Examiner Tips and Tricks

Make sure you don't confuse the system with your surroundings!

The system consists of the molecules that are reacting in a chemical reaction

The surroundings are everything else such as the solvent, the air around the reaction, test-tube, etc

Entropy Changes

- All elements have positive standard molar entropy values
- The order of entropy for the different states of matter are as follows:

gas > liquid > solid

- There are some exceptions such as calcium carbonate (solid) which has a higher entropy than mercury (liquid)
- **Simpler substances** with fewer atoms have **lower entropy** values than complex substances with more atoms
  - For example, calcium oxide (CaO) has a smaller entropy than calcium carbonate ($CaCO_3$)
- **Harder** substances have **lower entropy** than softer substances of the **same type**
  - For example, diamond has a smaller entropy than graphite

Change in state

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- The entropy of a substance changes during a **change in state**

Solid to liquid

- The entropy **increases** when a substance melts
  - Increasing the temperature of a solid causes the particles to vibrate more
  - The **regularly** arranged lattice of particles changes into an **irregular** arrangement of particles
  - These particles are still close to each other but can now **rotate** and **slide** over each other in the liquid
  - As a result, there is an **increase in disorder**

Liquid to gas

- The entropy **increases** when a substance boils
  - The particles in a gas can now freely move around and are far apart from each other
  - The entropy increases **significantly** as the particles become very disordered

Gas to liquid and liquid to solid

- Similarly, the entropy **decreases** when a substance **condenses** (change from **gas** to **liquid**) or freezes (change from **liquid** to **solid**)
  - The particles are brought together and get arranged in a more regular arrangement
  - The ability of the particles to move decreases as the particles become more ordered
  - There are fewer ways of arranging the energy so the entropy decreases

Graph of entropy against temperature

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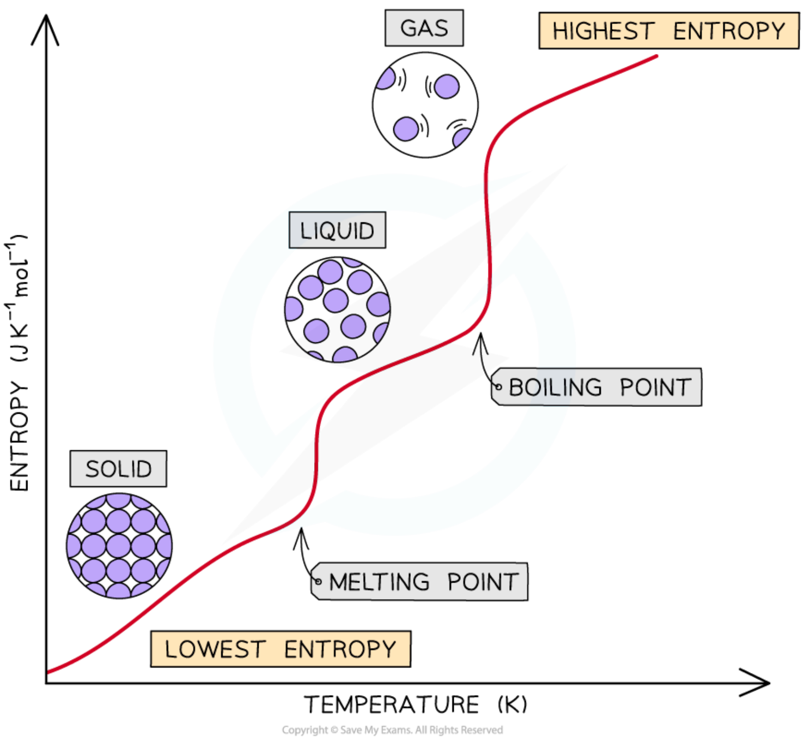


The entropy of a substance increases when the temperature is raised as particles become more disordered

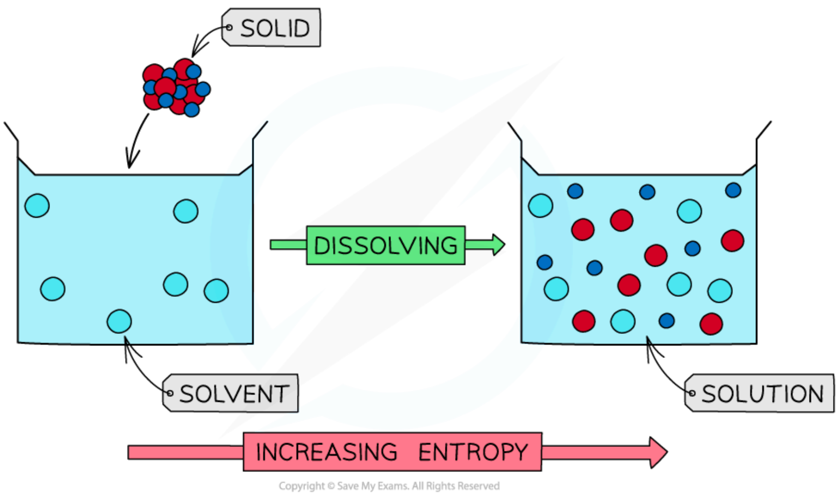
Dissolving

- The entropy also **increases** when a solid is **dissolved** in a solvent
- The solid particles are more ordered in the solid lattice as they can only slightly vibrate
- When dissolved to form a dilute solution, the entropy increases as:
  - The particles are more spread out
  - There is an increase in the number of ways of arranging the energy

Crystallisation

- The **crystallisation** of a salt from a solution is associated with a **decrease** in entropy
  - The particles are spread out in solution but become more **ordered** in the solid

Entropy changes during the dissolving of a solid



When a solid is dissolved in a solvent to form a dilute solution, the entropy increases as the particles become more disordered

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Entropy changes in reactions

- **Gases** have higher entropy values than **solids**
- So, if the number of **gaseous molecules** in a reaction changes, there will also be a change in entropy
- The greater the number of gas molecules, the greater the number of ways of arranging them, and thus the greater the entropy

Examples

- The decomposition of calcium carbonate ($CaCO_3$)

$$CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2\ (g)$$

- The CO_2 gas molecule is more disordered than the solid reactant ($CaCO_3$) as it can freely move around whereas the particles in $CaCO_3$ are in fixed positions in which they can only slightly vibrate
    - The system has therefore become more **disordered** and there is an **increase** in **entropy**
- The formation of ammonia in the Haber process

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$$

- In this case, all of the reactants and products are gases
    - Before the reaction occurs, there are **four gas molecules** (1 nitrogen and 3 hydrogen molecules) in the reactants
    - After the reaction has taken place, there are now only **two gas molecules** (2 ammonia molecules) in the products
    - So there are fewer ways of arranging the energy of the system over the products

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- The system has become **more ordered** causing a **decrease in entropy**
- The reactants (N_2 and H_2) are **energetically more stable** than the product (NH_3)

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Entropy Change Calculations

- The standard entropy change ($\Delta S_{system}^{\theta}$) for a given reaction can be calculated using the standard entropies (S^{θ}) of the reactants and products
- The equation to calculate the standard entropy change of a system is:

$$\Delta S_{system}^{\theta} = \sum S_{products}^{\theta} - \sum S_{reactants}^{\theta}$$

(where $\sum$ = sum of)

- For example, the standard entropy change for the formation of ammonia (NH_3) from nitrogen (N_2) and hydrogen (H_2) can be calculated using this equation

$$N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$$

$$\Delta S_{system}^{\theta} = (2 \times \Delta S^{\theta}(NH_3)) - (\Delta S^{\theta}(N_2) + 3 \times \Delta S^{\theta}(H_2))$$

Worked Example

Calculate the entropy change of the system for the following reaction:

$$2Mg (s) + O_2 (g) \rightarrow 2MgO (s)$$

- S^{θ} [Mg (s)] = 32.60 J K^{-1} mol^{-1}
- S^{θ} [O_2 (s)] = 205.0 J K^{-1} mol^{-1}
- S^{θ} [MgO (s)] = 38.20 J K^{-1} mol^{-1}

Answer:

- $\Delta S_{system}^{\theta} = \Sigma\Delta S_{products}^{\theta} - \Sigma\Delta S_{reactants}^{\theta}$
- $\Delta S_{system}^{\theta} = (2 \times 38.20) - (2 \times 32.60 + 205.0)$
- $\Delta S_{system}^{\theta} = -193.8$ J K^{-1} mol^{-1}

Examiner Tips and Tricks

Use the **stoichiometry** of the equation and the correct state of the compounds when calculating the entropy change of a reaction

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