Edexcel International A Level (IAL) Chemistry

Your notes

Entropy

Contents

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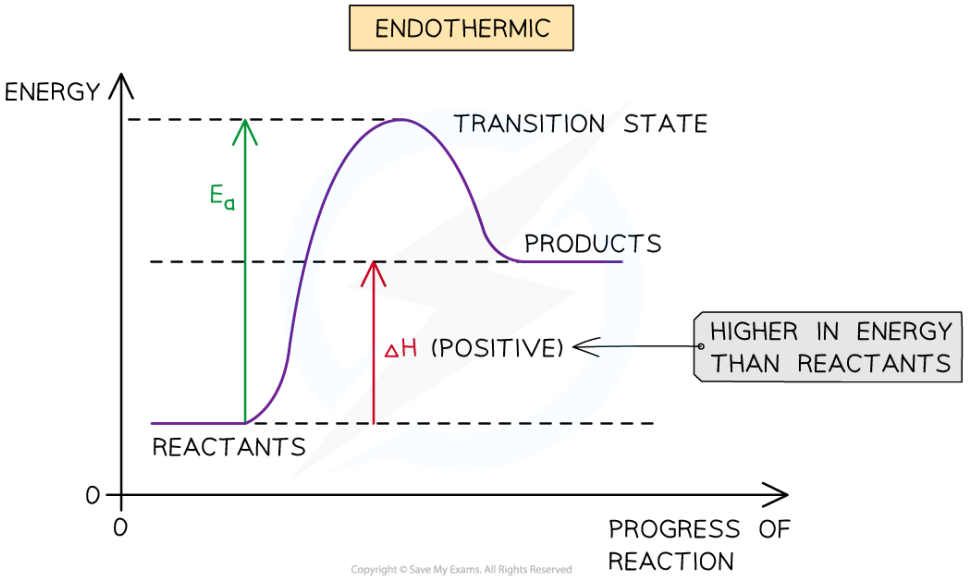
Entropy – Introduction

- You may have wondered why it is that **endothermic** reactions occur at all, after all, what can be the driving force behind endothermic reactions if the products end up in a less stable, higher energy state?
- Although the majority of chemical reactions we experience everyday are **exothermic**, $\Delta H^{\ominus}$ alone is not enough to explain why endothermic reactions occur



The driving force behind chemical reactions cannot be explained by enthalpy changes alone as it makes not sense for chemical to end up in a less stable higher energy state in endothermic reactions

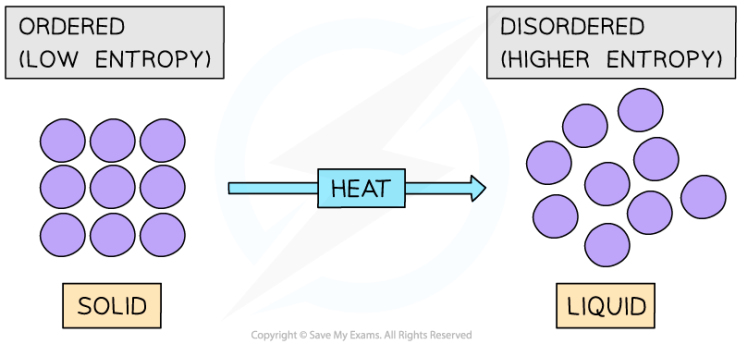
- The answer is **entropy**

Chaos in the universe

- 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** or **chaotic** 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**
- An example of a system that becomes more disordered is when a solid is **melted**
- For example, melting ice to form liquid water:

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

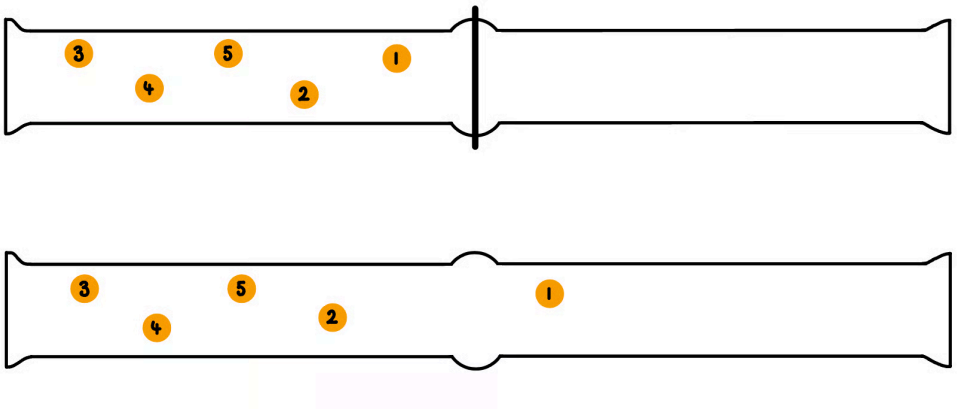
- The water molecules in ice are in fixed positions and can only vibrate about those positions
- In the liquid state, the particles are still quite close together but are arranged more randomly, in that they can move around each other
- Water molecules in the liquid state are therefore more **disordered**
- 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 favourable** (as the energy of the system is more spread out when it is in a disordered state)



Melting a solid will cause the particles to become more disordered resulting in a higher entropy state

Distribution of Molecules

- Consider two gas jars, separated by a cover slip and one of the gas jars containing five molecules of orange bromine gas
- When the cover slip between two gas jars is removed, molecules of gas will spread out evenly throughout both of the gas jars



The first two gas jars are separated by a glass cover slip, the second two gas jars are not separated allowing molecules to spread evenly between the two

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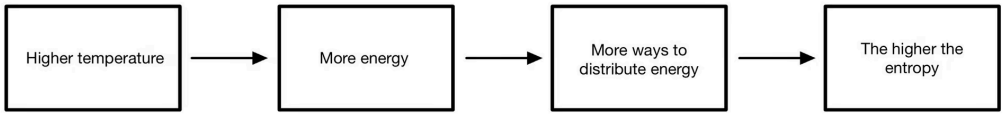
- Each molecule can either be in the left or the right hand gas jar, so therefore has two possible arrangements
- So the number of possible arrangements is 2
- If there are 5 molecules in one jar to begin with, the total number of ways, *W*, the five molecules can be arranged is
  - $W = W_1 \times W_2 \times W_3 \times W_4 \times W_5$
  - $W = 2 \times 2 \times 2 \times 2 \times 2$
  - $W = 2^5$
  - $W = 32$
- If we increased the number of molecules to 100, W becomes 2^{100}
- Therefore as the number of particles increases the number of possible arrangements increases rapidly
- Entropy (S) is linked to *W* by the equation

$$S = k \ln W$$

- k = Boltzmann distribution constant 1.38×10^{-23} J K^{-1} mol^{-1}
  - The units for entropy (S) are J K^{-1} mol^{-1}

Distribution of energy

- The spreading out of molecules in diffusion is an increase in entropy as the molecules are becoming more randomly dispersed
- Spreading out heat energy also represents an increase in entropy
- Energy exists in 'packets' called **quanta**
  - Only whole numbers of quanta are possible
- The more quanta, the more ways of arrange the particles
- The more particles the more ways of sharing quanta



Flow chart to show the effect of increasing temperature on entropy

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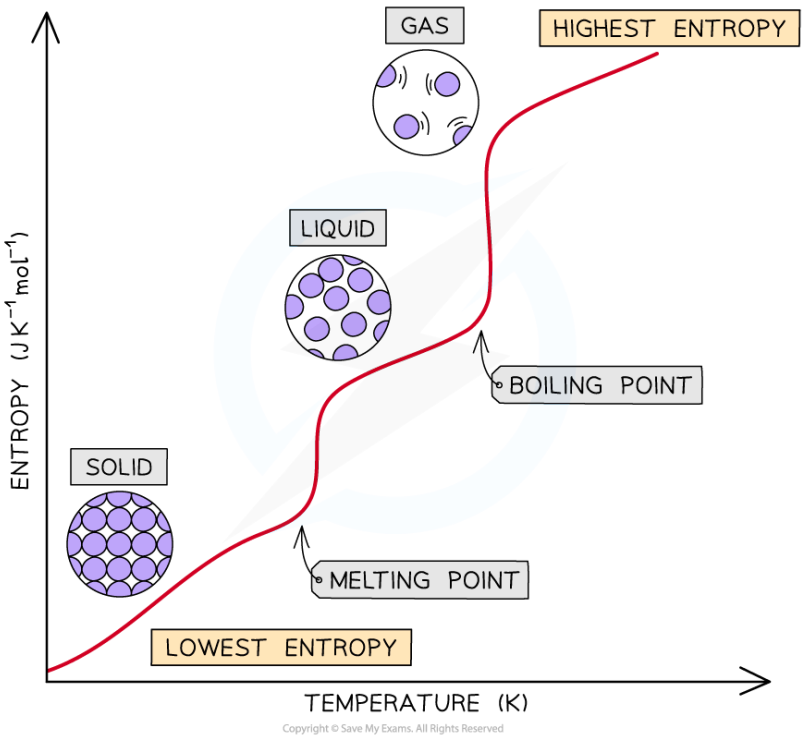
Entropy – Changes

Changes of State

- The entropy of a substance changes during a **change in state**
- The entropy **increases** when a substance melts (change from **solid** to **liquid**)
  - 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**
- The entropy **increases** when a substance boils (change from **liquid** to **gas**)
  - 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
- 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



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

Production of a gas

- During the thermal decomposition of calcium carbonate ($CaCO_3$) the entropy of the system increases:

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

- 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
- As a result, the system has become more **disordered** and there is an **increase** in **entropy**
- Another example is the reaction of **ethanoic acid** with **ammonium carbonate**

$$(NH_4)_2CO_3\,(s) + 2CH_3COOH\,(aq) \rightarrow 2CH_3COO^-\,(aq) + 2NH_4^+\,(aq) + CO_2\,(g) + H_2O\,(l)$$

- There is a slight fall in temperature during the reaction indicating the process is endothermic
  - Energy is taken in from the surroundings
- The particles are well-ordered in the solid, and the disorder increases because a solution and, especially, a gas is formed so entropy increases during the reaction

Dissolving a solid

- When ammonium nitrate is dissolved in water, the temperature of the solution decreases, therefore the process is endothermic
  - Energy is taken in from the surroundings

$$NH_4NO_3\,(s) + aq \rightarrow NH_4^+\,(aq) + NO_3^-\,(aq) \quad \Delta H = 25.7\ kJ\ mol^{-1}$$

- The level of disorder increases as the particles are no longer in a fixed position and are now free to move
- However, it is not always this simple!
- When an **ionic** solid dissolves
  - Bonds between the particles are broken increasing the disorder and taking in energy
  - Bonds between the solvent and particles are made reducing the disorder and releasing energy
- Therefore it is difficult to predict whether the process will be endothermic or exothermic

Endothermic reactions between two solids

- When barium hydroxide and ammonium chloride are mixed, they form a paste and the temperature drops significantly
- Therefore this is an endothermic process
  - Energy is taken in from the surroundings

$$2NH_4Cl\,(s) + Ba(OH)_2.8H_2O\,(s) \rightarrow BaCl_2.2H_2O\,(s) + 2NH_3\,(g) + H_2O\,(l)$$

- The gas produced is ammonia and this can be detected by the smell and it will turn damp red litmus paper blue
- When two solids are mixed and react together, the entropy change will depend on the physical state of the compounds made and not just on the energy changes in the reaction
- Two solids will of course have a very low entropy due to the high order
- If a liquid or gas is produced the entropy will have increased due to the increased disorder of the particles

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Total Entropy Calculations

- If we take the reaction between sodium and chorine, we know that this is a very exothermic reaction and also involves a decrease in entropy as a solid is produced from a solid and a gas (provided a flame is used to supply the necessary activation energy)

$$2Na\,(s) + Cl_2\,(g) \rightarrow 2NaCl\,(s)$$

- If there is a decrease in entropy, how can the reaction be spontaneous?
- We need to take into account the entropy of the surroundings as well
  - The energy being released causes a substantial increase in entropy of the surroundings because there are more ways of arranging the quanta (packets of energy) in the surroundings than the system alone
- Therefore, the total entropy change for a reaction is

$$\Delta S^{\ominus}_{total} = \Delta S^{\ominus}_{sys} + \Delta S^{\ominus}_{surr}$$

(sys = system and surr = surroundings)

- So, in the case of sodium and chlorine, the large amounts of energy released makes $\Delta S^{\ominus}_{surr}$ very positive, which will outweigh the negative value of $\Delta S^{\ominus}_{sys}$

Worked Example

Calculating total entropy change

- Calculate the total entropy change in the formation of 1 mole of sodium chloride from its elements in their standard state

$\Delta S^{\ominus}_{sys} = -90.1\ J\ K^{-1}\ mol^{-1}$

$\Delta S^{\ominus}_{surr} = +1379\ J\ K^{-1}\ mol^{-1}$

Answer

$\Delta S^{\ominus}_{total} = \Delta S^{\ominus}_{sys} + \Delta S^{\ominus}_{surr}$

$\Delta S^{\ominus}_{total} = -90.1 + 1379 = \mathbf{1289\ J\ K^{-1}\ mol^{-1}}$

Entropy Change in the System

- Entropy changes are an order of magnitude smaller than enthalpy changes, so entropy is measured in joules rather than kilojoules. The full unit for entropy is $\mathbf{J\ K^{-1}\ mol^{-1}}$
- The standard entropy change ($\Delta S^{\ominus}_{system}$) for a given reaction can be calculated using the standard entropies ($S^{\ominus}$) of the reactants and products
- The equation to calculate the standard entropy change of a system is:

$$\Delta S^{\ominus}_{system} = \Sigma S^{\ominus}_{products} - \Sigma S^{\ominus}_{reactants}$$

(where Σ = 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

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

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

- Notice that, unlike enthalpy of formation for elements, entropy for elements is **not** zero and you can find entropy values for elements and compounds in data books

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Worked Example

Calculating entropy changes

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

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

$S^{\ominus}[Mg(s)] = 32.60\ J\ K^{-1}\ mol^{-1}$

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

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

Answer

$\Delta S^{\ominus}_{system} = \Sigma S^{\ominus}_{products} - \Sigma S^{\ominus}_{reactants}$

$\Delta S^{\ominus}_{system} = (2 \times 38.20) - (2 \times 32.60 + 205.0)$

$= \mathbf{-193.8\ J\ K^{-1}\ mol^{-1}}$

Worked Example

Calculating entropy changes

What is the entropy change when ammonia is formed **from** nitrogen and hydrogen?

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

$S^{\ominus}[N_2\,(g)] = 191.6\ J\ K^{-1}\ mol^{-1}$

$S^{\ominus}[H_2\,(g)] = 131\ J\ K^{-1}\ mol^{-1}$

$S^{\ominus}[NH_3] = 192.3\ J\ K^{-1}\ mol^{-1}$

Answer:

$\Delta S^{\ominus}_{system} = \Sigma S^{\ominus}_{products} - \Sigma S^{\ominus}_{reactants}$

$\Delta S^{\ominus}_{system} = [2 \times S^{\ominus}(NH_3)] - [S^{\ominus}(N_2) + (3 \times S^{\ominus}(H_2))]$

$\Delta S^{\ominus}_{system} = [2 \times 192.3] - [191.6 + (3 \times 131)]$

$\Delta S^{\ominus}_{system} = 384.6 - 584.6$

$\Delta S^{\ominus}_{system} = \mathbf{-200\ J\ K^{-1}\ mol^{-1}}$

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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.

Entropy Change in the Surroundings

- To calculate the entropy change of the surroundings, $\mathbf{\Delta S^{\ominus}_{surr}}$, we need to know the energy that has been transferred to them
- This is given by the enthalpy change, **ΔH**, and the relationship can be expressed as:

$$\Delta S^{\theta}_{sur} = -\frac{\Delta H}{T}$$

- ***T*** is the absolute temperature
- The entropy change of the surroundings depends upon temperature
  - The transfer of a given quantity of energy to surroundings at a low temperature will produce a greater entropy change than the transfer of the same amount of energy to the surroundings at a higher temperature

Worked Example

Calculating entropy of surroundings

Calculating entropy of surroundings for the reaction between aluminium oxide and carbon at 298 K

$$\mathbf{Al_2O_3\,(s) + 3C\,(s) \rightarrow 2Al\,(s) + 3CO\,(g)}$$

$\Delta H^{\theta} = +1336\ kJ\ mol^{-1}$

$T = 298\ K$

Answer

$$\Delta S^{\ominus}_{sur} = -\frac{\Delta H}{T}$$

Convert ΔH from $kJ\ mol^{-1}$ to $J\ mol^{-1}$ by multiplying by 1000

$= -\frac{1336000}{298}$

$= -4483\ J\ K^{-1}\ mol^{-1}$

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Reaction Feasibility

Summary

- For ΔS_{total} to be positive and therefore the reaction feasible:
  - Both ΔS_{system} and $\Delta S_{surroundings}$ are positive
  - $\Delta S_{surroundings}$ is positive and ΔS_{system} is negative, but $\Delta S_{surroundings} > \Delta S_{system}$
  - $\Delta S_{surroundings}$ is negative and ΔS_{system} is positive, but $\Delta S_{surroundings} < \Delta S_{system}$

Feasibility

- Generally, entropy will increase in the order:
- solid < liquid < gas
- Therefore we can determine the change in entropy and the feasibility by considering the change in state of reactants to products
- Example 1: the reaction between magnesium and oxygen at 293 K is feasible

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

- This reaction produces a solid from a solid and a gas. Therefore entropy of the system is negative ($\Delta S_{system} < \Delta S_{surroundings}$)
- But since the entropy of the surroundings is very large as this reaction is very exothermic
- This outweighs the entropy of the system, so the total entropy is positive therefore the reaction is spontaneous
- Example 2: the reaction between ethanoic acid and ammonium carbonate

$$2CH_3COOH\,(aq) + (NH_4)_2CO_3\,(s) \rightarrow 2CH_3COONH_4\,(aq) + H_2O\,(l) + CO_2\,(g)$$

- This reaction is **endothermic**, therefore $\Delta S_{surroundings}$ is negative
- However, a gas is produced from a solid and liquid, so ΔS_{system} is positive
- $\Delta S_{system} > \Delta S_{surroundings}$ and the reaction is spontaneous

Gibbs free energy

- We can also use Gibbs free energy to work out if a reaction is feasible or not (this is not required as a part of the course)
- The feasibility of a reaction is determined by two factors
  - The **enthalpy** and **entropy change**
- The two factors come together in a fundamental thermodynamic concept called the **Gibbs free energy (G)**

- The Gibbs equation is:

$$\Delta G^{\ominus} = \Delta H_{reaction}^{\ominus} - T\Delta S_{system}^{\ominus}$$

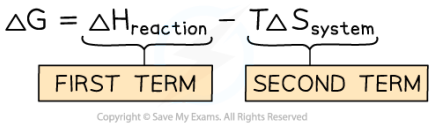
- The units of $\Delta G^{\ominus}$ are in kJ mol^{-1}
  - The units of $\Delta H_{reaction}^{\ominus}$ are in kJ mol^{-1}
  - The units of T are in K
  - The units of $\Delta S_{system}^{\ominus}$ are in J K^{-1} mol^{-1} (and must therefore be converted to kJ K^{-1} mol^{-1} by dividing by 1000)
- For a reaction to be feasible, $\Delta G^{\ominus}$ must be **equal or less than zero**

Temperature & feasibility

- We can look at the the values for ΔH and ΔS to determine whether the reaction is spontaneous / feasible at a given temperature (T)
- The Gibbs equation can explain what will affect the spontaneity / feasibility of a reaction for exothermic and endothermic reactions

Exothermic reactions

- In exothermic reactions, $\Delta H_{reaction}^{\ominus}$ is **negative**
- If the $\Delta S_{system}^{\ominus}$ is **positive:**
  - Both the first and second term will be **negative**
  - Resulting in a **negative** $\Delta G^{\ominus}$ so the reaction is **feasible**
  - Therefore, regardless of the temperature, an exothermic reaction with a positive $\Delta S_{system}^{\ominus}$ will **always be feasible**



- If the $\Delta S_{system}^{\ominus}$ is **negative:**
  - The first term is **negative** and the second term is **positive**
  - At very high temperatures, the $-T\Delta S_{system}^{\ominus}$ will be very **large** and **positive** and will overcome $\Delta H_{reaction}^{\ominus}$
  - Therefore, at high temperatures $\Delta G^{\ominus}$ is **positive** and the reaction is **not feasible**
- Since the relative size of an entropy change is much smaller than an enthalpy change, it is unlikely that $T\Delta S > \Delta H$ as temperature increases
- These reactions are therefore usually spontaneous at normal conditions

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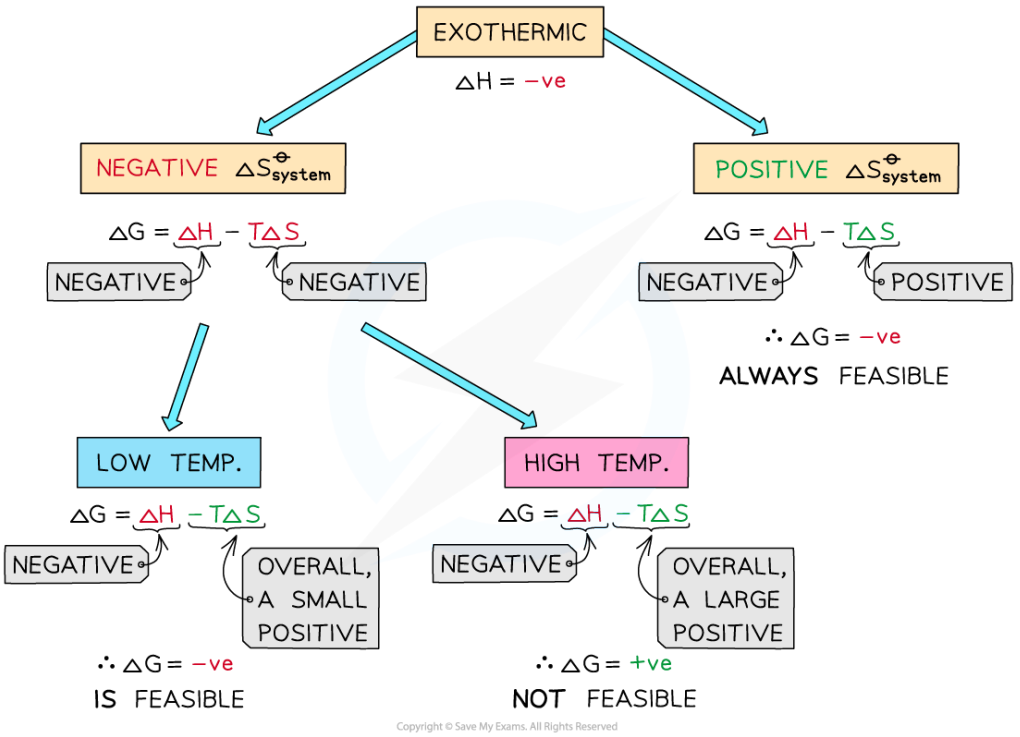

The diagram shows under which conditions exothermic reactions are feasible

Endothermic reactions

- In endothermic reactions, $\Delta H_{reaction}^{\ominus}$ is **positive**
- If the $\Delta S_{system}^{\ominus}$ is **negative:**
  - Both the first and second term will be **positive**
  - Resulting in a **positive** $\Delta G^{\ominus}$ so the reaction is **not feasible**
  - Therefore, regardless of the temperature, endothermic with a negative $\Delta S_{system}^{\ominus}$ will **never be feasible**
- If the $\Delta S_{system}^{\ominus}$ is **positive:**
  - The first term is **positive** and the second term is **negative**
  - At low temperatures, the $-T\Delta S_{system}^{\ominus}$ will be **small** and **negative** and will not overcome the larger $\Delta H_{reaction}^{\ominus}$
  - Therefore, at low temperatures $\Delta G^{\ominus}$ is **positive** and the reaction is not feasible
  - The reaction is **more feasible** at **high temperatures** as the second term will become negative enough to overcome the $\Delta H_{reaction}^{\ominus}$ resulting in a negative $\Delta G^{\ominus}$
- This tells us that for certain reactions which are not feasible at room temperature, they can become feasible at higher temperatures
  - An example of this is found in metal extractions, such as the extraction if iron in the blast furnace, which will be unsuccessful at low temperatures but can occur at

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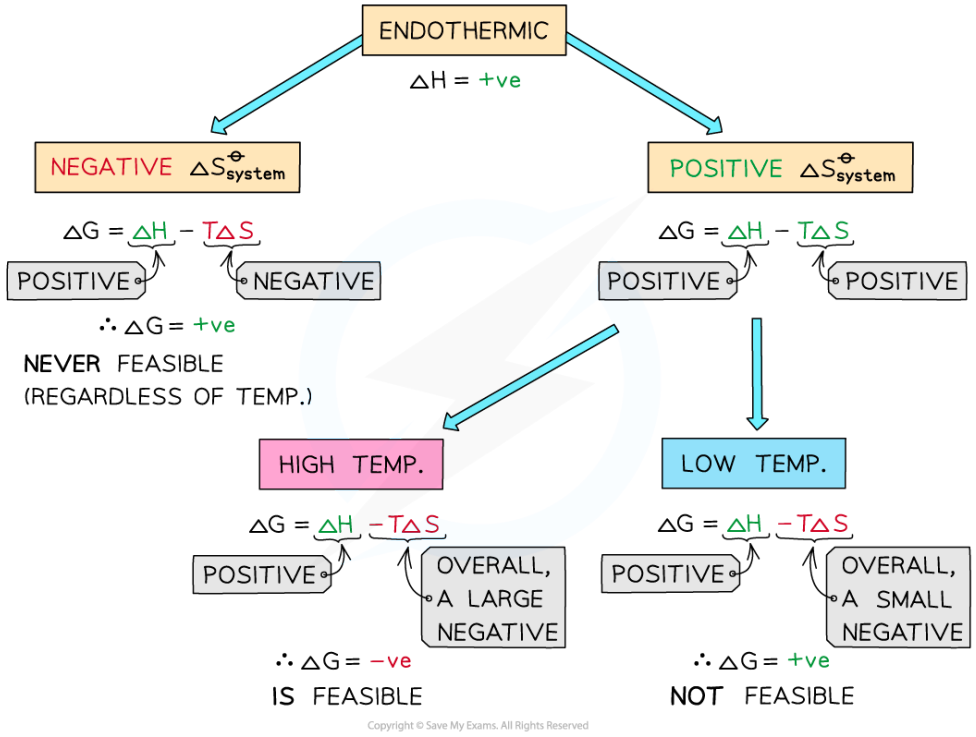
higher temperatures (~1500 °C in the case of iron)



The diagram shows under which conditions endothermic reactions are feasible

Summary of factors affecting Gibbs free energy

If ΔH...	And if ΔS...	Then ΔG is...	Spontaneous...	Because
Is negative < 0 exothermic	Is positive > 0 More disorder	Always negative < 0	Always	Forward reaction spontaneous at any T
Is positive > 0 endothermic	Is negative < 0 More order	Always positive > 0	Never	Reverse reaction spontaneous at any T
Is negative < 0 exothermic	Is negative < 0 More order	Negative at low T Positive at high T	Depending on T	Spontaneous only at low T TΔS < H
Is positive > 0 endothermic	Is positive > 0 More disorder	Negative at high T Positive at low T	Depending on T	Spontaneous only at high T TΔS > H

Worked Example

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The reaction between aluminium oxide and carbon is not feasible at room temperature.

$Al_2O_3 + 3C(s) \rightarrow 2Al(s) + 3CO_2(g)$

Given that $\Delta H = +1336\ kJmol^{-1}$ and $\Delta S = +581\ JK^{-1}mol^{-1}$, calculate the temperature at which the reaction becomes feasible.

Answer

- As both ΔH and ΔS are positive, ΔG will become negative if $T\Delta S > \Delta H$.
- The temperature at which this reaction becomes spontaneous can be calculated. This will be when $\Delta G = 0$.
- If $\Delta G = 0$, then $T = \Delta H / \Delta S$*
- $T = \frac{1336}{0.581}$
- $T = 2299\ K$

*Don't forget to convert this into kJ

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Thermodynamic & Kinetic Stability

Thermodynamic Stability

- Refers to whether a reaction is feasible under given conditions
- A reaction is thermodynamically feasible if the Gibbs free energy change (ΔG) is negative

$$\Delta G = \Delta H - T\Delta S$$

- This means:
  - Reactions are more likely to be feasible if **enthalpy change (ΔH)** is **negative** (exothermic)
  - Or if **entropy change (ΔS)** is **positive** (increase in disorder)
- Thermodynamic feasibility does **not** necessarily mean the reaction will happen quickly

Kinetic Stability

- Refers to how fast a reaction occurs (i.e. the rate of reaction)
- Depends on the **activation energy ($E\equiv$)**:
  - Reactions with a **high $E\equiv$** are **kinetically stable** and may not occur at room temperature
- Even if a reaction is thermodynamically feasible, it might not happen without enough energy to overcome the activation barrier

Examples

- Combustion of methane, CH_4
  - Thermodynamically feasible but kinetically stable

- Methane (CH_4) will not spontaneously form CO_2 and H_2O unless ignited ($E\equiv$ is high)

- Decomposition of hydrogen peroxide at 298 K
- This reaction is thermodynamically feasible:

$$H_2O_2\,(l) \rightarrow H_2O\,(l) + \tfrac{1}{2}O_2\,(g)$$

- The activation energy, E_a, is high, so a **catalyst** must be used (MnO_2)
- If the reaction was left for long enough, the hydrogen peroxide would eventually decompose, however the addition of the MnO_2 allows the reaction to take place via an alternative route with a lower E_a

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