

DP IB Chemistry: HL


Your notes

15.2 Entropy & Spontaneity

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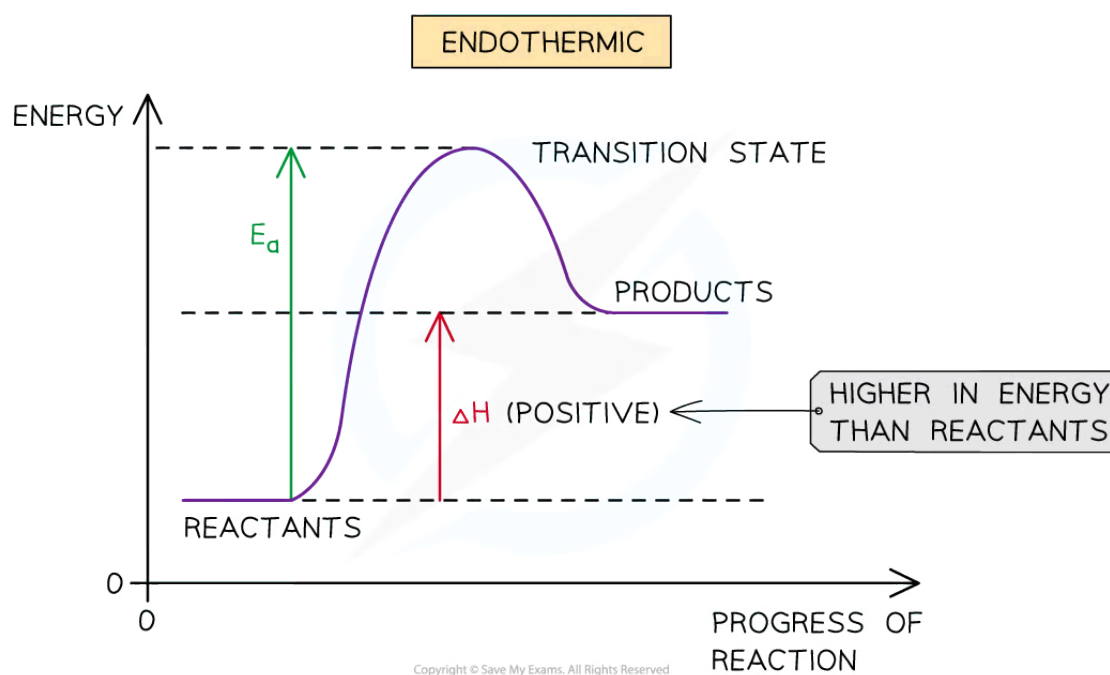
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15.2.1 Entropy

Entropy

Entropy

- 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, ΔH^\ddagger 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 does not sense for chemical to end up in a less stable higher energy state in endothermic reactions

- The answer is entropy

Predicting Entropy Changes

Chaos in the universe

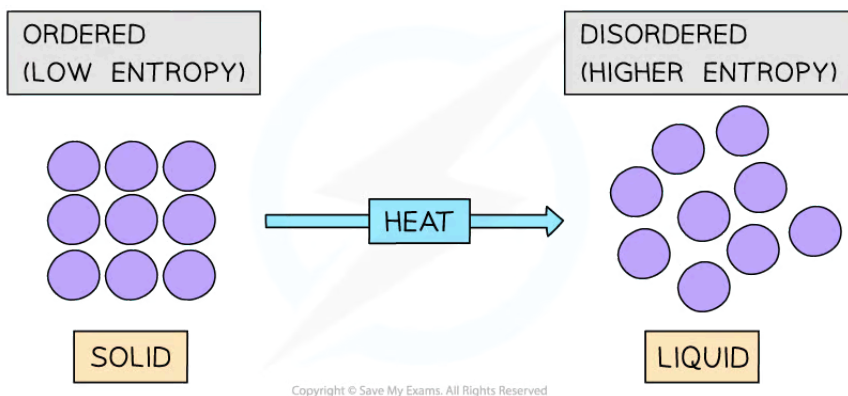
- The **entropy (S)** of a given system is the number of possible arrangements of the particles and their energy in a given system
 - In other words, it is a measure of how **disordered** or **chaotic** a system is
- When a system becomes more disordered, its entropy will increase
- An increase in entropy means that the system becomes **energetically more stable**
- For example, during the thermal decomposition of calcium carbonate (CaCO_3) 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
- As a result, the system has become more disordered and there is an increase in entropy
- Another typical example of a system that becomes more disordered is when a solid melts
 - For example, melting ice to form liquid water:
$$\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{l})$$
 - 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)



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



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15.2.2 Calculating Entropy Change

Calculating Standard Entropy Change

- The standard molar enthalpy values, S^\ominus , relate to standard conditions of temperature and pressure
- The entropy change, ΔS^\ominus , can be calculated from thermodynamic data using the following equation:

$$\Delta S^\ominus_{298}(\text{reaction}) = \Sigma S^\ominus_{298}(\text{products}) - \Sigma S^\ominus_{298}(\text{reactants})$$

- This equation is provided in the data booklet
- The units of $\Delta S_{\text{system}}^\ominus$ are in $\text{J K}^{-1} \text{mol}^{-1}$
- Entropy will change depending on the state of the matter
- Taking water as an example the values for S^\ominus will be different for the liquid and gaseous phases
 - $S^\ominus_{298}(\text{H}_2\text{O}(\text{l})) = 70.0 \text{ J K}^{-1} \text{mol}^{-1}$
 - $S^\ominus_{298}(\text{H}_2\text{O}(\text{g})) = 188.8 \text{ J K}^{-1} \text{mol}^{-1}$
- When calculating ΔS^\ominus , the coefficients used to balance the equation must be applied when calculating the overall entropy change
- For example, when calculating the ΔS^\ominus for the reaction below we need to double the value for $S^\ominus(\text{NO}(\text{g}))$
 - $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$
 - $\Delta S^\ominus_{298}(\text{reaction}) = \Sigma S^\ominus_{298}(\text{products}) - \Sigma S^\ominus_{298}(\text{reactants})$
 - $\Delta S^\ominus = [(2 \times S^\ominus_{298}(\text{NO}_2))] - S^\ominus_{298}(\text{N}_2\text{O}_4)$

Worked example

What is the entropy change when calcium carbonate decomposes?



- $S^\ominus_{298}(\text{CaCO}_3(\text{s})) = 92.9 \text{ J K}^{-1} \text{mol}^{-1}$
- $S^\ominus_{298}(\text{CaO}(\text{s})) = 39.7 \text{ J K}^{-1} \text{mol}^{-1}$
- $S^\ominus_{298}(\text{CO}_2(\text{g})) = 213.6 \text{ J K}^{-1} \text{mol}^{-1}$

Answer:

Step 1: Write out equation to calculate $\Delta S^\ominus_{298}(\text{reaction})$

- $\Delta S^\ominus_{298}(\text{reaction}) = \Sigma S^\ominus_{298}(\text{products}) - \Sigma S^\ominus_{298}(\text{reactants})$

Step 2: Substitute in formulas and then values for S^\ominus

- $\Delta S_{298}^{\ominus}(\text{reaction}) = [S_{298}^{\ominus}(\text{CaO}) + S_{298}^{\ominus}(\text{CO}_2)] - S_{298}^{\ominus}(\text{CaCO}_3)$
- $\Delta S^{\ominus}(\text{reaction}) = (39.7 + 213.6) - 92.9$
- $\Delta S^{\ominus}(\text{reaction}) = +160.4 \text{ J K}^{-1} \text{ mol}^{-1}$



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Worked example

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



- $S_{298}^{\ominus}(\text{N}_2(\text{g})) = 191.6 \text{ J K}^{-1} \text{ mol}^{-1}$
- $S_{298}^{\ominus}(\text{H}_2(\text{g})) = 131 \text{ J K}^{-1} \text{ mol}^{-1}$
- $S_{298}^{\ominus}(\text{NH}_3) = 192.3 \text{ J K}^{-1} \text{ mol}^{-1}$

Answer:

Step 1: Write out equation to calculate $\Delta S_{298}^{\ominus}(\text{reaction})$

- $\Delta S_{298}^{\ominus}(\text{reaction}) = \Sigma S_{298}^{\ominus}(\text{products}) - \Sigma S_{298}^{\ominus}(\text{reactants})$

Step 2: Substitute in formulas and then values for S^{\ominus} taking into account the coefficients

- $\Delta S_{298}^{\ominus}(\text{reaction}) = [2 \times S_{298}^{\ominus}(\text{NH}_3)] - [S_{298}^{\ominus}(\text{N}_2) + (3 \times S_{298}^{\ominus}(\text{H}_2))]$
- $\Delta S_{298}^{\ominus}(\text{reaction}) = [2 \times 192.3] - [191.6 + (3 \times 131)]$
- $\Delta S_{298}^{\ominus}(\text{reaction}) = 384.6 - 584.6$
- $\Delta S_{298}^{\ominus}(\text{reaction}) = -200 \text{ J K}^{-1} \text{ mol}^{-1}$



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15.2.3 Gibbs Free Energy

Gibbs Free Energy Change

Gibbs free energy

- The feasibility of a reaction is determined by two factors, the enthalpy change and the entropy change
- The two factors come together in a fundamental thermodynamic concept called the **Gibbs free energy (G)**
- The Gibbs equation is:

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

- The units of ΔG^{\ominus} are in kJ mol^{-1}
- The units of $\Delta H_{\text{reaction}}^{\ominus}$ are in kJ mol^{-1}
- The units of T are in K
- The units of $\Delta S_{\text{system}}^{\ominus}$ are in $\text{J K}^{-1} \text{mol}^{-1}$ (and must therefore be converted to $\text{kJ K}^{-1} \text{mol}^{-1}$ by dividing by 1000)

Calculating ΔG^{\ominus}

- There are two ways you can calculate the value of ΔG^{\ominus}
 1. From the Gibbs equation, using enthalpy change, ΔH^{\ominus} , and entropy change, ΔS^{\ominus} , values
 2. From ΔG^{\ominus} values of all the substances present

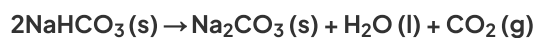
Calculating ΔG° from the Gibbs Equation



Your notes

Worked example

ΔG^\ominus from ΔH^\ominus and ΔS^\ominus values Calculate the free energy change for the following reaction:



- $\Delta H^\ominus = +135 \text{ kJ mol}^{-1}$
- $\Delta S^\ominus = +344 \text{ J K}^{-1} \text{ mol}^{-1}$

Answer:

Step 1: Convert the entropy value in kilojoules

- $\Delta S^\ominus = +344 \text{ J K}^{-1} \text{ mol}^{-1} \div 1000 = +0.344 \text{ kJ K}^{-1} \text{ mol}^{-1}$

Step 2: Substitute the terms into the Gibbs Equation

- $\Delta G^\ominus = \Delta H_{\text{reaction}}^\ominus - T\Delta S_{\text{system}}^\ominus$
 - $= +135 - (298 \times 0.344)$
 - $= +32.49 \text{ kJ mol}^{-1}$

The temperature is 298 K since standard values are quoted in the question

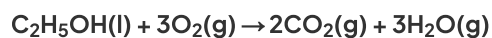


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Calculating ΔG^\ominus from ΔG^\ominus Formation

Worked example

ΔG^\ominus from other ΔG^\ominus values What is the standard free energy change, ΔG^\ominus , for the following reaction?

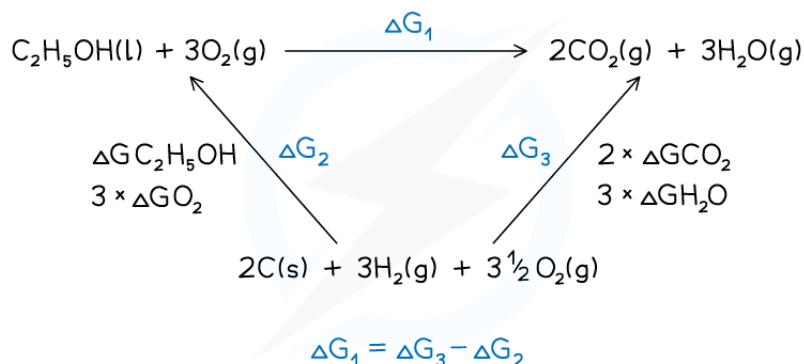


Substance	$\Delta G^\ominus \text{ kJ mol}^{-1}$
$\text{C}_2\text{H}_5\text{OH}(\text{l})$	-175
$\text{O}_2(\text{g})$	0
$\text{CO}_2(\text{g})$	-394
$\text{H}_2\text{O}(\text{g})$	-229

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Answer:

- This can be calculated in the same way as you complete enthalpy calculations
- $\Delta G^\ominus = \sum \Delta G_{\text{products}}^\ominus - \sum \Delta G_{\text{reactants}}^\ominus$
 - $\Delta G^\ominus = [(2 \times \text{CO}_2) + (3 \times \text{H}_2\text{O})] - [(\text{C}_2\text{H}_5\text{OH}) + (3 \times \text{O}_2)]$
 - $\Delta G^\ominus = [(2 \times -394) + (3 \times -229)] - [-175 + 0]$
 - $\Delta G^\ominus = -1300 \text{ kJ mol}^{-1}$
- This can also be done by drawing a Hess cycle - find the way that is best for you



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 **Exam Tip**

The idea of free energy is what's 'leftover' to do useful work when you've carried out the reaction. The enthalpy change is the difference between the energy you put in to break the chemical bonds and the energy out when making new bonds. The entropy change is the 'cost' of carrying out the reaction, so free energy is what you are left with!



Your notes



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15.2.4 Spontaneous Reactions

Spontaneous Reactions

- Gibbs free energy provides an effective way of focusing on a reaction system at constant temperature and pressure to determine its spontaneity
- For a reaction to be spontaneous, Gibbs free energy must have a **negative** value ($\Delta G^\ddagger \leq 0$)
- We can use the Gibbs equation to calculate whether a reaction is **spontaneous** / feasible or not

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

- When ΔG^\ddagger is **negative**, the reaction is **spontaneous / feasible** and likely to occur
- When ΔG^\ddagger is **positive**, the reaction is **not spontaneous / feasible** and unlikely to occur
- We can also look at the values for enthalpy change, ΔH , and entropy change, ΔS
 - Depending on the value for ΔH and ΔS we can determine whether the reaction is spontaneous at a given temperature (T)

If $\Delta H...$	And if $\Delta S...$	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 $T\Delta S < H$
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 $T\Delta S > H$

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Factors affecting ΔG and the spontaneity / feasibility of a reaction



Your notes

Worked example

Determining if a reaction is feasible / spontaneous

1. Calculate the Gibbs free energy change for the following reaction at 298 K
2. Determine whether the reaction is feasible.



- $S^\ominus[\text{Ca(s)}] = 41.00 \text{ J K}^{-1} \text{ mol}^{-1}$
- $S^\ominus[\text{O}_2\text{(g)}] = 205.0 \text{ J K}^{-1} \text{ mol}^{-1}$
- $S^\ominus[\text{CaO(s)}] = 40.00 \text{ J K}^{-1} \text{ mol}^{-1}$

Answers:

Answer 1:

Step 1: Calculate $\Delta S_{\text{system}}^\ominus$

- $\Delta S_{\text{system}}^\ominus = \sum \Delta S_{\text{products}}^\ominus - \sum \Delta S_{\text{reactants}}^\ominus$
- $$\begin{aligned} \Delta S_{\text{system}}^\ominus &= (2 \times \Delta S^\ominus[\text{CaO(s)}]) - (2 \times \Delta S^\ominus[\text{Ca(s)}] + \Delta S^\ominus[\text{O}_2\text{(g)}]) \\ &= (2 \times 40.00) - (2 \times 41.00 + 205.0) \\ &= -207.0 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

Step 2: Convert ΔS^\ominus to $\text{kJ K}^{-1} \text{ mol}^{-1}$

- $\Delta S_{\text{system}}^\ominus = -207.0 \text{ J K}^{-1} \text{ mol}^{-1} \div 1000 = -0.207 \text{ kJ mol}^{-1}$

Step 3: Calculate ΔG^\ominus

- $\Delta G^\ominus = \Delta H_{\text{reaction}}^\ominus - T\Delta S_{\text{system}}^\ominus$
- $$\begin{aligned} \Delta G^\ominus &= -635.5 - (298 \times -0.207) \\ &= -573.8 \text{ kJ mol}^{-1} \end{aligned}$$

Answer 2:

- Since ΔG^\ominus is **negative**, the reaction is **feasible**

Factors affecting ΔG and the spontaneity / feasibility of a reaction



Your notes

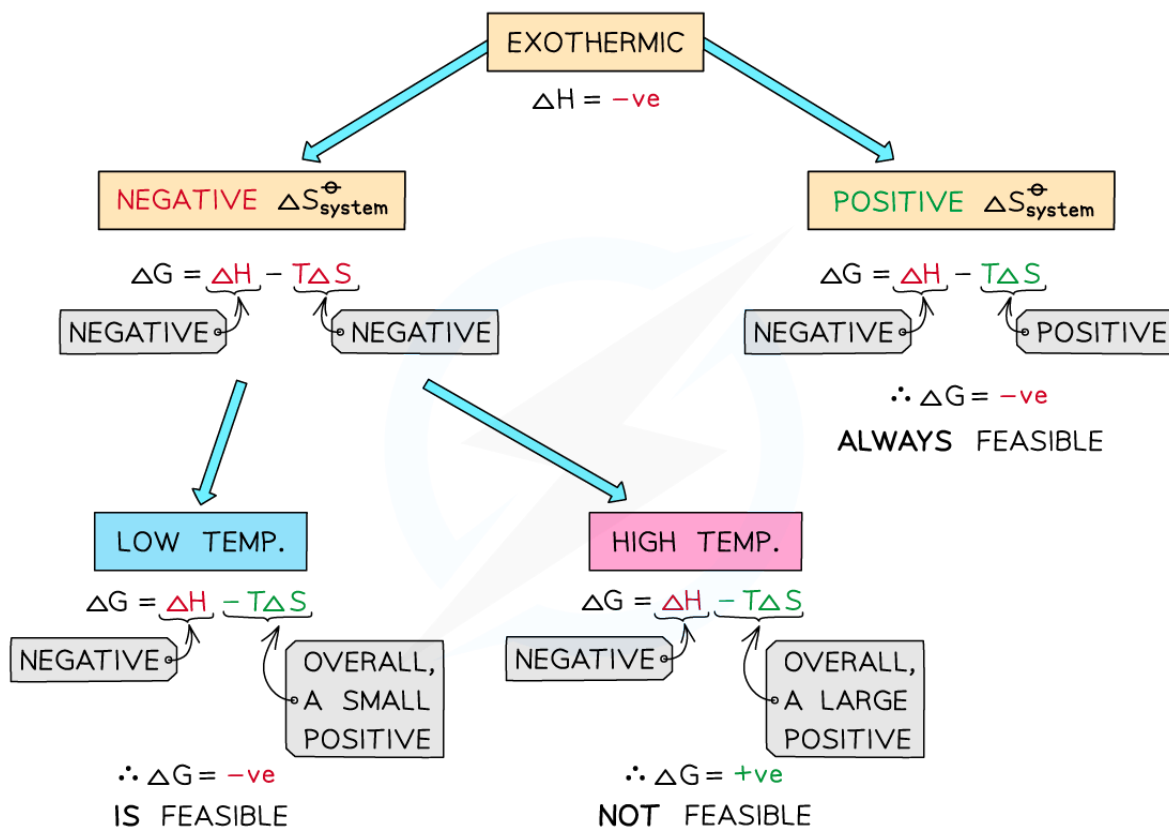
- We can also look at the values for ΔH and ΔS to determine whether the reaction is spontaneous / feasible at a given temperature (T)
- The Gibbs equation will be used to explain what will affect the spontaneity / feasibility of a reaction for exothermic and endothermic reactions

$$\Delta G = \underbrace{\Delta H_{\text{reaction}}}_{\text{FIRST TERM}} - T \underbrace{\Delta S_{\text{system}}}_{\text{SECOND TERM}}$$

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Exothermic reactions

- In exothermic reactions, $\Delta H_{\text{reaction}}$ is **negative**
- If the ΔS_{system} is **positive**:
 - Both the first and second term will be **negative**
 - Resulting in a **negative** ΔG so the reaction is **feasible**
 - Therefore, regardless of the temperature, an exothermic reaction with a positive ΔS_{system} will **always be feasible**
- If the ΔS_{system} is **negative**:
 - The first term is **negative** and the second term is **positive**
 - At very high temperatures, the $-T\Delta S_{\text{system}}$ will be very **large** and **positive** and will overcome $\Delta H_{\text{reaction}}$
 - Therefore, at high temperatures ΔG 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



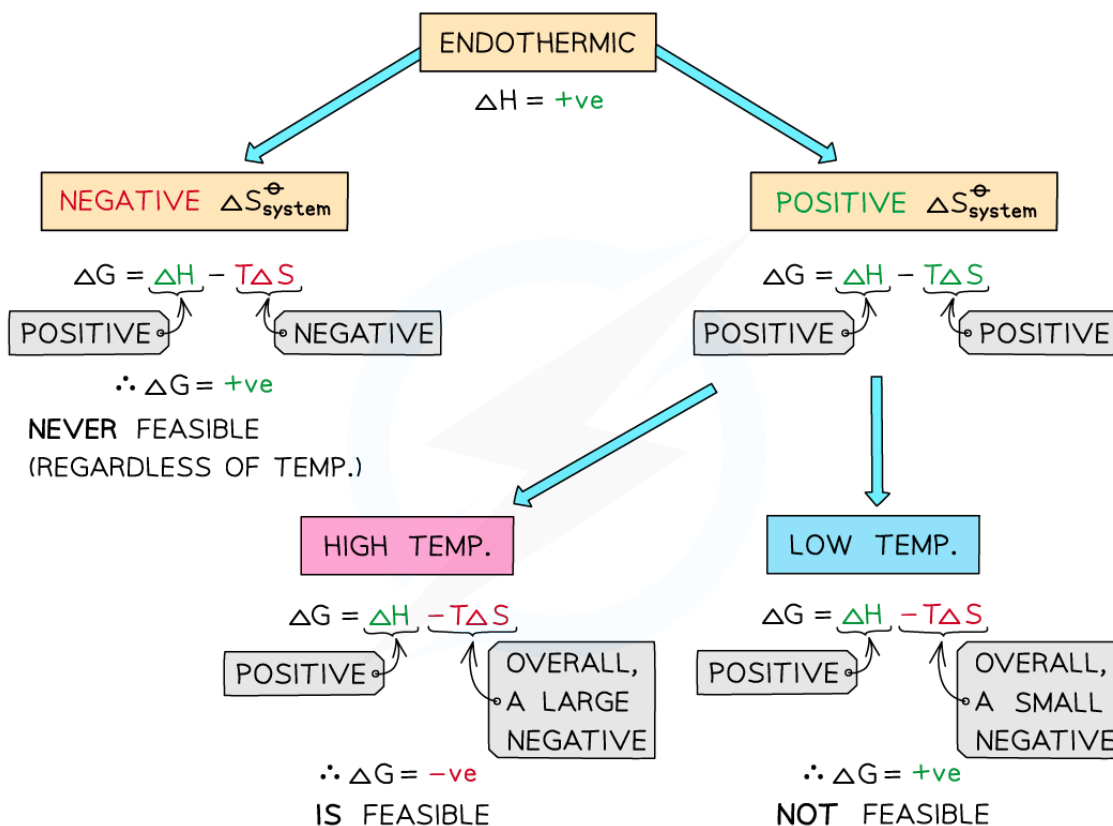
The diagram shows under which conditions exothermic reactions are feasible

Endothermic reactions

- In endothermic reactions, $\Delta H_{reaction}$ is **positive**
- If the ΔS_{system} is **negative**:
 - Both the first and second term will be **positive**
 - Resulting in a **positive** ΔG so the reaction is **not feasible**
 - Therefore, regardless of the temperature, endothermic with a negative ΔS_{system} will **never be feasible**
- If the ΔS_{system} is **positive**:
 - The first term is **positive** and the second term is **negative**
 - At low temperatures, the $-T\Delta S_{system}$ will be **small** and **negative** and will not overcome the larger $\Delta H_{reaction}$
 - Therefore, at low temperatures ΔG 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 $\Delta H_{reaction}$ resulting in a negative ΔG



- 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 of iron in the blast furnace, which will be unsuccessful at low temperatures but can occur at higher temperatures (~1500 °C in the case of iron)



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The diagram shows under which conditions endothermic reactions are feasible

Summary of factors affecting Gibbs free energy



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If $\Delta H...$	And if $\Delta S...$	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
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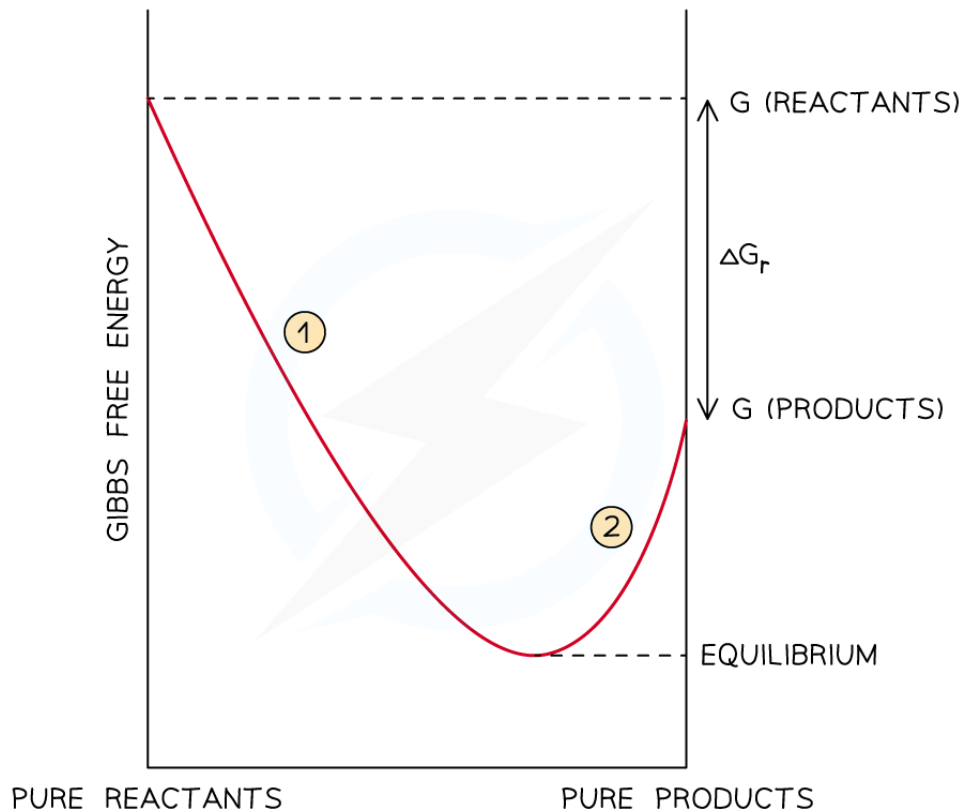


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15.2.5 Free Energy & Equilibrium

Free Energy & Equilibrium

- When $\Delta G < 0$ for a reaction at constant temperature and pressure, the reaction is spontaneous
- When a reversible reaction reaches equilibrium, the Gibbs free energy is changing as the ratio of reactants to products changes
- For non-reversible reactions:
 - As the amount of products increases, the reaction moves towards completion
 - This leads to a decrease in Gibbs free energy
- For reversible reactions:
 - As the amount of products increases, the reaction moves towards equilibrium
 - This causes a decrease in Gibbs free energy
- At the point of equilibrium, Gibbs free energy is at its lowest as shown on the graph:



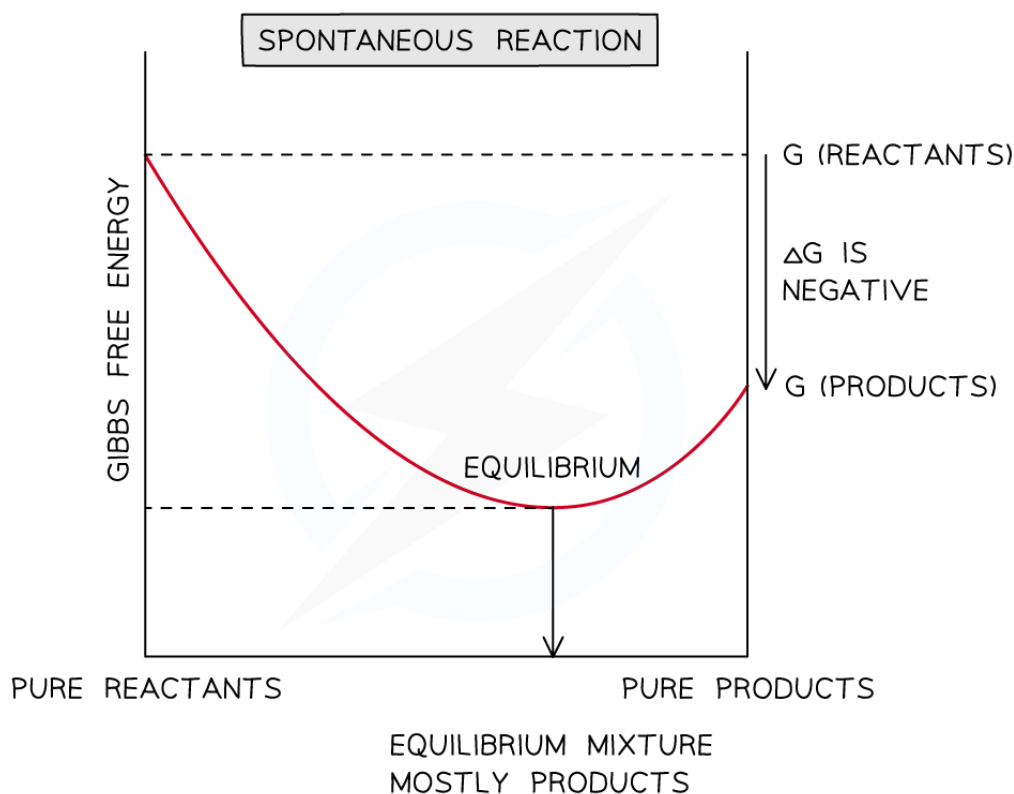
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Gibbs free energy changes as the reaction proceeds

- In section 1 of the graph, the forward reaction is favoured and the reaction proceeds towards a minimum value
- Having reached a point of equilibrium, the Gibbs free energy increases
 - This is when the reaction becomes non-spontaneous (section 2)
- The reverse reaction now becomes spontaneous and the Gibbs free energy again reaches the minimum value, so heads back towards equilibrium
- The reaction will be spontaneous in the direction that results in a decrease in free energy (becomes more negative)
- When the equilibrium constant, K , is determined for a given reaction, its value indicates whether the products or reactants are favoured at equilibrium
- ΔG is an indication of whether the forward or backward reaction is favoured

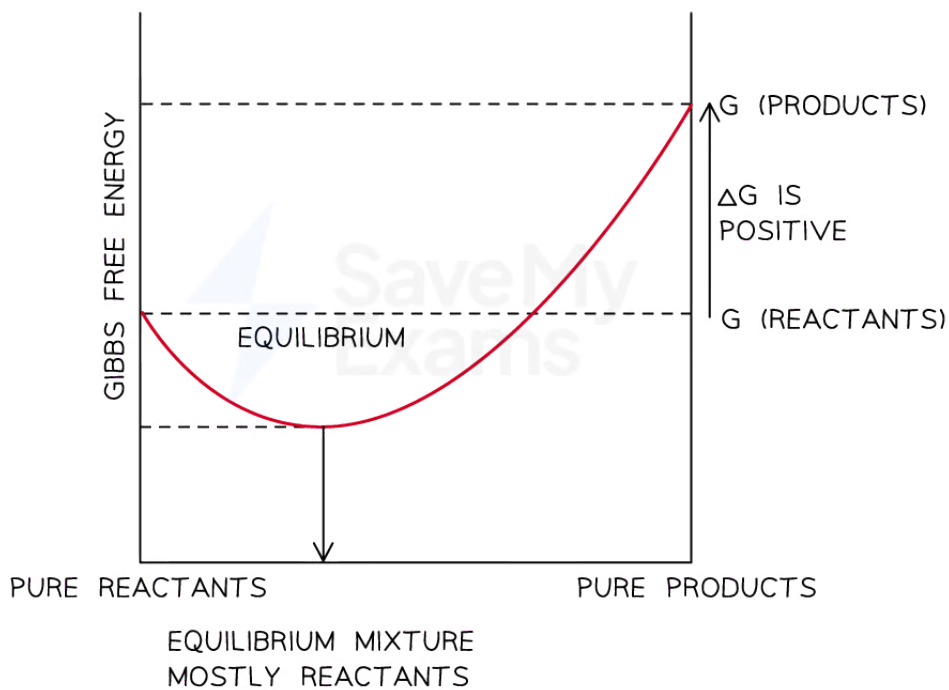


Graph for a spontaneous reaction



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NOT THERMODYNAMICALLY FAVORED REACTION



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Graph for a non-spontaneous reaction

- The quantitative relationship between standard Gibbs free energy change, temperature and the equilibrium constant is represented by:

$$\Delta G^\ominus = -RT \ln K$$