HL IB Chemistry

Your notes

Entropy & Spontaneity

Contents

Your notes

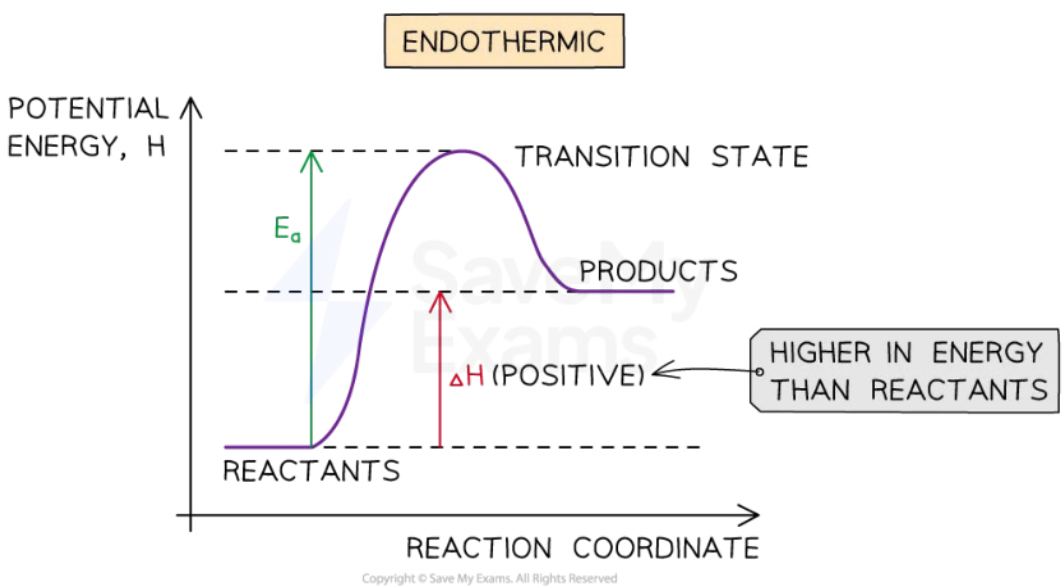
Entropy (HL)

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 every day are exothermic, $\Delta H^{\ominus}$ alone is not enough to explain why endothermic reactions occur

Endothermic reaction profile



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

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:

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

Your notes

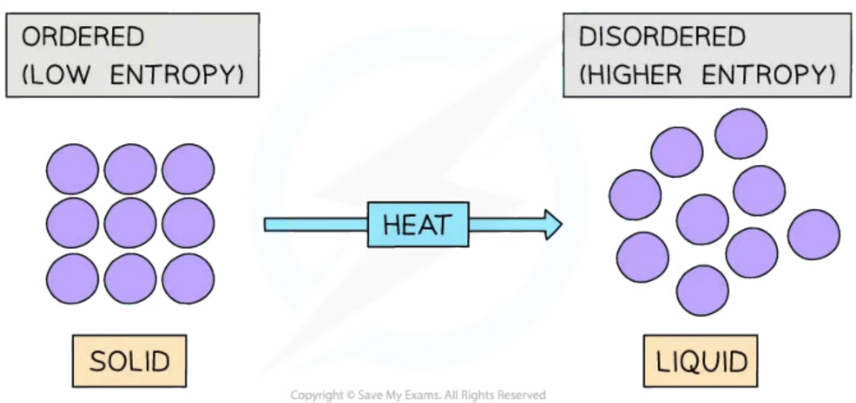
- In this decomposition reaction, a gas molecule (CO_2) is formed
- The CO_2 gas molecule is more disordered than the solid reactant ($CaCO_3$), as it is constantly moving around
- As a result, the system has become more disordered and there is an increase in entropy

- Another typical example of a system that becomes more disordered is when a solid melts
  - For example, melting ice to form liquid water:

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

  - 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)

Low entropy to high entropy



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

Calculating Standard Entropy Changes (HL)

Your notes

Calculating Standard Entropy Changes

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

$$\mathbf{\Delta S^{\ominus}_{298}(reaction) = \Sigma S^{\ominus}_{298}(products) - \Sigma S^{\ominus}_{298}(reactants)}$$

  - This equation is provided in the data booklet
- The units of $\Delta S_{system}{}^{\ominus}$ are in **J K^{-1} 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
    - $S^{\ominus}_{298}(H_2O\ (l)) = 70.0\ J\ K^{-1}\ mol^{-1}$
    - $S^{\ominus}_{298}(H_2O\ (g)) = 188.8\ J\ K^{-1}\ mol^{-1}$
- When calculating $\Delta S^{\ominus}$, the coefficients used to balance the equation must be applied when calculating the overall entropy change
- For example, when calculating the $\Delta S^{\ominus}$ for the reaction below we need to double the value for $S^{\ominus}$(NO (g))
  - $N_2O_4\ (g) \rightarrow \mathbf{2}NO_2\ (g)$
  - $\Delta S^{\ominus}_{298}(reaction) = \Sigma S^{\ominus}_{298}(products) - \Sigma S^{\ominus}_{298}(reactants)$
  - $\Delta S^{\ominus} = [(\mathbf{2} \times S^{\ominus}_{298}(NO_2)] - S^{\ominus}_{298}(N_2O_4)$

Worked example

What is the entropy change when calcium carbonate decomposes?

$$\mathbf{CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2\ (g)}$$

- $S^{\ominus}_{298}(CaCO_3\ (s)) = 92.9\ J\ K^{-1}\ mol^{-1}$
- $S^{\ominus}_{298}(CaO\ (s)) = 39.7\ J\ K^{-1}\ mol^{-1}$
- $S^{\ominus}_{298}(CO_2\ (g)) = 213.6\ J\ K^{-1}\ mol^{-1}$

Answer:

Step 1: Write out the equation to calculate $\Delta S^{\ominus}_{298}$(reaction)

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

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

- $\Delta S^{\ominus}_{298}(reaction) = [S^{\ominus}_{298}(CaO) + S^{\ominus}_{298}(CO_2)] - S^{\ominus}_{298}(CaCO_3)$
- $\Delta S^{\ominus}(reaction) = (39.7 + 213.6) - 92.9$
- $\Delta S^{\ominus}(reaction) = \mathbf{+160.4\ J\ K^{-1}\ mol^{-1}}$

Your notes

Worked example

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

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

- $S^{\circ}_{298}(N_2(g))$ = 191.6 J K^{-1} mol^{-1}
- $S^{\circ}_{298}(H_2(g))$ = 131 J K^{-1} mol^{-1}
- $S^{\circ}_{298}(NH_3)$ = 192.3 J K^{-1} mol^{-1}

Answer:

Step 1: Write out the equation to calculate ΔS°_{298}(reaction)

- ΔS°_{298}(reaction) = ΣS°_{298}(products) - ΣS°_{298}(reactants)

Step 2: Substitute in formulas and then values for S° taking into account the coefficients

- ΔS°_{298}(reaction) = [2 x $S^{\circ}_{298}(NH_3)$] - [$S^{\circ}_{298}(N_2)$+ (3 x $S^{\circ}_{298}(H_2)$)]
- ΔS°_{298}(reaction) = [2 x 192.3] - [191.6 + (3 x 131)]
- ΔS°_{298}(reaction) = 384.6 - 584.6
- ΔS°_{298}(reaction) = **–200 J K^{-1} mol^{-1}**

Gibbs Free Energy (HL)

Gibbs Free Energy

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:

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

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

Calculating $\Delta G^{\equiv}$

- There are two ways you can calculate the value of $\Delta G^{\equiv}$
  1. From the Gibbs equation, using enthalpy change, $\Delta H^{\equiv}$, and entropy change, $\Delta S^{\equiv}$, values
  2. From $\Delta G^{\equiv}$ values of all the substances present

Worked example

$\Delta G^{\equiv}$ from $\Delta H^{\equiv}$ and $\Delta S^{\equiv}$ values

Calculate the free energy change for the following reaction at 298 K:

$$2NaHCO_3\,(s) \rightarrow Na_2CO_3\,(s) + H_2O\,(l) + CO_2\,(g)$$

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

Answer:

- **Step 1:** Convert the entropy value in kilojoules
  - $\Delta S^{\equiv} = \dfrac{+344\ \text{J K}^{-1}\ \text{mol}^{-1}}{1000}$ = +0.344 kJ K^{-1} mol^{-1}
- **Step 2:** Substitute the terms into the Gibbs Equation
  - $\Delta G^{\equiv} = \Delta H_{reaction}{}^{\equiv} - T\Delta S_{system}{}^{\equiv}$
  - $\Delta G^{\equiv}$ = +135 – (298 x 0.344)
  - $\Delta G^{\equiv}$ = **+32.49 kJ mol^{-1}**

Your notes

Worked example

$\Delta G^{\ominus}$ from other $\Delta G^{\ominus}$ values

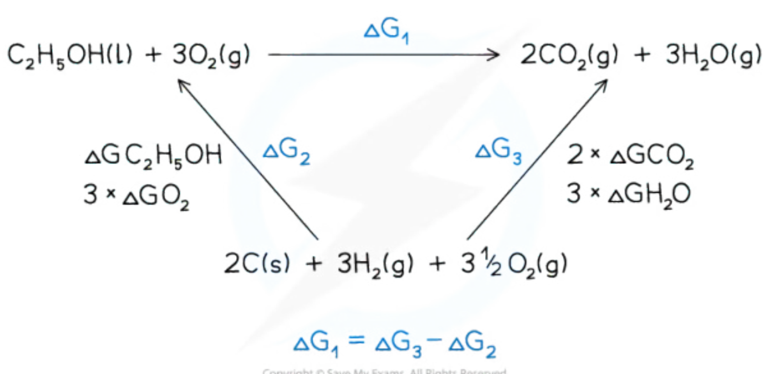
What is the standard free energy change, $\Delta G^{\ominus}$, for the following reaction?

$$C_2H_5OH\ (l) + 3O_2\ (g) \rightarrow 2CO_2\ (g) + 3H_2O\ (g)$$

Substance	$\Delta G^{\ominus}$ kJ mol^{-1}
C_2H_5OH (l)	-175
O_2 (g)	0
CO_2 (g)	-394
H_2O (g)	-229

Answer:

- This can be calculated in the same way as you complete enthalpy calculations
    - $\Delta G^{\ominus} = \Sigma\Delta G_{products}{}^{\ominus} - \Sigma\Delta G_{reactants}{}^{\ominus}$
    - $\Delta G^{\ominus} = [(2 \times CO_2) + (3 \times H_2O)] - [(C_2H_5OH) + (3 \times O_2)]$
    - $\Delta G^{\ominus} = [(2 \times -394) + (3 \times -229)] - [-175 + 0]$
    - $\Delta G^{\ominus}$ = **-1300 kJ mol^{-1}**
- This can also be done by drawing a Hess cycle - find the way that is best for you



Examiner 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

Spontaneous Reactions (HL)

Your notes

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 ($\Delta G^{\ominus} \leq 0$)
- We can use the Gibbs equation to calculate whether a reaction is **spontaneous** / feasible or not

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

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

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.

$$\mathbf{2Ca\ (s) + O_2\ (g) \rightarrow 2CaO\ (s)} \qquad \Delta H = -635.5\ \text{kJ mol}^{-1}$$

- $S^{\ominus}$[Ca(s)] = 41.00 J K^{-1} mol^{-1}
- $S^{\ominus}$[O_2(g)] = 205.0 J K^{-1} mol^{-1}
- $S^{\ominus}$[CaO(s)] = 40.00 J K^{-1} mol^{-1}

Answer 1:

Step1: Calculate $\Delta S_{system}^{\ominus}$

- $\Delta S_{system}^{\ominus} = \Sigma\Delta S_{products}^{\ominus} - \Sigma\Delta S_{reactants}^{\ominus}$
- $\Delta S_{system}^{\ominus}$ = (2 x $\Delta S^{\ominus}$ [CaO(s)]) – (2 x $\Delta S^{\ominus}$ [Ca(s)] + $\Delta S^{\ominus}$ [O_2(g)])
  - = (2 x 40.00) – (2 x 41.00 + 205.0)
  - = -207.0 J K^{-1} mol^{-1}

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

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

Step 3: Calculate $\Delta G^{\ominus}$

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

  $\Delta G^{\ominus}$ = -635.5 – (298 x -0.207)

  = **-573.8 kJ mol^{-1}**

Answer 2:

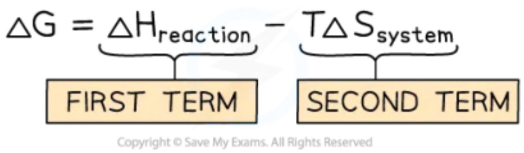
- Since $\Delta G^{\ominus}$ is **negative**, the reaction is **feasible**

Factors affecting ΔG and the spontaneity / feasibility of a reaction

- 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

Gibbs free energy equation

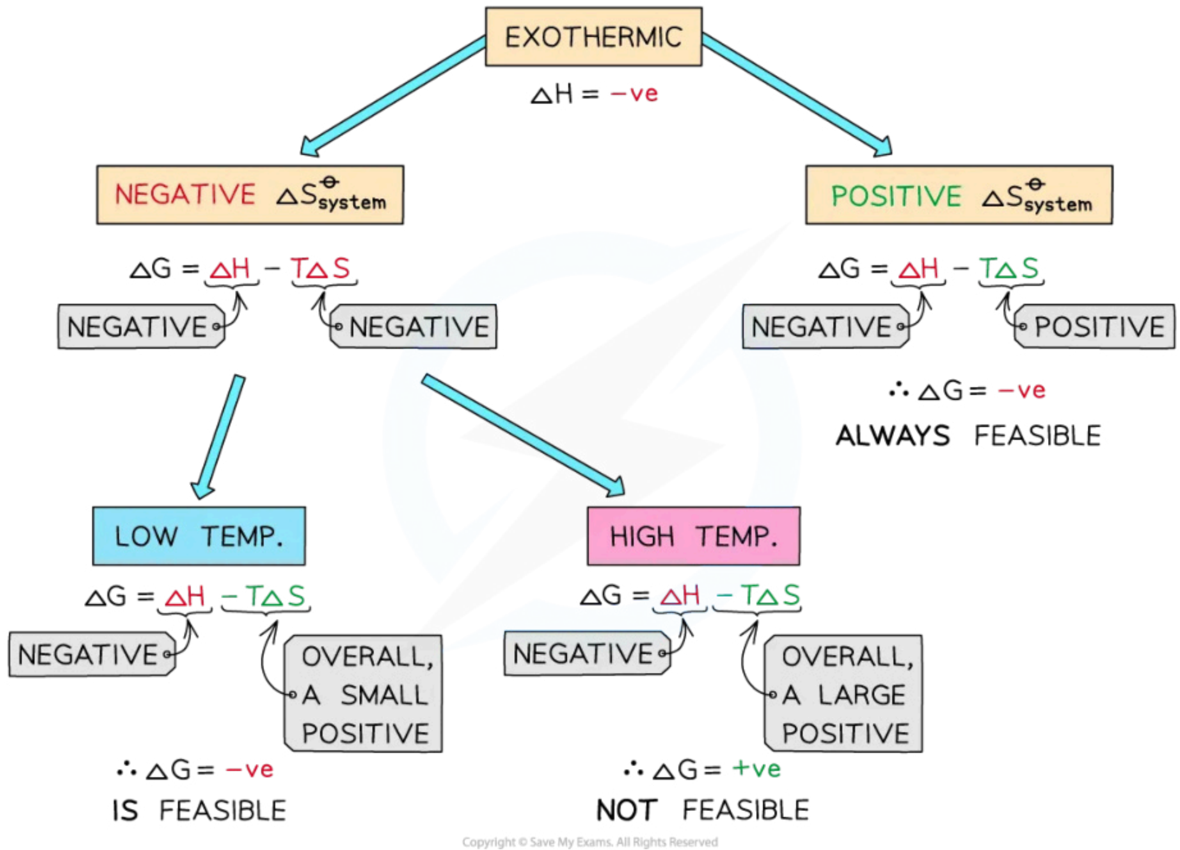
Your notes



Exothermic reactions

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

Flow chart to determine the feasibility of exothermic reactions



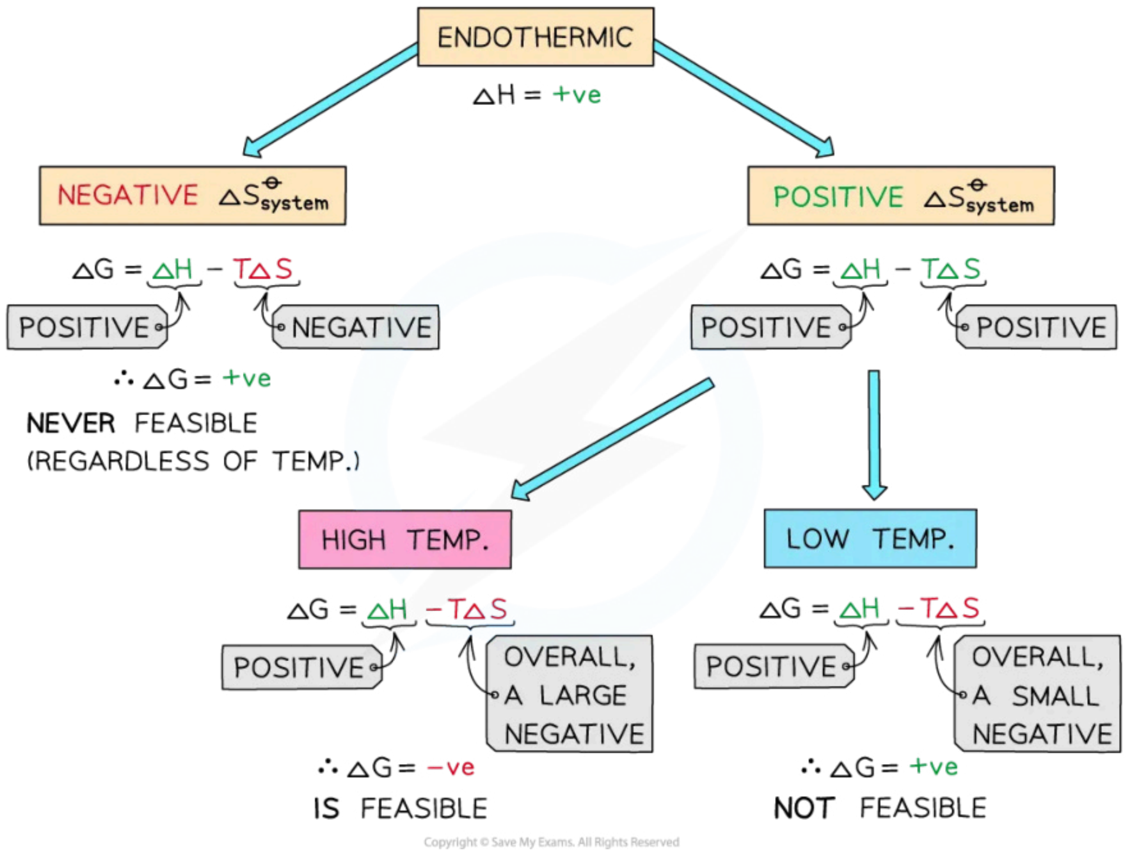
The diagram shows under which conditions exothermic reactions are feasible

Endothermic reactions

- In endothermic reactions, $\Delta H_{reaction}^{\equiv}$ is **positive**
- If the $\Delta S_{system}^{\equiv}$ is **negative:**
  - Both the first and second term will be **positive**
  - Resulting in a **positive** $\Delta G^{\equiv}$ so the reaction is **not feasible**
  - Therefore, regardless of the temperature, endothermic with a negative $\Delta S_{system}^{\equiv}$ will **never be feasible**
- If the $\Delta S_{system}^{\equiv}$ is **positive:**
  - The first term is **positive** and the second term is **negative**
  - At low temperatures, the $-T\Delta S_{system}^{\equiv}$ will be **small** and **negative** and will not overcome the larger $\Delta H_{reaction}^{\equiv}$
  - Therefore, at low temperatures $\Delta G^{\equiv}$ 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 $\Delta H_{reaction}^{\equiv}$ resulting in a negative $\Delta G^{\equiv}$
- 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 higher temperatures (~1500 °C in the case of iron)

Flow chart to determine the feasibility of endothermic reactions



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*

Your notes

is negative < 0 exothermic	is negative < 0 more order	negative at low *T* positive high *T*	Dependent on *T*	Spontaneous only at low *T* ***T*ΔS < *H***
is positive > 0 endothermic	is positive > 0 more disorder	negative at high *T* positive low *T*	Dependent on *T*	Spontaneous only at high *T* ***T*ΔS > *H***

Temperature & Spontaneity

- Rearranging the Gibbs equation allows you to determine the temperature at which a non-spontaneous reaction become feasible

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

- Remember, for a reaction to be feasible ΔG^⊖≣ must be zero or negative
  - 0 = Δ*H*≣ - TΔ*S*≣
  - Δ*H*≣ = TΔ*S*≣
  - $T = \dfrac{\Delta H^{\theta}}{\Delta S^{\theta}}$

Worked example

At what temperature will the reduction of aluminium oxide with carbon become spontaneous?

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

Δ*H*≣ = +1336 kJ mol^{-1}

Δ*S*≣ = +581 J K^{-1} mol^{-1}

Answer:

- If ΔG≣ = 0 then $T = \dfrac{\Delta H^{\theta}}{\Delta S^{\theta}}$
- Covert Δ*S*≣ to kJ K^{-1} mol^{-1} by dividing by 1000
- $T = \dfrac{1336}{\left(\dfrac{581}{1000}\right)}$ **= 2299 K**

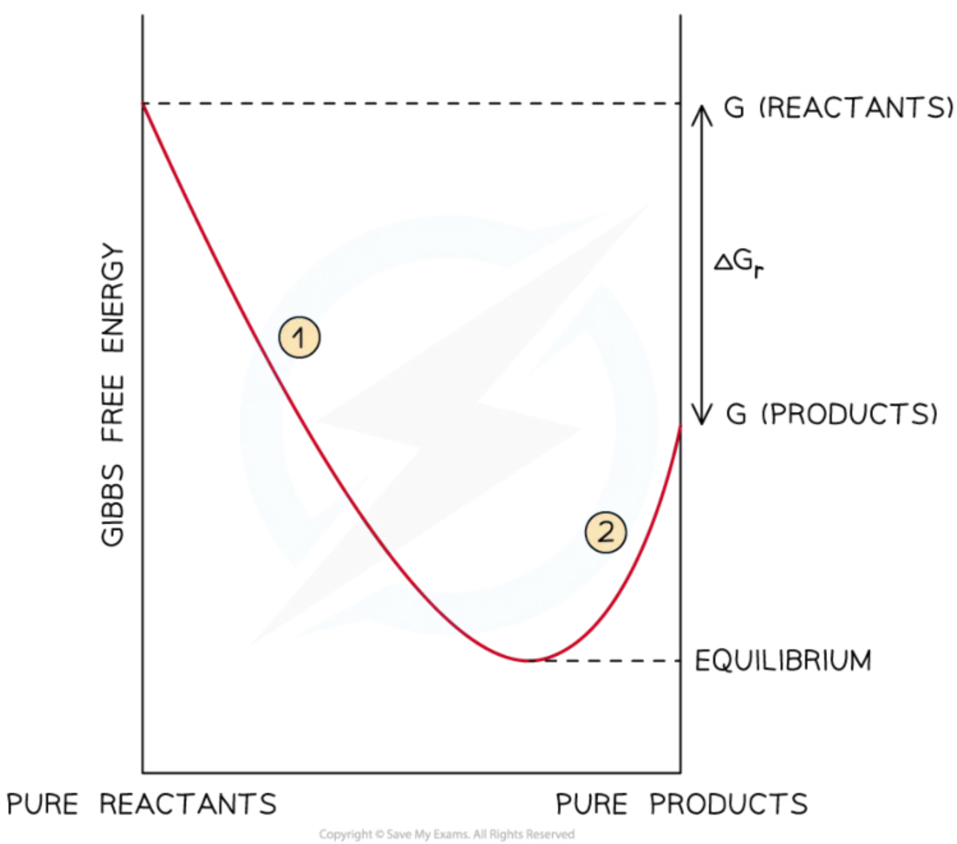
Your notes

Gibbs Free Energy & Equilibrium Constant (HL)

Gibbs Free Energy & Equilibrium Constant

- 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:

Gibbs free energy and equilibrium relationship



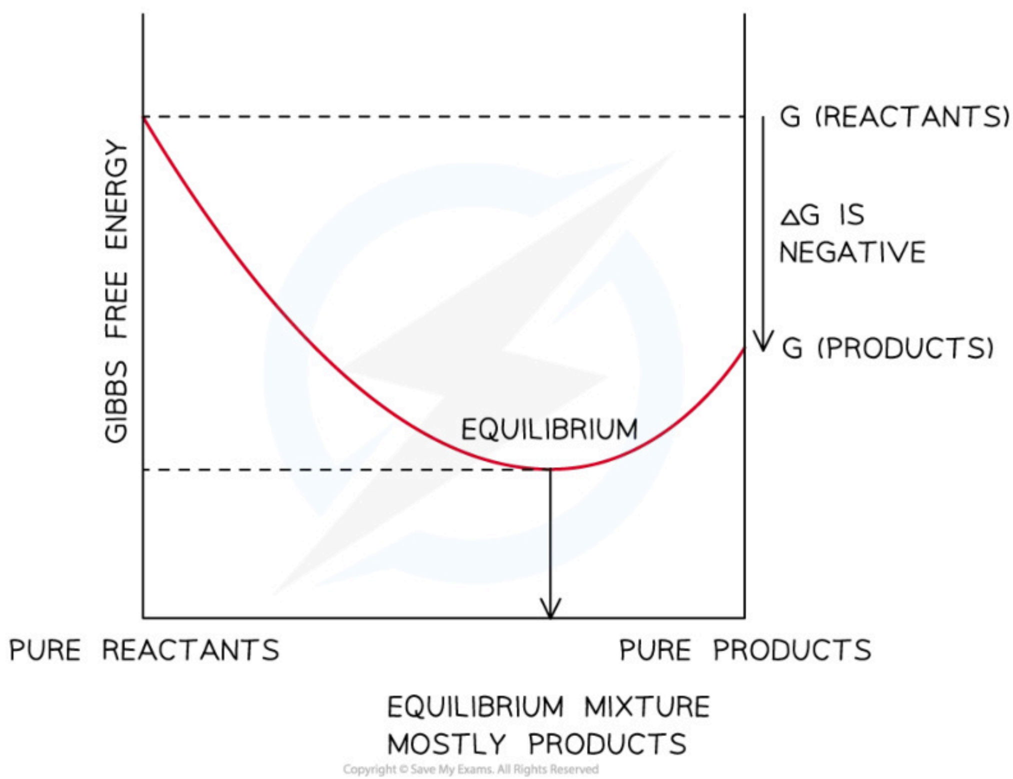
Gibbs free energy changes as the reaction proceeds

Your notes

- 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

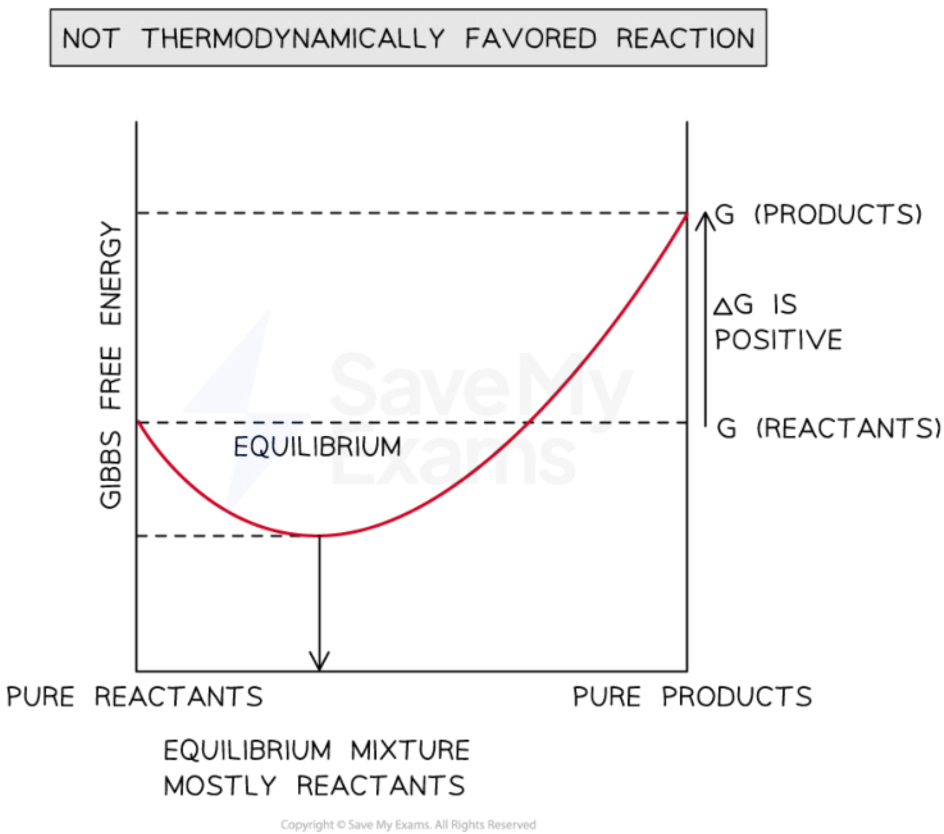
- The reaction will be spontaneous in the direction that results in a decrease in free energy (becomes more negative)
- When the equilibrium constant, *K*, is determined for a given reaction, its value indicates whether the products or reactants are favoured at equilibrium
- ΔG is an indication of whether the forward or backward reaction is favoured

Free energy graph for a spontaneous reaction



Free energy graph for a non-spontaneous reaction

Your notes



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

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

The rearrangement of this equation makes it possible to:

- Calculate the equilibrium constant
- Deduce the position of equilibrium for the reaction

$$\ln K = -\frac{\Delta G^{\ominus}}{RT}$$

- The **reaction quotient**, **Q**, is calculated using the same equation as the equilibrium constant expression, but with non-equilibrium concentrations of reactants and products
- It is a useful concept because the size of **Q** can tell us how far a reaction is from equilibrium and in which direction the reaction proceeds

So how is the reaction quotient related to Gibbs free energy?

- They are related by the following expression:

$$\Delta G = \Delta G^{\theta} + RT \ln Q$$

Your notes

- At non-equilibrium conditions ΔG and ΔG^{θ} are not the same; ΔG is the driver that pushes a reaction toward equilibrium
- When a reaction reaches equilibrium, Q = K and $\Delta G = 0$, so

$$\mathbf{0 = \Delta G^{\theta} + RT \ln K}$$

$$\mathbf{\Delta G^{\theta} = - RT \ln K}$$

Your notes

Worked example

Calculating K_c

Ethanoic acid and ethanol react to form the ester ethyl ethanoate and water as follows:

$$CH_3COOH\ (l) + C_2H_5OH\ (l) \rightleftharpoons CH_3COOC_2H_5\ (l) + H_2O\ (l)$$

At 25 °C, the free energy change, $\Delta G^{\ominus}$, for the reaction is -4.38 kJ mol^{-1}. (R = 8.31 J K^{-1} mol^{-1})

1. Calculate the value of K_c for this reaction
2. Using your answer to part (1), predict and explain the position of the equilibrium

Answers

Answer 1:

Step 1: Convert any necessary values

- $\Delta G^{\ominus}$ into J mol^{-1}:
  - -4.38 x 1000 = -4380 J mol^{-1}
- T into Kelvin
  - 25 + 273 = 298 K

Step 2: Write the equation:

- $\boldsymbol{\Delta G^{\ominus} = -RT \ln K}$

Step 3: Substitute the values:

- -4380 = -8.31 x 298 x lnK_c

Step 4: Rearrange and solve the equation for K_c:

- ln K = -4380 ÷ (-8.31 x 298)
- ln K = 1.77
- $K = e^{1.77}$
- K = 5.87

Answer 2:

From part (1), the value of K_c is 5.87

Therefore, the equilibrium lies to the right / products side because the value of K_c is positive

Worked example

Finding ΔG

Sulfur dioxide reacts with oxygen to form sulfur trioxide in the following reversible reaction:

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons + 2SO_3\,(g)$$

ΔG^{θ} is = -142 kJmol^{-1}

In an experiment, the concentrations of $[SO_2]$, $[O_2]$, $[SO_3]$, were found to be 0.100 mol dm^{-3}, 0.200 mol dm^{-3}, and 0.950 mol dm^{-3} respectively at 1455 K. R = 8.31 J K mol^{-1}

Calculate the value of ΔG at this temperature.

Answer

Step 1 - Write the Q expression

$$Q = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

$$Q = \frac{[0.950]^2}{[0.100]^2[0.200]}$$

Step 2 - Solve Q

$$Q = 451.25$$

Step 3 - Substitution

$$\Delta G = \Delta G^{\theta} + RT \ln Q$$

$$\Delta G = -142 + (8.31 \times 1455 \times 451.25)/1000$$

$$\Delta G = -142 + 73.9 = -68.1 \text{ kJ mol}^{-1}$$

Remember to divide by 1000, because R is in J mol^{-1}K^{-1} not kJ mol^{-1}K^{-1}

Examiner Tip

These equations are given in the data booklet

Your notes