



# Cambridge (CIE) A Level Chemistry



## Gibbs Free Energy Change, $\Delta G$

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# The Gibbs Equation

## Gibbs free energy

- The feasibility of a reaction does not only depend on the entropy change of the reaction but can also be affected by the enthalpy change
- Therefore, using the entropy change of a reaction **only** to determine the feasibility of a reaction is inaccurate
- The **Gibbs free energy (G)** is the energy change that takes into account **both** the **entropy** change of a reaction and the **enthalpy** change
- The Gibbs equation is:

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

- The units of  $\Delta G^\theta$  are in **kJ mol<sup>-1</sup>**
  - The units of  $\Delta H_{\text{reaction}}^\theta$  are in **kJ mol<sup>-1</sup>**
  - The units of T are in K
  - The units of  $\Delta S_{\text{system}}^\theta$  are in **JK<sup>-1</sup>mol<sup>-1</sup>**



## Worked Example

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



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

**Answer:**

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



## Examiner Tips and Tricks

**Careful:** When calculating  $\Delta G^\theta$  the value for  $\Delta S_{\text{system}}^\theta$  must be divided by 1000

$$\text{J K}^{-1}\text{mol}^{-1} \xrightarrow{\div 1000} \text{kJ K}^{-1}\text{mol}^{-1}$$



## The Gibbs Equation: Calculations

- The Gibbs equation can be used to calculate the Gibbs free energy change of a reaction

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

- The equation can also be rearranged to find values of  $\Delta H_{\text{reaction}}^\theta$ ,  $\Delta S_{\text{system}}^\theta$  or the temperature,  $T$
- For example, if for a given reaction, the values of  $\Delta G^\theta$ ,  $\Delta H_{\text{reaction}}^\theta$  and  $\Delta S_{\text{system}}^\theta$  are given, the temperature can be found by rearranging the Gibbs equation as follows:

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



### Worked Example

Calculate the Gibbs free energy for the reaction of methanol, CH<sub>3</sub>OH, with hydrogen bromide, HBr, at 298 K.



- $\Delta S^\theta[\text{CH}_3\text{OH}(\text{l})] = +240 \text{ J K}^{-1}\text{mol}^{-1}$
- $\Delta S^\theta[\text{HBr}(\text{g})] = +99.0 \text{ J K}^{-1}\text{mol}^{-1}$
- $\Delta S^\theta[\text{H}_2\text{O}(\text{l})] = +70.0 \text{ J K}^{-1}\text{mol}^{-1}$
- $\Delta S^\theta[\text{CH}_3\text{Br}(\text{g})] = +246 \text{ J K}^{-1}\text{mol}^{-1}$

**Answer:**

- Step 1: Calculate  $\Delta S_{\text{system}}^\theta$**

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

$$\Delta S_{\text{system}}^\theta = (\Delta S^\theta[\text{CH}_3\text{Br}(\text{g})] + \Delta S^\theta[\text{H}_2\text{O}(\text{l})]) - (\Delta S^\theta[\text{CH}_3\text{OH}(\text{l})] + \Delta S^\theta[\text{HBr}(\text{g})])$$

$$\Delta S_{\text{system}}^\theta = (246 + 70.0) - (240 + 99.0)$$

$$\Delta S_{\text{system}}^\theta = -23.0 \text{ J K}^{-1}\text{mol}^{-1}$$

- Step 2: Convert  $\Delta S^\theta$  into  $\text{kJ K}^{-1}\text{mol}^{-1}$**

$$\Delta S_{\text{system}}^\theta = \frac{-23.0}{1000} = 0.023 \text{ kJ K}^{-1}\text{mol}^{-1}$$

- Step 3: Calculate  $\Delta G^\theta$**

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

$$\Delta G^\theta = -47 - (298 \times -0.023)$$

$$\Delta G^\theta = -40.146 \text{ kJ mol}^{-1}$$



$\Delta G^\theta = -40.1 \text{ kJ mol}^{-1}$



Your notes



# Reaction Feasibility

- The Gibbs equation can be used to calculate whether a reaction is **feasible** or not

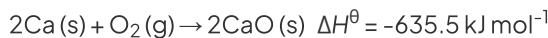
$$\Delta G^\theta = \Delta H_{\text{reaction}}^\theta - T\Delta S_{\text{system}}^\theta$$

- When  $\Delta G^\theta$  is **negative**, the reaction is **feasible** and likely to occur
- When  $\Delta G^\theta$  is **positive**, the reaction is **not feasible** and unlikely to occur



### Worked Example

Calculate the Gibbs free energy for the following reaction at 298 K and determine whether the reaction is feasible.



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

**Answer:**

- Step 1:** Calculate  $\Delta S_{\text{system}}^\theta$

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

$$\Delta S_{\text{system}}^\theta = (2 \times \Delta S^\theta[\text{CaO}(\text{s})]) - (2 \times \Delta S^\theta[\text{Ca}(\text{s})] + \Delta S^\theta[\text{O}_2(\text{g})])$$

$$\Delta S_{\text{system}}^\theta = (2 \times 40.00) - (2 \times 41.00 + 205.0)$$

$$\Delta S_{\text{system}}^\theta = -207.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

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

$$\Delta S^\theta = \frac{-207.0}{1000} = -0.207 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

- Step 3:** Calculate  $\Delta G^\theta$

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

$$\Delta G^\theta = -635.5 - (298 \times -0.207)$$

$$\Delta G^\theta = -573.8 \text{ kJ mol}^{-1}$$

- Step 4:** Determine whether the reaction is feasible

- Since the  $\Delta G^\theta$  is **negative** the reaction is **feasible** and likely to occur

## Reaction Feasibility & Temperature Changes

- The feasibility of a reaction can be affected by the **temperature**
- The Gibbs equation will be used to explain what will affect the feasibility of a reaction for exothermic and endothermic reactions



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

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## Exothermic reactions

- In exothermic reactions,  $\Delta H_{\text{reaction}}^{\theta}$  is **negative**
- If the  $\Delta S_{\text{system}}^{\theta}$  is **positive**:
  - Both the first and second term will be **negative**
  - Resulting in a **negative**  $\Delta G^{\theta}$  so the reaction is **feasible**
  - Therefore, regardless of the temperature, an exothermic reaction with a positive  $\Delta S_{\text{system}}^{\theta}$  will **always be feasible**
- If the  $\Delta S_{\text{system}}^{\theta}$  is **negative**:
  - The first term is **negative** and the second term is **positive**
  - At high temperatures, the  $-T\Delta S_{\text{system}}^{\theta}$  will be very **large** and **positive** and will overcome  $\Delta H_{\text{reaction}}^{\theta}$
  - Therefore, at **high temperatures**  $\Delta G^{\theta}$  is **positive** and the reaction is not feasible
  - The reaction is more **feasible** at low temperatures, as the second term will not be large enough to overcome  $\Delta H_{\text{reaction}}^{\theta}$  resulting in a negative  $\Delta G^{\theta}$
- This corresponds to Le Chatelier's principle which states that for **exothermic reactions** an increase in temperature will cause the equilibrium to shift position in favour of the reactants, i.e. in the endothermic direction
  - In other words, for exothermic reactions, the products will **not be formed** at high temperatures
  - The reaction is **not feasible** at high temperatures

## Summary of factors affecting Gibbs free energy for exothermic reactions

If $\Delta H \dots$	And if $\Delta S \dots$	Then $\Delta G$ is	Spontaneous?	Because



Your notes

is negative $< 0$ exothermic	is positive $> 0$ more disorder	always negative $< 0$	Always	Forward reaction spontaneous at any $T$
is negative $< 0$ exothermic	is negative $< 0$ more order	negative at low $T$ positive high $T$	Dependent on $T$	Spontaneous only at low $T$ $T\Delta S < H$

## Endothermic reactions

- In endothermic reactions,  $\Delta H_{\text{reaction}}^\theta$  is **positive**
- If the  $\Delta S_{\text{system}}^\theta$  is **negative**:
  - Both the first and second term will be **positive**
  - Resulting in a **positive**  $\Delta G^\theta$  so the reaction is **not feasible**
  - Therefore, regardless of the temperature, endothermic with a negative  $\Delta S_{\text{system}}^\theta$  will **never be feasible**
- If the  $\Delta S_{\text{system}}^\theta$  is **positive**:
  - The first term is **positive** and the second term is **negative**
  - At low temperatures, the  $-T\Delta S_{\text{system}}^\theta$  will be **small** and **negative** and will not overcome the larger  $\Delta H_{\text{reaction}}^\theta$
  - Therefore, at low temperatures  $\Delta G^\theta$  is **positive** and the reaction is less feasible
  - The reaction is **more feasible at high temperatures** as the second term will become negative enough to overcome the  $\Delta H_{\text{reaction}}^\theta$  resulting in a negative  $\Delta G^\theta$
- This again corresponds to Le Chatelier's principle which states that for **endothermic reactions** an increase in temperature will cause the equilibrium to shift position in favour of the products
  - In other words, for endothermic reactions, the products will **be formed** at high temperatures
  - The reaction is therefore **feasible**

## Summary of factors affecting Gibbs free energy for endothermic reactions

If $\Delta H \dots$	And if $\Delta S \dots$	Then $\Delta G$ is	Spontaneous?	Because



is positive > 0 endothermic	is negative < 0 more order	always positive > 0	Never	Reverse reaction spontaneous at any $T$
is positive > 0 endothermic	is positive > 0 more disorder	negative at high $T$ positive low $T$	Dependent on $T$	Spontaneous only at high $T$ $T\Delta S > H$