

Cambridge (CIE) A Level Chemistry



Your notes

Gibbs Free Energy Change, ΔG

Contents

- * Gibbs Free Energy Change & Gibbs Equation
- * Reaction Feasibility



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 ΔG^θ are in kJ mol^{-1}
 - The units of $\Delta H_{\text{reaction}}^\theta$ are in kJ mol^{-1}
 - The units of T are in K
 - The units of $\Delta S_{\text{system}}^\theta$ are in $\text{J K}^{-1} \text{mol}^{-1}$



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 ΔG^θ the value for $\Delta S_{\text{system}}^\theta$ must be divided by 1000

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



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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 ΔG^θ , $\Delta H_{\text{reaction}}^\theta$ 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_3OH , with hydrogen bromide, HBr , at 298 K.



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

Answer:

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

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

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

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

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

- Step 2: Convert ΔS^θ 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 ΔG^θ**

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

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

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



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



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Reaction Feasibility

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

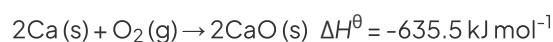
$$\Delta G^\theta = \Delta H_{\text{reaction}}^\theta - T\Delta S_{\text{system}}^\theta$$

- When ΔG^θ is **negative**, the reaction is **feasible** and likely to occur
- When ΔG^θ 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.



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

Answer:

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

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

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

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

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

- Step 2:** Convert ΔS^θ 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 ΔG^θ

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

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

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

- Step 4:** Determine whether the reaction is feasible
 - Since the ΔG^θ 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



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

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Exothermic reactions

- In exothermic reactions, $\Delta H_{\text{reaction}}^{\theta}$ is **negative**
- If the $\Delta S_{\text{system}}^{\theta}$ is **positive**:
 - Both the first and second term will be **negative**
 - Resulting in a **negative** ΔG^{θ} 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** ΔG^{θ} 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 ΔG^{θ}
- 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 ΔH	And if ΔS	Then ΔG is	Spontaneous?	Because



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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, $\Delta H_{\text{reaction}}^{\ominus}$ is **positive**
- If the $\Delta S_{\text{system}}^{\ominus}$ is **negative**:
 - Both the first and second term will be **positive**
 - Resulting in a **positive** ΔG^{\ominus} so the reaction is **not feasible**
 - Therefore, regardless of the temperature, endothermic with a negative $\Delta S_{\text{system}}^{\ominus}$ will **never be feasible**
- If the $\Delta S_{\text{system}}^{\ominus}$ is **positive**:
 - The first term is **positive** and the second term is **negative**
 - At low temperatures, the $-T\Delta S_{\text{system}}^{\ominus}$ will be **small** and **negative** and will not overcome the larger $\Delta H_{\text{reaction}}^{\ominus}$
 - Therefore, at low temperatures ΔG^{\ominus} 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 $\Delta H_{\text{reaction}}^{\ominus}$ resulting in a negative ΔG^{\ominus}
- 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 ΔH	And if ΔS	Then ΔG 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 $T\Delta S > H$



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