

Equilibrium HL

IB CHEMISTRY HL

<p>25 Mn Manganese 54.938045</p>	<p>16 S Sulfur 32.065</p>	<p>J</p>	<p>6 C Carbon 12.0107</p>	<p>2 He Helium 4.002602</p>	<p>25 Mn Manganese 54.938045</p>
---	--	-----------------	--	--	---

17.1 The equilibrium law

Understandings:

- Le Châtelier's principle for changes in concentration can be explained by the equilibrium law.
- The position of equilibrium corresponds to a maximum value of entropy and a minimum in the value of the Gibbs free energy.
- The Gibbs free energy change of a reaction and the equilibrium constant can both be used to measure the position of an equilibrium reaction and are related by the equation:

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

Applications and skills:

- Solution of homogeneous equilibrium problems using the expression for K_c .
- Relationship between ΔG and the equilibrium constant.
- Calculations using the equation:

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

- Relationship of ΔG^\ominus to the position of equilibrium

Guidance:

- The expression $\Delta G^\ominus = -RT \ln K$ is given in the data booklet in section 1.
- Students will not be expected to derive the expression
- The use of quadratic equations will not be assessed.

Syllabus checklist

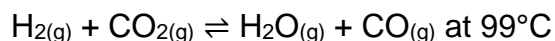
Objective	I am confident with this	I need to review this	I need help with this
Calculate the value of K_c for homogeneous equilibria			
Calculate equilibrium concentrations of reactants and products using an ICE box			
Use the equation $\Delta G^\ominus = -RT \ln K$ to calculate the change in Gibbs free energy for a reaction.			
Explain the relationship between the change in Gibbs free energy and the position of equilibrium.			

Determining the value of K_c

- The value of K_c can be determined in different ways, depending on what data you are given.

Given the concentration of products and reactants at equilibrium.

Calculate the K_c given the reaction:



with the following equilibrium concentrations:

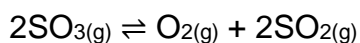
$$[\text{H}_2] = 0.61 \text{ mol dm}^{-3}, [\text{CO}_2] = 1.6 \text{ mol dm}^{-3}, [\text{H}_2\text{O}] = 1.1 \text{ mol dm}^{-3}, [\text{CO}] = 1.4 \text{ mol dm}^{-3}$$

$$K_c =$$

Given the initial concentration of one species and the equilibrium concentration of another.

Before equilibrium is reached, a 1 dm^3 flask contains 0.350 mol of $\text{SO}_3(\text{g})$ at 832°C .

What is the K_c for the reaction at equilibrium if 0.093 mol of oxygen is present?



Make an ICE box. ICE stands for Initial, Change, Equilibrium

	$2\text{SO}_3(\text{g})$	\rightleftharpoons	$\text{O}_2(\text{g})$	$2\text{SO}_2(\text{g})$
Initial (mol dm^{-3})	0.350			
Change (mol dm^{-3})				
Equilibrium (mol dm^{-3})				

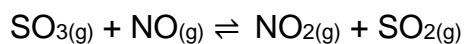
Next, calculate the K_c value.

Calculating the equilibrium concentrations given K_c and initial concentrations

The K_c for the following reaction is 6.78 at a certain temperature.

The initial concentrations of NO and SO_3 are both $0.0300 \text{ mol dm}^{-3}$.

Calculate the equilibrium concentration of each reactant.



	$\text{SO}_3(\text{g})$	$\text{NO}(\text{g})$	$\text{NO}_2(\text{g})$	$\text{SO}_2(\text{g})$
Initial (mol dm^{-3})				
Change (mol dm^{-3})				
Equilibrium (mol dm^{-3})				

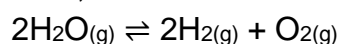
Calculating equilibrium concentrations when K_c is very small

- In some chemical reactions, K_c is a small value, less than 1×10^{-3} . In these reactions, the forward reaction has barely proceeded and the equilibrium mixture consists of mostly reactants.

The change in the initial concentration of reactants is almost zero and the equilibrium concentrations of reactants are almost equal to their initial concentrations.

Example:

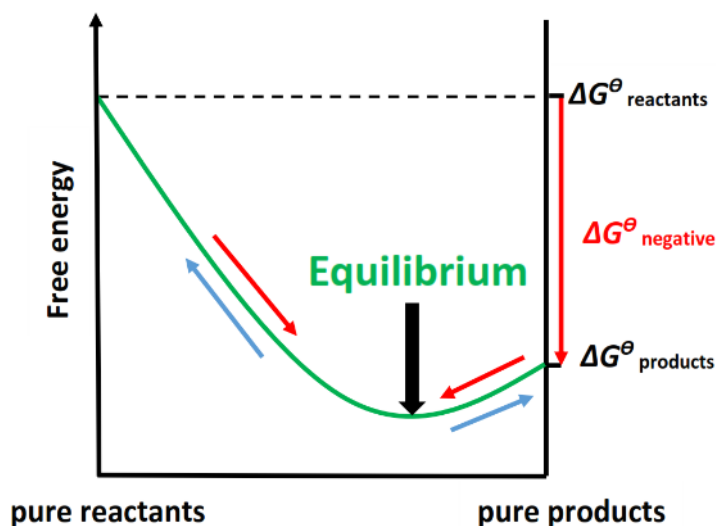
The thermal decomposition of water has a K_c value of 7.3×10^{-18} at 1000°C . If the initial concentration of H_2O is 0.10 mol dm^{-3} , calculate the concentration of O_2 at equilibrium.



	$2\text{H}_2\text{O}(\text{g})$	$2\text{H}_2(\text{g})$	$\text{O}_2(\text{g})$
Initial (mol dm^{-3})			
Change (mol dm^{-3})			
Equilibrium (mol dm^{-3})			

The assumption made in this previous question is that subtracting x from the initial concentration will not make a difference within the precision used (to 2 significant figures). In general, if the value of K_c is less than 1×10^{-3} , this assumption can be made.

ΔG^\ominus and position of equilibrium



- At the **minimum** value of Gibbs free energy, the reaction is at equilibrium.
- This corresponds to a **maximum** value of entropy.

A reaction at equilibrium has a minimum value of Gibbs free energy and a maximum value of entropy.

- The following equation is given in section 1 of the data booklet and can be used to show the relationship between the ΔG^\ominus and the equilibrium constant K_c .

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

ΔG^\ominus = standard change in Gibbs free energy

R = universal gas constant ($8.31 \text{ JK}^{-1}\text{mol}^{-1}$)

T = temperature in kelvin

$\ln K$ = natural log of K

The above equation can be arranged to give the following:

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

Examples:

1. Calculate the value of K_c at 298 K for a reaction given that $\Delta G^\ominus = -32.96 \text{ kJ mol}^{-1}$

2. Calculate the ΔG^\ominus for a reaction given that the K_c is 45.6 at 761 K.

The table below shows the relationship between the ΔG^\ominus and the equilibrium constant K .

- The trend that can be seen from the table is that as the ΔG^\ominus becomes more negative (more spontaneous), the value for the equilibrium constant increases.
- Conversely as the ΔG^\ominus becomes more positive (less spontaneous), the value for the equilibrium constant K decreases.

Reaction (298 K)	ΔG^\ominus (kJ mol ⁻¹)	K_c
$2\text{SO}_{3(g)} \rightleftharpoons 2\text{SO}_{2(g)} + \text{O}_{2(g)}$	+141.7	1.4×10^{-25}
$\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}^+_{(aq)} + \text{OH}^-_{(aq)}$	+79.9	1.0×10^{-14}
$\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$	-32.9	5.8×10^5
$\text{Zn}_{(s)} + \text{Cu}^{2+}_{(aq)} \rightarrow \text{Zn}^{2+}_{(aq)} + \text{Cu}_{(s)}$	-211	1.4×10^{37}

- For a reaction with a larger negative value for the ΔG^\ominus , the equilibrium position lies to the right and the reaction almost goes to completion (as in the reaction of Zn and Cu^{2+}), and the equilibrium mixture will contain mostly products.
- For a reaction with a larger positive value for the ΔG^\ominus , the equilibrium position lies to the left and the equilibrium mixture will contain mostly reactants (as in the decomposition of SO_3).