

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>
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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:

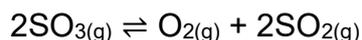
$$[\text{H}_2] = 0.61 \text{ mol dm}^{-3}, [\text{CO}_2] = 1.6 \text{ mol dm}^{-3}, [\text{H}_2\text{O}] = 1.1 \text{ mol dm}^{-3}, [\text{CO}] = 1.4 \text{ mol dm}^{-3}$$

$$K_c =$$

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

Before equilibrium is reached, a 1.00 dm^3 flask contains 0.350 mol of $\text{SO}_3(\text{g})$ at 832°C .

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



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

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

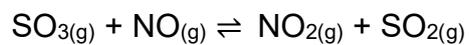
Next, calculate the K_c value.

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.



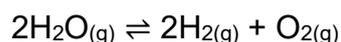
	$\text{SO}_{3(g)}$	$\text{NO}_{(g)}$	$\text{NO}_{2(g)}$	$\text{SO}_{2(g)}$
Initial (mol dm^{-3})				
Change (mol dm^{-3})				
Equilibrium (mol dm^{-3})				

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:

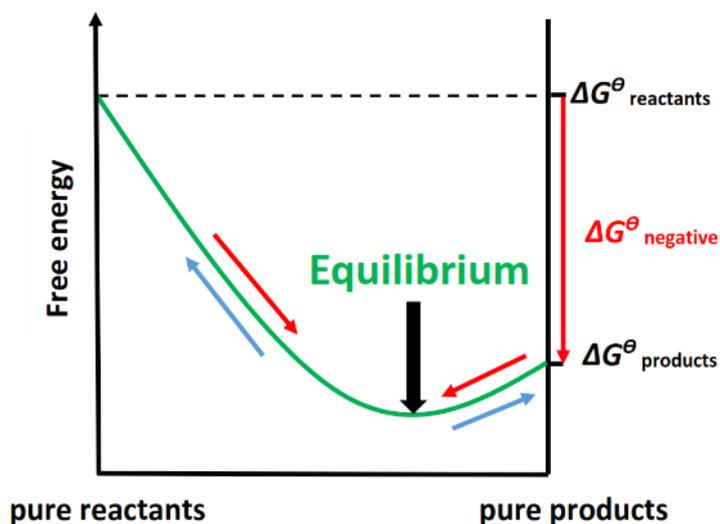
The thermal decomposition of water has a K_c value of 7.3×10^{-18} at 1000°C . If the initial concentration of H_2O is 0.10 mol dm^{-3} , calculate the concentration of O_2 at equilibrium.



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

The assumption made in this example 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 Gibbs free energy change

R – universal gas constant ($8.31 \text{ J K}^{-1} \text{ mol}^{-1}$)

T – temperature in kelvin (K)

$\ln K$ – natural log of K

- The above equation can be arranged to give the following:

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

Exercises:

1. Calculate the value of K_c at 298 K for a reaction given that $\Delta G^\circ = -32.96 \text{ kJ mol}^{-1}$
2. Calculate the ΔG° for a reaction given that the K_c is 45.6 at 298 K.

The table below shows the relationship between the ΔG° and the equilibrium constant K .

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

Reaction (298 K)	ΔG° (kJ mol ⁻¹)	K_c
$2\text{SO}_3(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$	+141.7	1.4×10^{-25}
$\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$	+79.9	1.0×10^{-14}
$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$	-32.9	5.8×10^5
$\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$	-211	1.4×10^{37}

- For a reaction with a larger negative value for the ΔG° , 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° , the equilibrium position lies to the left and the equilibrium mixture will contain mostly reactants (as in the decomposition of SO_3).