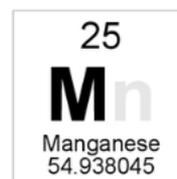
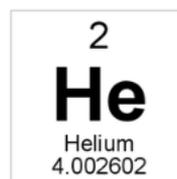
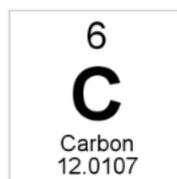
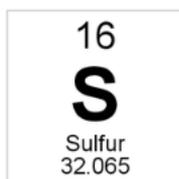
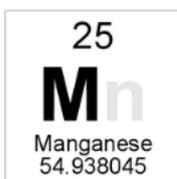


Equilibrium HL (answers)

IB CHEMISTRY HL



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:

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

Applications and skills:

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

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

- Relationship of ΔG to the position of equilibrium.

Guidance:

- The expression $\Delta G = -RT \ln K$ 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 concentration 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:

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

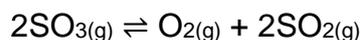
Write the expression for the K_c and plug in the equilibrium concentrations;

$$K_c = (1.1 \times 1.4) \div (0.61 \times 1.6) = 1.6$$

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

Before equilibrium is reached, a 1 dm³ flask contains 0.350 mol of SO_{3(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

	2SO _{3(g)}	O _{2(g)}	2SO _{2(g)}
Initial (mol dm ⁻³)	0.350	0	0
Change (mol dm ⁻³)	-2 × 0.093	+0.093	+ 2 × 0.093
Equilibrium (mol dm ⁻³)	0.164	0.093	0.186

Next, calculate the K_c value.

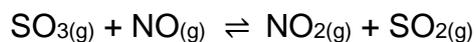
$$K_c = (0.093 \times 0.186^2) \div (0.164^2) = 0.12$$

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 were 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})	0.0300	0.0300	0	0
Change (mol dm^{-3})	-x	-x	+x	+x
Equilibrium (mol dm^{-3})	$0.0300 - x$	$0.0300 - x$	x	x

$$6.78 = (x^2) \div (0.0300 - x)^2$$

take the square root of both sides

$$2.60 = x \div (0.0300 - x)$$

Solve for x

$$x = 0.0217$$

$$[\text{SO}_3] = 0.0300 - 0.0217 = 0.00830 \text{ mol dm}^{-3}$$

$$[\text{NO}] = 0.0300 - 0.0217 = 0.00830 \text{ mol dm}^{-3}$$

$$[\text{NO}_2] = 0.0217 \text{ mol dm}^{-3}$$

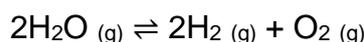
$$[\text{SO}_2] = 0.0217 \text{ mol dm}^{-3}$$

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.



	$2\text{H}_2\text{O(g)}$	$2\text{H}_2\text{(g)}$	$\text{O}_2\text{(g)}$
Initial (mol dm^{-3})	0.10	0	0
Change (mol dm^{-3})	$-2x$	$+2x$	$-x$
Equilibrium (mol dm^{-3})	$0.10 - 2x$	$2x$	x

Because value of K_c is so small, the equilibrium concentration of the H_2O is the same as the initial concentration.

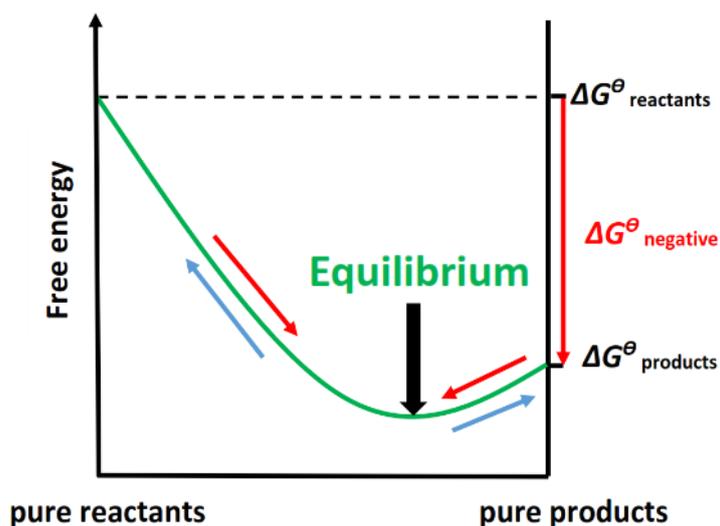
Solve for x

$$x = 2.6 \times 10^{-7}$$

Equilibrium concentration of $\text{H}_2 = 2x = 5.2 \times 10^{-7} \text{ mol dm}^{-3}$

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 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:

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

Example:

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

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

$$K = e^{-32960 \div (8.31 \times 298)}$$

$$K = e^{13.3}$$

$$K = 5.98 \times 10^5$$

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

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

$$\Delta G^\ominus = -8.31 \times 761 \times \ln 45.6$$

$$\Delta G^\ominus = -24.2 \text{ kJ mol}^{-1}$$

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 of the equilibrium constant increases.
- Conversely as the ΔG^\ominus becomes more positive (less spontaneous), the value of the equilibrium constant K decreases.

Reaction (298 K)	ΔG^\ominus (kJ mol ⁻¹)	K
$2\text{SO}_3(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$	+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^\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).