HL IB Chemistry

Your notes

How Far? The Extent of Chemical Change

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The Characteristics of Dynamic Equilibrium

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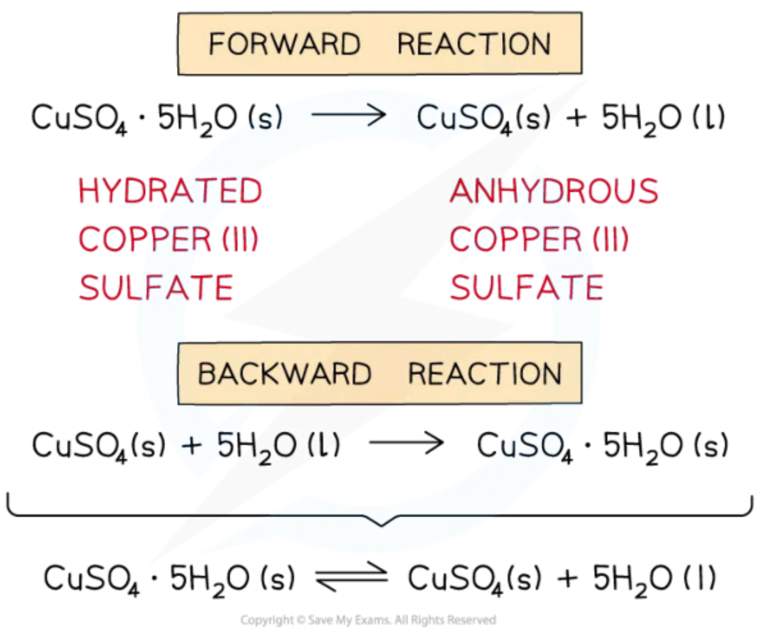
The Characteristics of Dynamic Equilibrium

What are reversible reactions?

- Some reactions go to completion where the reactants are used up to form the products and the reaction stops when all of the reactants are used up
- In **reversible reactions,** the products can react to reform the original reactants
- To show a reversible reaction, two half arrows are used: ⇌

A reversible reaction



The diagram shows an example of a forward and backward reaction that can be written as one equation using two half arrows

What is dynamic equilibrium?

- In a **dynamic equilibrium** the reactants and products are **dynamic** (they are constantly moving)
- In a dynamic equilibrium:
  - The **rate** of the **forward** reaction is the same as the rate of the **backward** reaction in a **closed system**
  - The **concentrations** of the **reactants** and **products** are **constant**
- There is no change in **macroscopic properties** such as colour and density as they depend on the concentration

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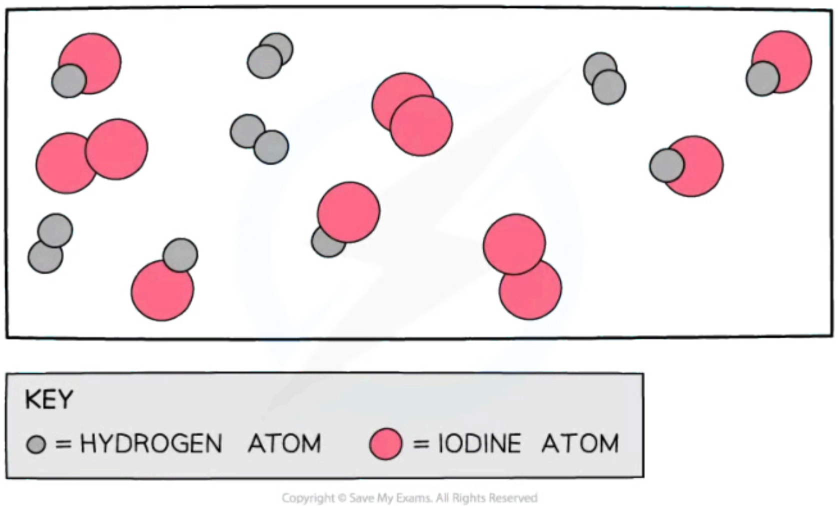
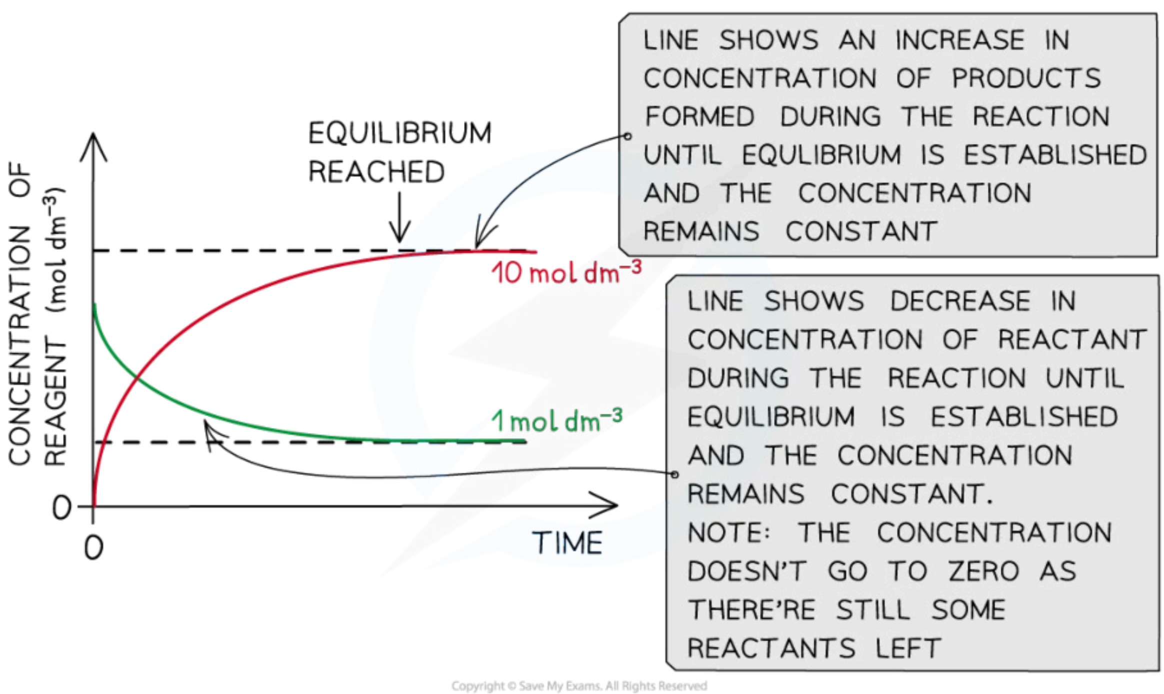
Dynamic equilibrium between hydrogen, iodine and hydrogen iodide



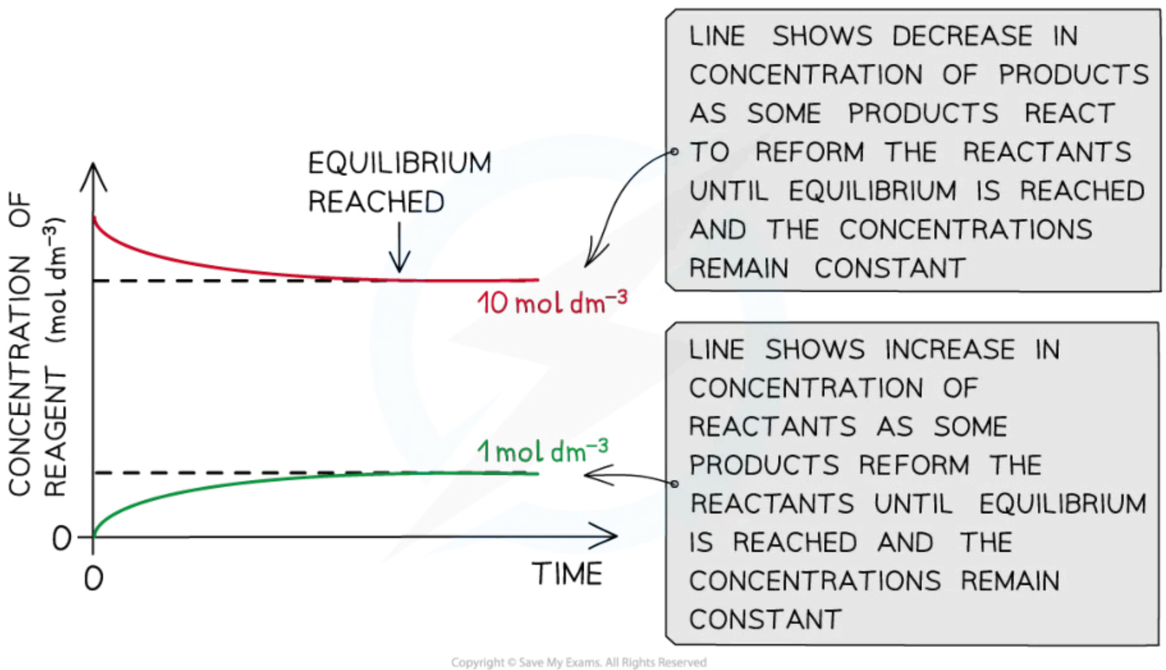
The diagram shows a snapshot of a dynamic equilibrium in which molecules of hydrogen iodide are breaking down to hydrogen and iodine at the same rate as hydrogen and iodine molecules are reacting together to form hydrogen iodide

Graph of concentration against time



The diagram shows that the concentration of the reactants and products does not change anymore once equilibrium has been reached (equilibrium was approached using reactants)

Graph of concentration against time



The same equilibrium can be approached starting with the products

Examiner Tip

- Dynamic equilibrium can also be established in physical systems, for example, in a bottle of ethanol
  - Some liquid ethanol will evaporate and some ethanol vapour will condense
  - An equilibrium exists between the two phases as the rate of evaporation = the rate of condensation.

$$C_2H_5OH\ (l) \rightleftharpoons C_2H_5OH\ (g)$$

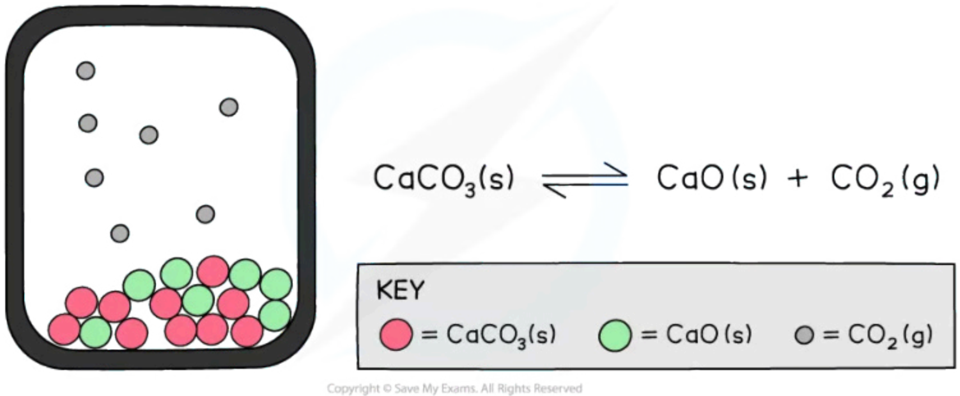
What is a closed system?

- A **closed system** is one in which none of the reactants or products escape from the reaction mixture
- In an **open system** some matter is lost to the surroundings
- When a reaction takes place entirely in solution, equilibrium can be reached in open flasks
- If the reaction involves gas, equilibrium can only be reached in a closed system

A closed system

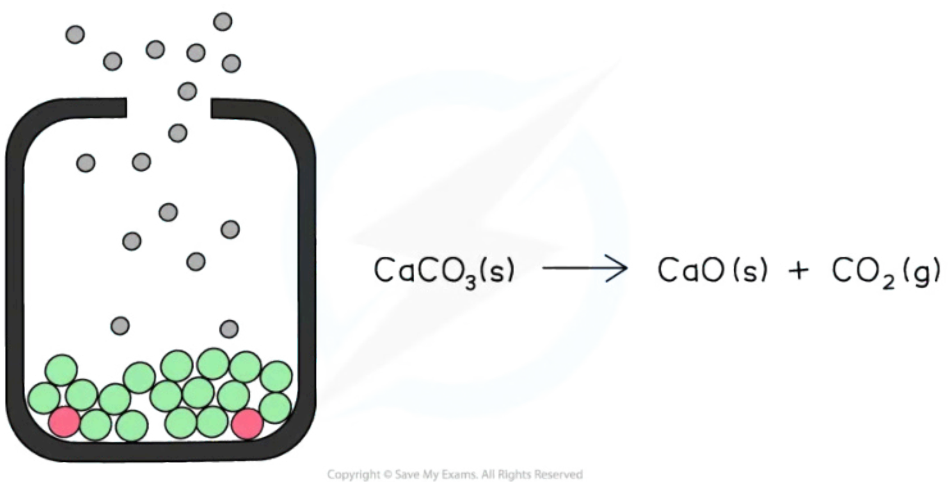
Your notes

Your notes



The diagram shows a closed system in which no carbon dioxide gas can escape and the calcium carbonate is in equilibrium with the calcium oxide and carbon dioxide

An open system



The diagram shows an open system in which the calcium carbonate is continually decomposing as the carbon dioxide is lost causing the reaction to eventually go to completion

Examiner Tip

- A common misconception is to think that the concentrations of the reactants and products are **equal**, however, they are **not** equal but **constant** (the concentrations are not changing)
  - Stating that the concentrations are equal will lose a mark in an exam
- The dynamic equilibrium can be reached by starting either with the reactants or products
  - In both cases, the concentrations of the reactants and products remain constant once dynamic equilibrium has been reached

The Equilibrium Law

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The Equilibrium Law

- **Equilibrium law** explains how the **equilibrium constant, *K*,** can be found from the stoichiometry of the reaction

The equilibrium constant equation

- The **equilibrium constant expression** is an expression that links the **equilibrium constant**, ***K***, to the **concentrations of reactants and products** at equilibrium taking the **stoichiometry** of the equation into account
- So, for a given reaction:

$$aA + bB \rightleftharpoons cC + dD$$

- The corresponding **equilibrium constant expression** is written as:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

  - Where:
    - [A] and [B] = equilibrium reactant concentrations (mol dm^{-3})
    - [C] and [D] = equilibrium product concentrations (mol dm^{-3})
    - a, b, c and d = number of moles of corresponding reactants and products
- **Solids** are ignored in equilibrium constant expressions
- The equilibrium constant, *K*, of a reaction is specific to a given equation

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Worked example

Deduce the equilibrium constant expression for the following reactions

1. $Ag^+ (aq) + Fe^{2+} (aq) \rightleftharpoons Ag (s) + Fe^{3+} (aq)$
2. $N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$
3. $2SO_2 (g) + O_2 (g) \rightleftharpoons 2SO_3 (g)$

Answer 1:

$$K = \frac{[Fe^{3+}(aq)]}{[Fe^{2+}(aq)][Ag^+(aq)]}$$

- [Ag (s)] is not included in the equilibrium constant expression as it is a solid

Answer 2:

$$K = \frac{[NH_3(g)]}{[N_2(g)][H_2(g)]^3}$$

Answer 3:

$$K = \frac{[SO_3(g)]^2}{[SO_2(g)]^2[O_2(g)]}$$

Examiner Tip

- You must use square brackets in equilibrium constant expressions as they have a specific meaning, representing concentrations
- In an exam answer, you would lose the mark if you used round brackets.

The Equilibrium Constant

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The Equilibrium Constant

The equilibrium constant, *K*

- The size of the equilibrium constant, *K*, tells us how the equilibrium mixture is made up with respect to reactants and products

$$K = \frac{[\text{ products }]_{eqm}}{[\text{ reactants }]_{eqm}}$$

- If ***K* > 1**, the concentration of products is **greater** than the concentration of reactants and we say that the equilibrium lies to the **right hand** side
  - When ***K* >> 1**, equilibrium lies far over to the right hand side and the reaction almost goes to completion
- If ***K* < 1**, then the concentration of reactants is **greater** than the concentration of products and we say that the equilibrium lies to **the left hand** side
  - When ***K* << 1**, equilibrium lies far over to the left hand side and the reaction hardly proceeds
- When ***K* = 1**, at equilibrium, there are significant amounts of both reactants and products and equilibrium does not lie in favour of either the reactants or products
- ***K*** is a constant at a specified temperature
- Since temperature can affect the position of equilibrium, it follows that ***K*** is dependent on temperature

Your notes

Worked example

When the following reactions reach equilibrium, state whether the equilibrium mixture contains mostly reactants or products. Assume the value of *K* corresponds to the temperature of the reaction mixture

1. $Ag^{+} (aq) + Fe^{2+} (aq) \rightleftharpoons Ag (s) + Fe^{3+} (aq)$ $\quad K = 7.3 \times 10^{-26}$
2. $N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$ $\quad K = 2.6 \times 10^{-18}$
3. $2SO_2 (g) + O_2 (g) \rightleftharpoons 2SO_3 (g)$ $\quad K = 5.0 \times 10^{13}$

Answer:

- **Reactions 1 and 2**:
  - *K* is very much smaller than 1
  - So, the denominator in the equilibrium constant expression must be much larger than the numerator
  - This means that the concentration of the reactants is much larger than the concentration of products
  - Therefore, the equilibrium lies far to the left and the equilibrium mixture contains **mostly reactants**

- **Reaction 3**:
  - *K* is very much larger than 1
  - So, the numerator in the equilibrium constant expression must be much larger than the denominator
  - This means that the concentration of the products is much larger than the concentration of reactants
  - Therefore, the equilibrium lies to the right-hand side and the reaction mixture contains **mostly products**

Examiner Tip

- Stronger acids dissociate more than weaker acids in solution, meaning that equilibrium lies towards the products
- So, stronger acids will have a higher value of *K* than weaker acids.

The relationship between *K* values for reactions that are the reverse of each other

- The equilibrium constant expression is dependent on a specific reaction
- For example, take the reaction between nitrogen and hydrogen to make ammonia:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

- The **equilibrium constant expression** for this reaction is:

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$$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

- If we reverse the equation:

$$2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$$

- The equilibrium constant expression for the **reverse** of this reaction, *K'*, is:

$$K' = \frac{[N_2][H_2]^3}{[NH_3]^2}$$

- What is the relationship between these two *K* values? At the same temperature, *K'* becomes the reciprocal of the original K value:

$$K' = \frac{1}{K} \text{ or } K' = K^{-1}$$

Worked example

The equilibrium constant for the following reaction is 7.1×10^{32}.

$$2NO_2\,(g) + F_2\,(g) \rightleftharpoons 2NO_2F\,(g)$$

What is the equilibrium constant for the reverse at the same temperature?

Answer:

- $K_{(\text{reverse})} = \frac{1}{K_{(\text{forward})}} = \frac{1}{7.1 \times 10^{32}} = \mathbf{1.41 \times 10^{-33}}$

Le Chatelier's Principle

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Le Chatelier's Principle

Position of equilibrium

- The **position of the equilibrium** refers to the relative amounts of products and reactants in an equilibrium mixture.
- When the position of equilibrium shifts to the **left**, it means the concentration of **reactants** increases
- When the position of equilibrium shifts to the **right**, it means the concentration of **products** increases

Le Chatelier's principle

- **Le Chatelier's principle** says that if a change is made to a system at dynamic equilibrium, the position of the equilibrium moves to minimise this change
- The principle is used to predict changes to the position of equilibrium when there are changes in temperature, pressure or concentration

Effects of concentration on the position of equilibrium

- When the concentration of a reactant increases, the rate of the forward reaction increases and the system is no longer in equilibrium
- When a new equilibrium is established, there will be more product and less reactant within the reaction mixture, so the equilibrium has shifted to the right
- This shift has reduced the effect of the increase by removing some of the reactant

Effects of Concentration Table

Change	How the equilibrium shifts
Increase in concentration of a reactant	Equilibrium shifts to the **right** to reduce the effect of an increase in the concentration of a reactant
Decrease in concentration of a reactant	Equilibrium shifts to the **left** to reduce the effect of a decrease in the concentration of a reactant
Increase in concentration of a product	Equilibrium shifts to the **left** to reduce the effect of an increase in the concentration of a product
Decrease in concentration of a product	Equilibrium shifts to the **right** to reduce the effect of a decrease in the concentration of a product

Effects of concentration of the value of *K*

Your notes

- If all other conditions stay the same, the equilibrium constant *K* is **not affected** by any changes in concentration of the reactants or products
- For example, the decomposition of hydrogen iodide:

$$2HI \rightleftharpoons H_2 + I_2$$

- The equilibrium expression is:

$$K = \frac{[H_2][I_2]}{[HI]^2} = 6.25 \times 10^{-3}$$

- Adding more HI makes the ratio of [products] to [reactants] smaller
- To restore equilibrium, $[H_2]$ and $[I_2]$ increases and [HI] decreases
- Equilibrium is restored when the ratio is 6.25×10^{-3} again

Your notes

Worked example

1. Using the reaction below:

$$CH_3COOH\ (l) + C_2H_5OH\ (l) \rightleftharpoons CH_3COOC_2H_5\ (l) + H_2O\ (l)$$

Explain what happens to the position of equilibrium when:

a. More $CH_3COOC_2H_5$ (l) is added
b. Some C_2H_5OH (l) is removed

2. Use the reaction below:

$$Ce^{4+}\ (aq) + Fe^{2+}\ (aq) \rightleftharpoons Ce^{3+}\ (aq) + Fe^{3+}\ (aq)$$

Explain what happens to the position of equilibrium when water is added to the equilibrium mixture

Answer 1a:

- The position of the equilibrium moves to the left and more ethanoic acid and ethanol are formed
- The reaction moves in this direction to oppose the effect of added ethyl ethanoate, so the ethyl ethanoate decreases in concentration

Answer 1b:

- The position of the equilibrium moves to the left and more ethanoic acid and ethanol are formed
- The reaction moves in this direction to oppose the removal of ethanol so more ethanol (and ethanoic acid) are formed from ethyl ethanoate and water

Answer 2:

- There is no effect as the water dilutes all the ions equally so there is no change in the ratio of reactants to products

Effects of pressure on the position of equilibrium

- Changes in pressure only affect reactions where the reactants or products are gases
- The pressure of a gas in a fixed volume increases as the number of gas molecules increases
- Changes in pressure will cause the equilibrium to shift to reduce the effect of this change

Effects of Pressure Table

Change	How the equilibrium shifts

Increase in pressure	Equilibrium shifts in the direction that produces the **smaller** number of molecules of gas to decrease the pressure again
Decrease in pressure	Equilibrium shifts in the direction that produces the **larger** number of molecules of gas to increase the pressure again

Effects of pressure on the value of *K*

- If all other conditions stay the same, the equilibrium constant K is **not affected** by any changes in pressure of the reactants and products

Examiner Tip

- If there are the same number of gas molecules on either side of the reaction, changes in pressure will not change the position of equilibrium

Your notes

Your notes

Worked example

Predict the effect of increasing the pressure on the following reactions:

1. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

2. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

Predict the effect of decreasing the pressure on the following reaction:

3. $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$

Answer 1:

- The equilibrium shifts to the left as there are fewer gas molecules on the left
- This causes a decrease in pressure

Answer 2:

- The equilibrium shifts to the left as there are no gas molecules on the left but there is CO_2 on the right
- This causes a decrease in pressure

Answer 3:

- The equilibrium shifts to the right as there is a greater number of gas molecules on the right
- This causes an increase in pressure

Effects of temperature on the position of equilibrium

- When the temperature changes, the equilibrium will respond by moving in the direction which will absorb or release energy

Effects of Temperature Table

Change	How the equilibrium shifts
Increase in temperature	Equilibrium shifts in the **endothermic** direction, absorbing energy to reverse the change
Decrease in temperature	Equilibrium shifts in the **exothermic** direction, releasing energy to reverse the change

Effects of temperature on the value of *K*

Your notes

- Changes in temperature **change** the equilibrium constant *K*
- For an endothermic reaction such as:

$$2HI (g) \rightleftharpoons H_2 (g) + I_2 (g) \qquad K = \frac{[H_2][I_2]}{[HI]^2}$$

- An increase in temperature:
  - $[H_2]$ and $[I_2]$ **increases**
  - [HI] **decreases**
- Because $[H_2]$ and $[I_2]$ are **increasing** and [HI] is **decreasing**, the equilibrium constant *K* **increases**

- For an exothermic reaction such as:

$$2SO2 (g) + O_2 (g) \rightleftharpoons 2SO_3 (g) \qquad K = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

- An increase in temperature:
  - $[SO_3]$ **decreases**
  - $[SO_2]$ and $[O_2]$ **increases**
- Because $[SO_3]$ **decreases** and $[SO_2]$ and $[O_2]$ **increases** the equilibrium constant *K* **decreases**

Your notes

Worked example

1. Using the reaction below:

$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g) \qquad \Delta H = +41.2 \text{ kJ mol}^{-1}$

Predict the effect of increasing the temperature on this reaction

2. Using the reaction below:

$Ag_2CO_3(s) \rightleftharpoons Ag_2O(s) + CO_2(g)$

Increasing the temperature increases the amount of CO_2(g) at constant pressure. Is this reaction exothermic or endothermic? Explain your answer.

Answer 1:

- The reaction will absorb the excess heat and since the forward reaction is endothermic, the equilibrium will shift to the right

Answer 2:

- The reaction will absorb the excess heat and since this causes a shift of the equilibrium towards the right (as more CO_2(g) is formed) this means that the reaction is endothermic (because endothermic reactions favour the products)

Effects of catalysts

- A catalyst is a substance that increases the rate of a chemical reaction (they increase the rate of the **forward** and **reverse** reaction **equally**)
- Catalysts only cause a reaction to reach its equilibrium **faster**
- Catalysts therefore have **no effect** on the **position of the equilibrium** or on the value of ***K***

Your notes

Examiner Tip

- When conditions of industrial processes are chosen, Le Chatelier's principle can be used to predict the conditions that would cause the equilibrium to lie towards the products, giving a high equilibrium yield
- However, the kinetics of the reaction must also be considered as the rate of reaction needs to be sufficiently fast.
- For example, consider a reversible reaction whose forward reaction is exothermic
  - According to Le Chatelier's principle, lower temperatures would produce a higher equilibrium yield
  - However, higher temperatures will give a faster rate of reaction
  - A compromise temperature is used which gives a **lower yield** of product but is made more quickly

Heterogeneous equilibria

- Le Chatelier's principle can also be applied to heterogeneous equilibria
- For example, in a fizzy drink bottle, an equilibrium exists between the dissolved CO_2 and gaseous CO_2:

$$\mathbf{CO_2\,(g) \rightleftharpoons CO_2\,(aq)}$$

- When the bottle is opened, some CO_2 (g) escapes, the equilibrium shifts to the left to reduce the effect of this change and bubbles of CO_2 (g) are observed

Your notes

The Reaction Quotient (HL)

The Reaction Quotient

What is the reaction quotient?

- The **reaction quotient**, **Q**, is calculated using the same equation as the equilibrium constant expression, but with non-equilibrium concentrations of reactants and products
- The expression for **Q** is therefore the same as ***K***

For more information on the equilibrium constant expression, see our revision notes on The Equilibrium Law

- It is a useful concept because the size of **Q** can tell us how far a reaction is from equilibrium and in which direction the reaction proceeds
- For example,
  - If **Q = *K*** then the reaction is **at equilibrium**, no net reaction occurs
  - If **Q < *K*** the reaction **proceeds to the right** in favour of the products
  - If **Q > *K*** the reaction **proceeds to the left** in favour of the reactants
- Using concentration values of the substances present, we can work out if a reaction is at equilibrium or not, as the following example shows:

Your notes

Worked example

The equilibrium constant for the reaction below is 5.1 x 10^{-2} at 298 K.

$$COI_2\,(g) \rightleftharpoons CO\,(g) + I_2\,(g)$$

Deduce whether the following reaction mixture concentrations represent a reaction at equilibrium and for those not at equilibrium indicate the direction is proceeding.

Reaction mixture	[COI_2 (g)]	[CO (g)]	[I_2 (g)]
1	0.012	0.050	0.050
2	0.020	0.032	0.032
3	0.150	0.025	0.025

Answer:

- The reaction quotient expression is:

$$Q = \frac{[CO\ (g)][I_2\ (g)]}{[COI_2\ (g)]}$$

- **For reaction mixture 1:**

$$Q = \frac{0.050 \times 0.050}{0.012} = 0.21$$

  - In this mixture Q **>>** ***K***, so Q has to decrease to reach *K*
  - This means the reaction must be moving to the left, in order to reach equilibrium, so the reactants are favoured

- **For reaction mixture 2:**

$$Q = \frac{0.032 \times 0.032}{0.020} = 0.051$$

  - In this mixture, the value of **Q** = ***K***, so the reaction is at equilibrium

- **For reaction mixture 3:**

$$Q = \frac{0.025 \times 0.025}{0.150} = 0.0042$$

- In this mixture ***Q* < *K***, so Q has to increase to reach *K*
- This means the reaction must be moving to the right, in order to reach equilibrium, so the products are favoured

Your notes

Examiner Tip

The value of Q is not a fixed value as it can be measured at any time but the value of *K* is constant at a given temperature.

Your notes

Equilibrium Law Problem Solving (HL)

Equilibrium Law Problem Solving

Calculations involving *K*

- In the equilibrium expression, each term inside a square bracket represents the concentration of that chemical in mol dm^{-3}
- Some questions give the number of moles of each of the reactants and products at equilibrium together with the volume of the reaction mixture
- The concentrations of the reactants and products can then be calculated from the number of moles and total volume, using the equation:

$$\text{concentration} \quad (\text{mol dm}^{-3}) = \frac{\text{amount of substance} \quad (\text{mol})}{\text{volume} \ (\text{dm}^3)}$$

Your notes

Worked example

Calculating *K* of ethanoic acid

Ethanoic acid and ethanol react to form the ester ethyl ethanoate and water as follows:

$$CH_3COOH\ (l) + C_2H_5OH\ (l) \rightleftharpoons CH_3COOC_2H_5\ (l) + H_2O\ (l)$$

At equilibrium, 500 cm^3 of the reaction mixture contained 0.235 mol of ethanoic acid and 0.035 mol of ethanol together with 0.182 mol of ethyl ethanoate and 0.182 mol of water.

Use this data to calculate a value of *K* for this reaction.

Answer:

- **Step 1:** Calculate the concentrations of the reactants and products:

$$[CH_3COOH\ (l)] = \frac{0.235}{0.500} = 0.470\ mol\ dm^{-3}$$

$$[C_2H_5OH\ (l)] = \frac{0.035}{0.500} = 0.070\ mol\ dm^{-3}$$

$$[CH_3COOC_2H_5\ (l)] = \frac{0.182}{0.500} = 0.364\ mol\ dm^{-3}$$

$$[H_2O\ (l)] = \frac{0.182}{0.500} = 0.364\ mol\ dm^{-3}$$

- **Step 2:** Write out the balanced symbol equation with the concentrations of each chemical underneath:

CH_3COOH (l)	+	C_2H_5OH (l)	$\rightleftharpoons$	$CH_3COOC_2H_5$ (l)	+	H_2O (l)
0.470 mol dm^{-3}		0.070 mol dm^{-3}		0.364 mol dm^{-3}		0.364 mol dm^{-3}

- **Step 3:** Write out the equilibrium constant for the reaction:

$$K = \frac{[H_2O][CH_3COOC_2H_5]}{[C_2H_5OH][CH_3COOH]}$$

- **Step 4:** Substitute the equilibrium concentrations into the expression and calculate the answer:

$$K = \frac{0.364 \times 0.364}{0.070 \times 0.470} = \mathbf{4.03}$$

- **Note:** The smallest number of significant figures used in the question is 3, so the final answer should also be given to 3 significant figures

Your notes

ICE tables

- Some questions do not give the initial and equilibrium concentrations of all of the reactants and products
- An initial, change and equilibrium (ICE) table should be used to determine the equilibrium concentration of the remaining reactants and products using the molar ratio in the stoichiometric equation
- **Step 1** in the worked example below shows how to use an ICE table to find the equilibrium concentrations

Your notes

Worked example

Calculating *K* of ethyl ethanoate

Ethyl ethanoate is hydrolysed by water:

$$CH_3COOC_2H_5\ (l) + H_2O\ (l) \rightleftharpoons CH_3COOH\ (l) + C_2H_5OH\ (l)$$

0.1000 mol of ethyl ethanoate is added to 0.1000 mol of water. A little acid catalyst is added and the mixture is made up to 1 dm^3. At equilibrium 0.0654 mol of water are present. Use this data to calculate a value of *K* for this reaction.

Answer:

- **Step 1:** Complete the ICE table for the reaction:
  - Write out the balanced chemical equation with the number of moles of each substance given in the question beneath using an initial, change and equilibrium table:
  - Calculate the change in moles of water and add to the table (an increase is shown by + and a decrease is shown by -)
    - Equilibrium amount = Initial amount + Change in amount
    - 0.0654 = 0.100 + Change in amount
    - Change in amount = 0.0654 - 0.100 = -0.0346
  - Use the stoichiometry of the equation to calculate the change in amounts of the remaining reactants/products and add to the table
    - There is a 1 : 1 reacting ratio between H_2O and all other reactants/products
    - As H_2O has **decreased** by 0.0346 mol, the other reactant $CH_3COOC_2H_5$ will **decrease** by 0.0346 mol
    - Since CH_3COOH and C_2H_5OH are products, they will both **increase** by 0.0346 mol
  - Calculate the number of moles at equilibrium of the remaining reactants / products to complete the table
    - Equilibrium amount = Initial amount + Change in amount
    - Equilibrium amount of $CH_3COOC_2H_5$ = 0.100 + (-0.0346) = 0.0654 mol
    - Equilibrium amount of CH_3COOH = 0.000 + 0.0346 = 0.0346 mol
    - Equilibrium amount of C_2H_5OH = 0.000 + 0.0346 = 0.0346 mol

	$CH_3COOC_2H_5$ (l) +	H_2O (l) ⇌	CH_3COOH (l) +	C_2H_5OH (l)
Initial moles	0.100	0.100	0.000	0.000
Change	-0.0346	-0.0346	+0.0346	+0.0346
Equilibrium moles	**0.0654**	0.0654	**0.0346**	**0.0346**

- **Step 2:** Calculate the concentrations of the reactants and products:

Your notes

$[CH_3COOH (l)] = \frac{0.0654}{1.000} =$ 0.0654 mol dm^{-3}

$[C_2H_5OH (l)] = \frac{0.0654}{1.000} =$ 0.0654 mol dm^{-3}

$[CH_3COOC_2H_5 (l)] = \frac{0.0346}{1.000} =$ 0.0346 mol dm^{-3}

$[H_2O (l)] = \frac{0.0346}{1.000} =$ 0.0346 mol dm^{-3}

- **Step 3**: Write the equilibrium constant for this reaction in terms of concentration:

$$K = \frac{[C_2H_5OH][CH_3COOH]}{[H_2O][CH_3COOC_2H_5]}$$

- **Step 4:** Substitute the equilibrium concentrations into the expression:

$$K = \frac{0.0346 \times 0.0346}{0.0654 \times 0.0654} = \mathbf{0.280}$$

Examiner Tip

- For reactions which have the same number of concentration terms in both the numerator and denominator in their equilibrium constant expression, such as the reaction in the worked example above, you do not need to know the volume to be able to calculate *K*.
- As concentration = moles ÷ volume, the volume terms will cancel in the *K* expression, and *K* can be calculated directly from the number of moles of reactants and products at equilibrium:

$$K = \frac{\left(\frac{mol_C}{\cancel{V}}\right)\left(\frac{mol_D}{\cancel{V}}\right)}{\left(\frac{mol_A}{\cancel{V}}\right)\left(\frac{mol_B}{\cancel{V}}\right)} = \frac{mol_C \times mol_D}{mol_A \times mol_B}$$

Calculating *K* when *K* is very small

- When $K < 10^{-3}$, the reaction lies far to the left and the equilibrium mixture contains mainly reactants
- The change from the initial amount of reactant to the equilibrium amount is close to zero

- The initial amount of reactant and the equilibrium amount of reactants are approximately the same
- Therefore the following approximation can also be made:

$$\textbf{[reactant]}_{\textbf{initial}} \approx \textbf{[reactant]}_{\textbf{equilibrium}}$$

- This approximation can be used in calculations involving *K*

Your notes

Your notes

Worked example

Ammonia decomposes to produce hydrogen and nitrogen. At 450 K, the equilibrium constant, *K*, for the reaction is 3.85 x 10^{-4}.

$$2NH_3 (g) \rightleftharpoons 3H_2 (g) + N_2 (g)$$

A reaction is set up at 450 K, where the initial concentration of ammonia is 0.20 mol dm^{-3}. Calculate the concentration of hydrogen at equilibrium.

Answer:

- Complete an ICE table. As the change in concentration is unknown, we can use algebra to find the equilibrium concentrations:
  - Assign the changes in concentration according to the stoichiometry of the reaction:
    - Change in concentration of NH_3 = $-2X$
    - Change in concentration of $3H_2$ = $+3X$
    - Change in concentration of N_2 = $+X$

	$2NH_3$ (g) ⇌	$3H_2$ (g) +	N_2 (g)
Initial (mol dm^{-3})	0.20	0.00	0.00
Change (mol dm^{-3})	$-2X$	$+3X$	$+X$
Equilibrium (mol dm^{-3})	$0.20 - 2X$ ≈ 0.20	$3X$	X

- As *K* is small, the change in concentration is small and $0.20 \gg 2X$, so the assumption $0.20 - 2X \approx 0.20$ is justified
- Write the expression for *K* and substitute in the equilibrium concentration:

$$K = \frac{[H_2]^3[N_2]}{[NH_3]^2} = \frac{(3x)^2 x}{(0.20)^2} = 3.85 \times 10^{-4}$$

- Rearrange to give X:

$$9X^3 = 3.85 \times 10^{-4} \times (0.20)^2$$

$$X = 1.196 \times 10^{-2}$$

- Calculate the equilibrium concentration of H_2:

$$[H_2]_{equilibrium} = 3X = \mathbf{3.6 \times 10^{-2}\ mol\ dm^{-3}}$$

Examiner Tip

When using this method, you must state in your answer the approximation that you have made and why you have been able to use it, i.e. because $K < 10^{-3}$.

Your notes

Your notes

The Equilibrium Constant & Gibbs Energy (HL)

The Equilibrium Constant & Gibbs Energy

How is Gibbs energy related to the equilibrium constant?

- The equilibrium constant, *K*, gives no information about the individual rates of reaction
  - It is independent of the kinetics of the reaction
- The equilibrium constant, *K*, is directly related to the Gibbs energy change, $\Delta G^{\ominus}$, according to the following Gibbs energy equation:

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

  - $\Delta G^{\ominus}$ = Gibbs energy change ($kJ\ mol^{-1}$)
  - R = gas constant ($8.31\ J\ K^{-1}\ mol^{-1}$)
  - T = temperature (Kelvin, K)
  - K = equilibrium constant
- This equation is provided in section 1 of the data booklet

- This relationship between the equilibrium constant, *K*, and Gibbs energy change, $\Delta G^{\ominus}$, can be used to determine whether the forward or backward reaction is favoured

The relationship between the equilibrium constant, K, and Gibbs energy change, ΔG

Equilibirum constant, *K*	Description	Gibbs energy change, ΔG
$K > 1$	Products favoured	$\Delta G < 0$ (negative)
$K = 1$	Reaction at equilibirum Neither reactants nor products are favoured	$\Delta G = 0$
$K < 1$	Reactants favoured	$\Delta G > 0$ (positive)

- At a given temperature, a **negative** ΔG value for a reaction indicates that:
  - The reaction is feasible / **spontaneous**
  - The equilibrium concentration of the products is greater than the equilibrium concentration of the reactants
  - The value of the equilibrium constant is greater than 1
- As ΔG becomes **more negative**:
  - The **forward** reaction is favoured more

- The value of the equilibrium constant **increases**

Examiner Tip

- When completing calculations using the $\Delta G^{\ominus} = -RT\ln K$ equation, you have to be aware that:
  - $\Delta G^{\ominus}$ is measured in **kJ** mol^{-1}
  - R is measured in **J** K^{-1} mol^{-1}
- This means that one of these values will need adjusting by a factor of 1000
- Gibbs energy is also referred to as 'Gibbs free energy', or just 'free energy'

Your notes

Free Energy & Equilibrium Calculations

- The relationship between Gibbs energy change, $\Delta G^{\ominus}$, temperature and the equilibrium constant, K, is described by the equation:

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

- The rearrangement of this equation makes it possible to:
  - Calculate the equilibrium constant
  - Deduce the position of equilibrium for the reaction

$$\ln K = -\frac{\Delta G}{RT}$$

Your notes

Worked example

Calculating *K*

Ethanoic acid and ethanol react to form the ester ethyl ethanoate and water as follows:

$$CH_3COOH\ (l) + C_2H_5OH\ (l) \rightleftharpoons CH_3COOC_2H_5\ (l) + H_2O\ (l)$$

At 25 °C, the free energy change, ΔG°, for the reaction is -4.38 kJ mol^{-1}. (R = 8.31 J K^{-1} mol^{-1})

1. Calculate the value of *K* for this reaction
2. Using your answer to part (1), predict and explain the position of the equilibrium

Answer 1:

- **Step 1:** Convert any necessary values
  - ΔG° into J mol^{-1}:
    - -4.38 x 1000 = -4380 J mol^{-1}
  - *T* into Kelvin
    - 25 + 273.15 = 298.15 K
- **Step 2:** Write the equation:
  - $\boldsymbol{\Delta G^{\circ} = -RT \ln K}$
- **Step 3:** Substitute the values:
  - -4380 = -8.31 x 298.15 x ln*K*
- **Step 4:** Rearrange and solve the equation for *K*:
  - ln *K* = -4380 ÷ (-8.31 x 298.15)
  - ln *K* = 1.7678
  - $K = e^{1.7678}$
  - *K* = 5.86

Answer 2:

- From part (1), the value of K_c is 5.86
- Therefore, the equilibrium lies to the right / products side because the value of *K* is positive