SL IB Chemistry

Your notes

How Far? The Extent of Chemical Change

Contents

The Characteristics of Dynamic Equilibrium

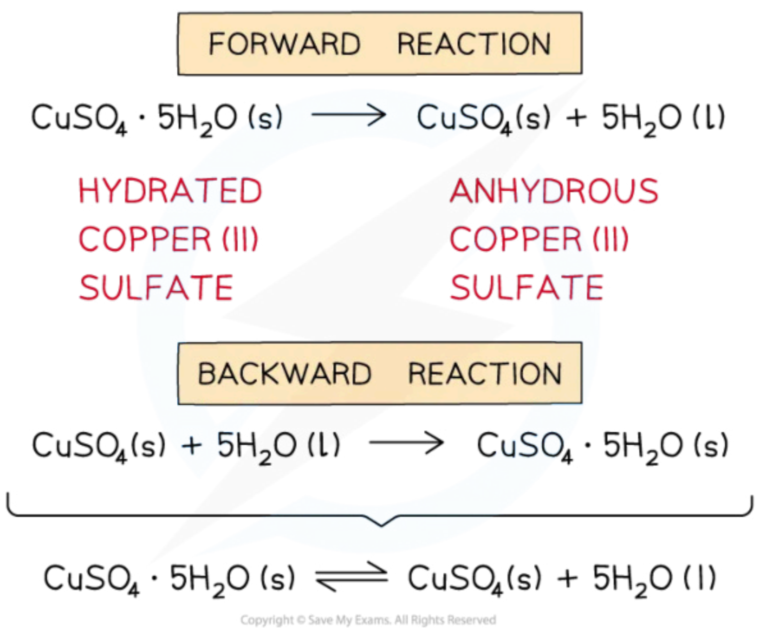
Your notes

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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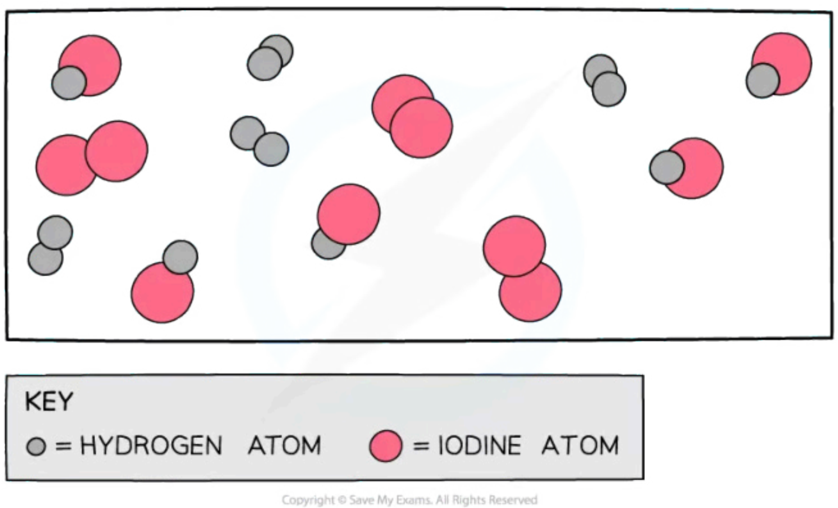
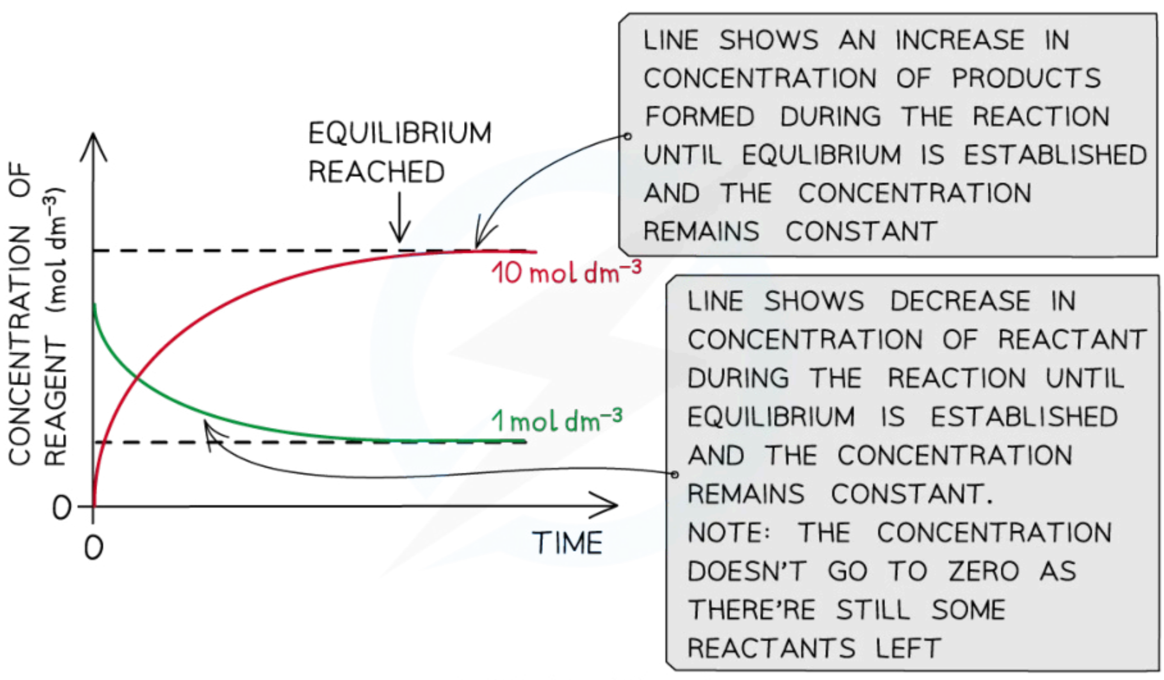
Dynamic equilibrium between hydrogen, iodine and hydrogen iodide



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



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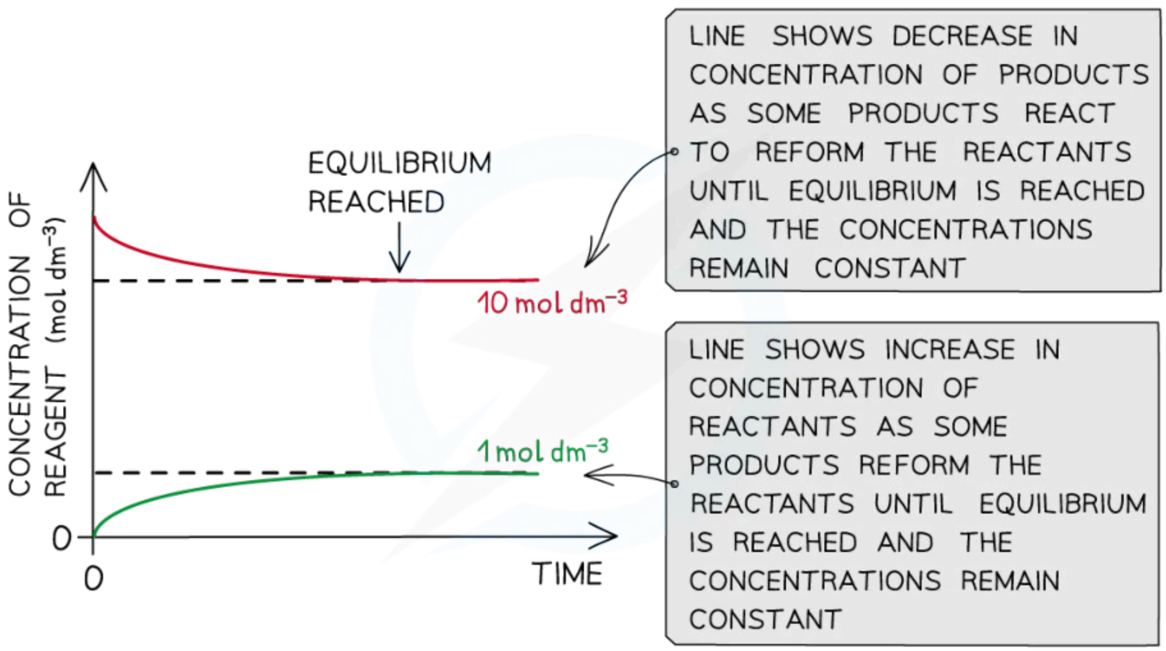
The diagram shows that the concentration of the reactants and products does not change anymore once equilibrium has been reached (equilibrium was approached using reactants)

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

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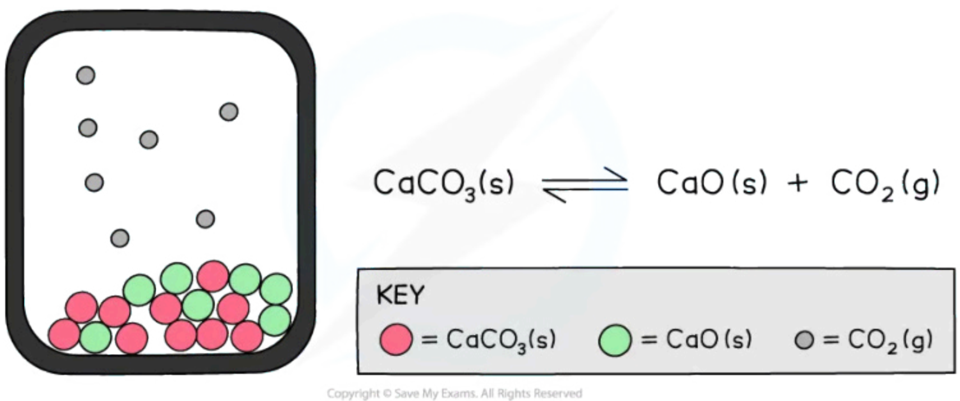
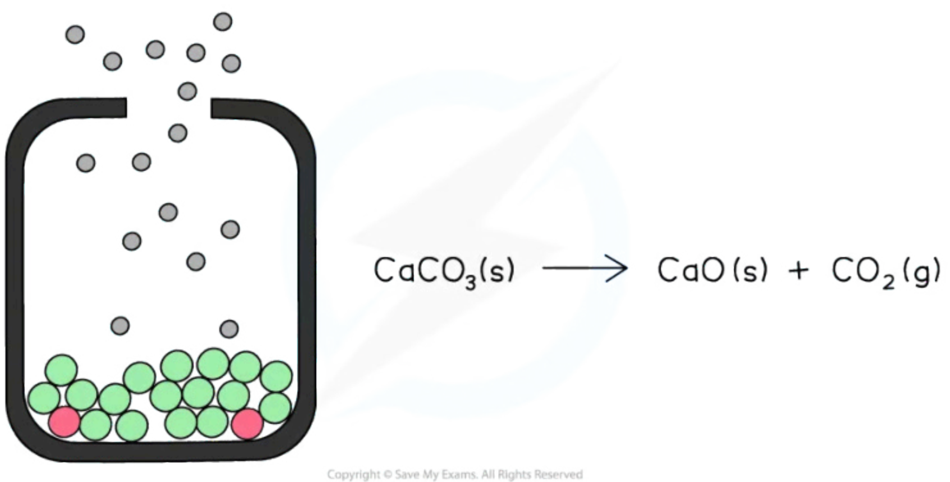


The diagram shows a closed system in which no carbon dioxide gas can escape and the calcium carbonate is in equilibrium with the calcium oxide and carbon dioxide

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

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.

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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

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

- 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

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

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*

- 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

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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

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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

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) ⇌ H_2 (g) + I_2 (g)

$$K = \frac{[H_2][I_2]}{[HI]^2}$$

- 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) ⇌ $2SO_3$ (g)

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

- 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***

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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