# DP IB Chemistry: HL

## 7.1 Equilibrium

Your notes

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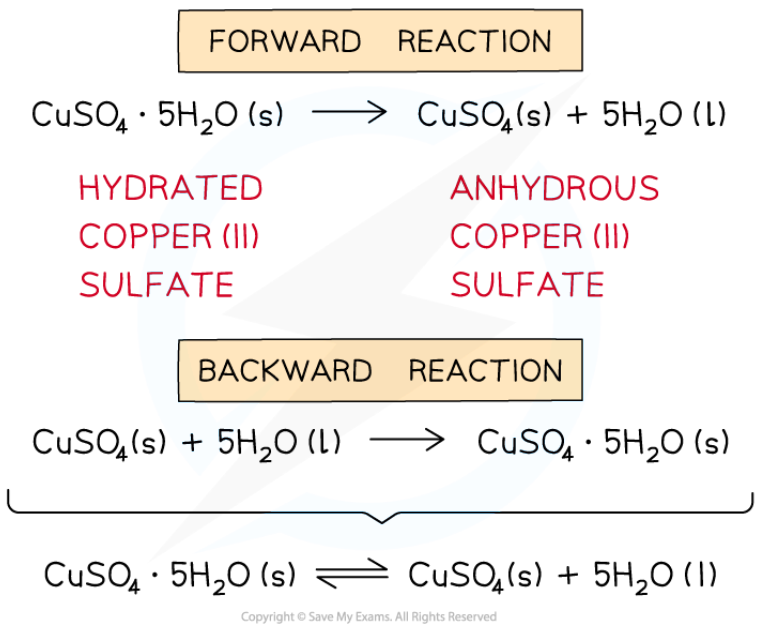
# 7.1.1 The State of Equilibrium

## The State of Equilibrium

### Reversible reaction

- 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: $\rightleftharpoons$




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

### 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** and the **concentrations** of the **reactants** and **products** is **constant**
- There is no change in **macroscopic properties** such as colour and density as they depend on concentration

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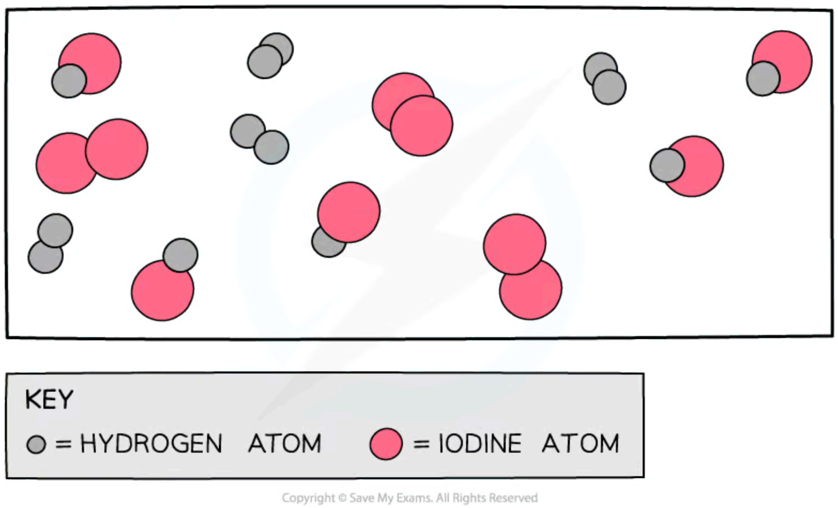
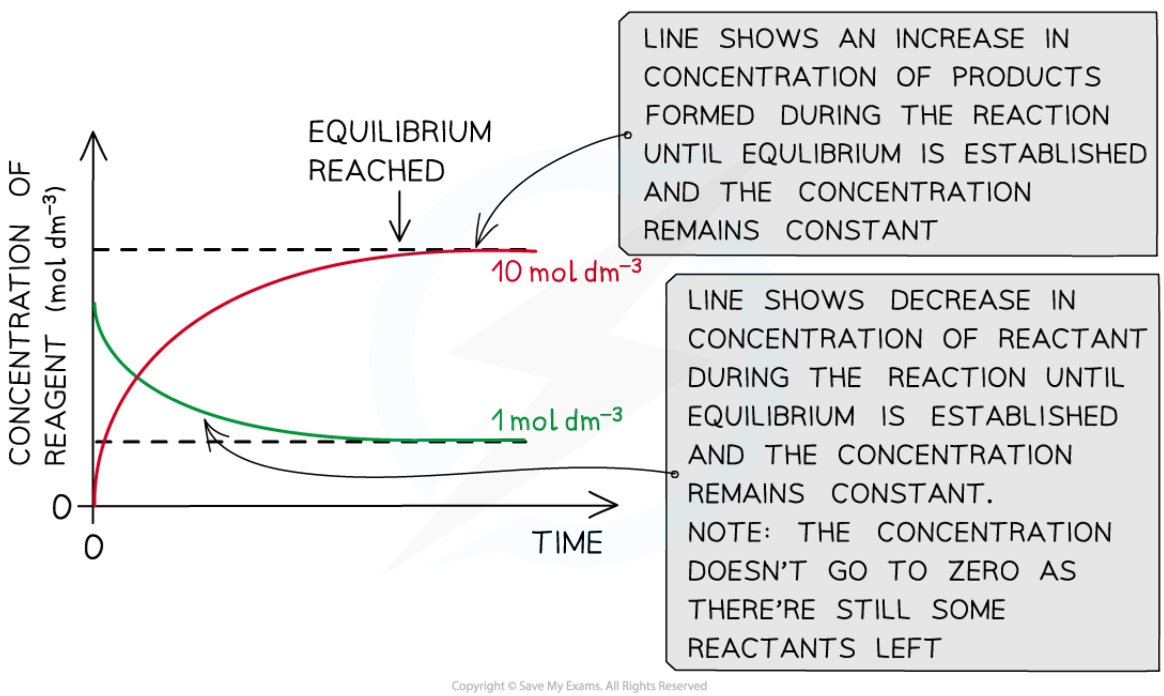



***The diagram shows a snapshot of a dynamic equilibrium in which molecules of hydrogen iodide are breaking down to hydrogen and iodine at the same rate as hydrogen and iodine molecules are reacting together to form hydrogen iodide***



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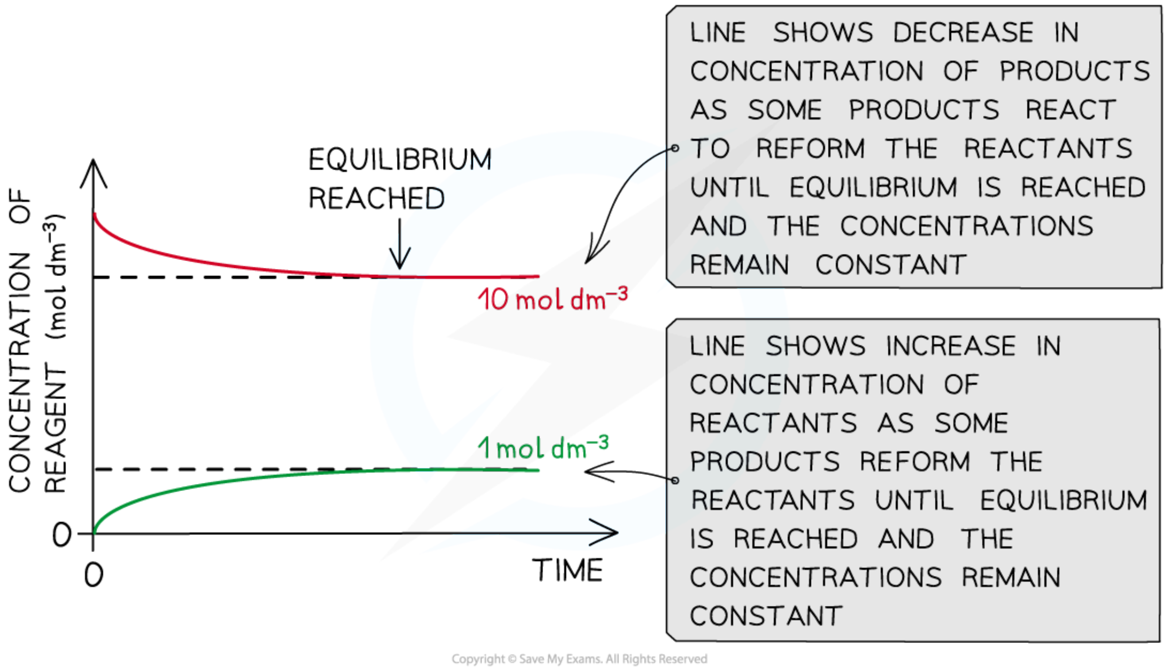
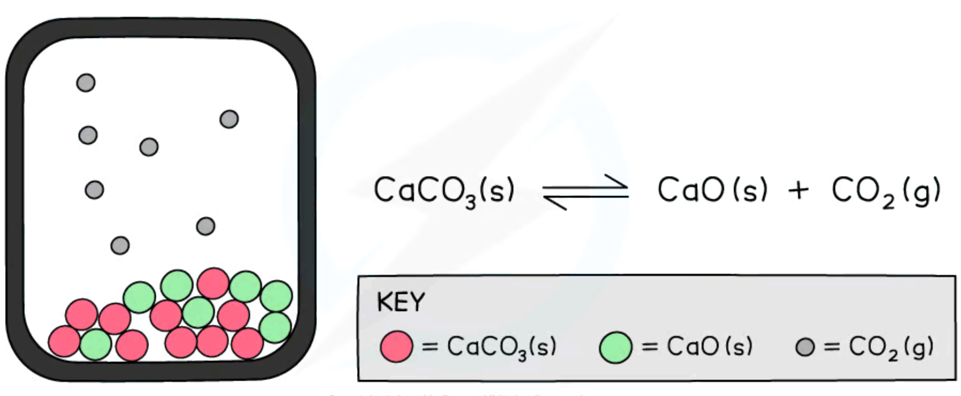
***The diagram shows that the concentration of the reactants and products does not change anymore once equilibrium has been reached (equilibrium was approached using reactants)***




***The same equilibrium can be approached starting with the products***

- 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



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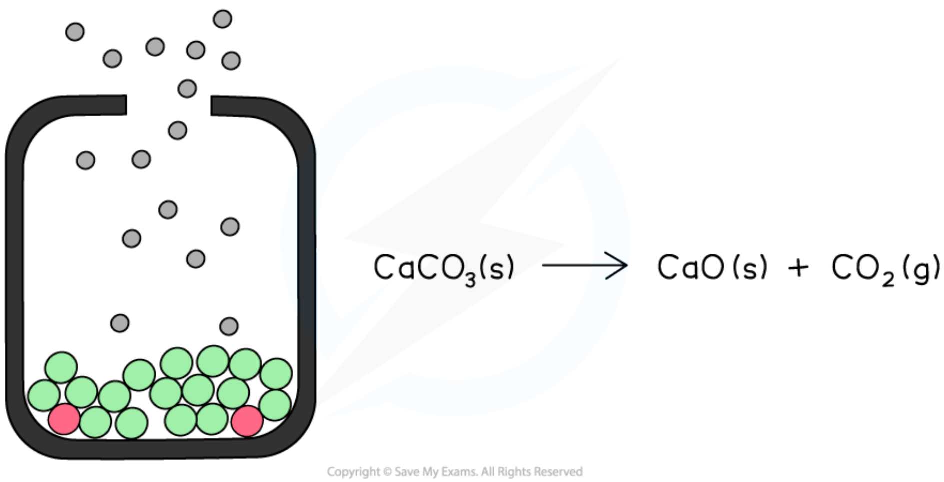
***The diagram shows a closed system in which no carbon dioxide gas can escape and the calcium carbonate is in equilibrium with the calcium oxide and carbon dioxide***




***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***

### Exam Tip

A common misconception is to think that the concentrations of the reactants and products is **equal**, however, they are **not** equal but **constant** (the concentrations are not changing).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.

## 7.1.2 The Equilibrium Law

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# The Equilibrium Constant

### Equilibrium expression & constant

- The **equilibrium expression** is an expression that links the **equilibrium constant**, $K_c$, 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 $K_c$ is expressed as follows:

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

[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 REACTANTS AND PRODUCTS



***Equilibrium expression linking the equilibrium concentration of reactants and products at equilibrium***

- **Solids** are ignored in equilibrium expressions
- The $K_c$ 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:**

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**Answer 1:**

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

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

**Answer 2:**

$$K_c = \frac{[NH_3(g)]^2}{[N_2(g)]\,[H_2(g)]^3}$$

**Answer 3:**

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

## The Size of Kc

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- The size of $K_c$ tells us how the equilibrium mixture is made up with respect to reactants and products

$$K_c = \frac{[PRODUCTS]_{eqm}}{[REACTANTS]_{eqm}}$$



- If $K_c > 1$, the concentration of products is **greater** than the concentration of reactants and we say that the equilibrium lies to the **right hand** side
- If $K_c < 1$, then the concentration of reactants is **greater** than the concentration of products and we say that the equilibrium lies to **the left hand** side
- $K_c$ is a constant at a specified temperature
- Since temperature can affect the position of equilibrium it follows that $K_c$ is dependent on temperature

### Worked example

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

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

**Answer:**

- 1 and 2: As $K_c$ is very much smaller than 1 the denominator in the equilibrium expression must be much larger than the numerator so the concentration of the reactants is much larger than the concentration of products. The equilibrium mixture contains **mostly reactants**
- 3: As $K_c$ is very much larger than 1 the numerator in the equilibrium expression must be much larger than the denominator so the concentration of the products is much larger than the concentration of reactants. The equilibrium mixture contains **mostly products**

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# 7.1.3 Equilibrium Constant Relationships

## Equilibrium Constant Relationships

- In the previous section we saw that the concentrations of the substances are raised to the **power of the coefficients** from the balanced equation
- This means the **$K_c$ expression** is dependent on a specific equation
- For example, take the reaction between nitrogen and hydrogen to make ammonia

$$\tfrac{1}{2}N_{2(g)} + 1\tfrac{1}{2}H_{2(g)} \rightleftharpoons NH_{3(g)}$$

- The **$K_c$ expression** for this reaction is:

$$K_c = \frac{[NH_3]}{[N_2]^{\frac{1}{2}}[H_2]^{\frac{3}{2}}}$$



- If you double the stoichiometry the equation becomes

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

- The new **$K_c$ expression** for this reaction is then:

$$\text{NEW } K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$



- What is the relationship between these two **$K_c$** values? You can probably see that when we double the coefficient the new **$K_c$** is the square of the original value:

$$\text{NEW } K_c = (\text{ORIGINAL } K_c)^2$$



- If we reverse the equation:

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

- $K_c$ becomes the reciprocal of the original $K_c$ value:

$$\text{REVERSE } K_c = \frac{[N_2][H_2]^3}{[NH_3]^2}$$

$$\text{REVERSE } K_c = \frac{1}{\text{ORIGINAL } K_c}$$



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- Test your understanding in the following example:

## Worked example

$K_c$ for $2NO_2\,(g) + F_2\,(g) \rightleftharpoons 2NO_2F\,(g)$ is $7.1 \times 10^{32}$What is $K_c$ for the following reaction, at the same temperature?

$NO_2F\,(g) \rightleftharpoons NO_2\,(g) + ½F_2\,(g)$

**A.** $7.1 \times 10^{32}$

**B.** $\frac{1}{\sqrt{7.1 \times 10^{32}}}$

**C.** $\frac{2}{7.1 \times 10^{32}}$

**D.** $\frac{1}{2 \times 7.1 \times 10^{32}}$

**Answer:**

The correct option is **B**.

- The original equation has been reversed and halved, so the $K_c$ value must be square rooted and inverted to obtain the reciprocal

### Exam 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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## 7.1.4 The Reaction Quotient

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### The Reaction Quotient

- The **reaction quotient**, **Q**, is the ratio of products and reactants for a reaction that has **NOT** yet reached equilibrium
- The expression for **Q** is very similar to **$K_c$**:

$$Q = \frac{[PRODUCTS]}{[REACTANTS]}$$



- 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 = Kc** then the reaction is **at equilibrium**, no net reaction occurs
  - If **Q < Kc** the reaction **proceeds to the right** in favour of the products
  - If **Q > Kc** the reaction **proceeds to the left** in favour of the reactants

- Using values of the concentrations of the substances present we can work out if a reaction is at equilibrium or not, as the following example shows:

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## Worked example

The equilibrium constant for the following reaction:

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

is $5.1 \times 10^{-2}$ at 298 K

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

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

**Reaction mixture 1:**

$$Q = \frac{[0.050]\ [\ 0.050]}{[\ 0.012]} = 0.21$$

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

**Reaction mixture 2:**

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$$Q = \frac{[0.032]\,[0.032]}{[0.020]} = 0.051$$

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

**Reaction mixture 3:**

$$Q = \frac{[0.025]\,[0.025]}{[0.150]} = 0.0042$$

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

## Exam Tip

The calculation of Q is not explicitly part of the SL course, just as calculating *Kc* values only comes in HL chemistry. However, a comparison of Q and *Kc* is relevant and the worked example is included only to illustrate how Q is determined from experimental data.

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# 7.1.5 Le Chatelier's Principle

## Le Chatelier's Principle

### Position of the 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

**Effects of Concentration Table**

| CHANGE | HOW THE EQUILIBRIUM SHIFTS |
|---|---|
| INCREASE IN CONCENTRATION | EQUILIBRIUM SHIFTS TO THE **RIGHT** TO REDUCE THE EFFECT OF INCREASE IN THE CONCENTRATION OF A REACTANT |
| DECREASE IN CONCENTRATION | EQUILIBRIUM SHIFTS TO THE **LEFT** TO REDUCE THE EFFECT OF A DECREASE IN REACTANT (OR AN INCREASE IN THE CONCENTRATION OF PRODUCT) |

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## Worked example

A. 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:

1. More $CH_3COOC_2H_5(l)$ is added
2. Some $C_2H_5OH(l)$ is removed

B. 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

3. Water is added to the equilibrium mixture

**Answer:**

**Answer 1:**

- 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 2:**

- 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 3:**

- 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

- Changes in pressure only affect reactions where the reactants or products are gases

**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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## 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:**

**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

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**Effects of Temperature Table**

| CHANGE | HOW THE EQUILIBRIUM SHIFTS |
|---|---|
| INCREASE IN TEMPERATURE | EQUILIBRIUM MOVES IN THE **ENDOTHERMIC** DIRECTION TO REVERSE THE CHANGE |
| DECREASE IN TEMPERATURE | EQUILIBRIUM MOVES IN THE **EXOTHERMIC** DIRECTION TO REVERSE THE CHANGE |

### Worked example

Using the reaction below:

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

1. Predict the effect of increasing the temperature on this reaction

Using the reaction below:

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

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

Explain your answer

**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** once this is reached

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### Exam Tip

You are not required to quote Le Chatelier's Principle in an exam, but you must know how to apply it to systems in equilibrium

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# 7.1.6 Catalysts & Equilibrium

## Catalysts & Equilibrium

### Changes in concentration

- If all other conditions stay the same, the equilibrium constant $K_c$ 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:

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

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 $6.25 \times 10^{-3}$ again

### Changes in pressure

- A change in pressure **only** changes the **position of the equilibrium** (see Le Chatelier's principle)
- If all other conditions stay the same, the equilibrium constant $K_c$ is **not affected** by any changes in pressure of the reactants and products

### Changes in temperature

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

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

An increase in temperature:

$[H_2]$ and $[I_2]$ **increases**

[HI] **decreases**

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Because $[H_2]$ and $[I_2]$ are **increasing** and [HI] is **decreasing**, the equilibrium constant $K_c$ **increases**

- For an exothermic reaction such as:

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

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 $K_c$ decreases

### Presence of a catalyst

- If all other conditions stay the same, the equilibrium constant $K_c$ is **not affected** by the presence of a catalyst
- A catalyst speeds up both the forward and reverse reactions at the same rate so the ratio of [ products ] to [ reactants ] remains unchanged

## Worked example

An equilibrium is established in the following reaction:

$$AB\,(aq) + CD\,(aq) \rightleftharpoons AC\,(aq) + BD\,(aq) \qquad \Delta H = +180\ kJ\ mol^{-1}$$

Which factors would affect the value of in this equilibrium?

**Answer:**

- Only a change in temperature will affect the value of $K_c$ and any other changes in conditions would result in the position of the equilibrium moving in such way to oppose this change.
- Adding a catalyst will increase the rate of reaction meaning the state of equilibrium will be reached faster but will have no effect on the position of the equilibrium and therefore $K_c$ is unchanged.