

# Cambridge (CIE) A Level Chemistry



Your notes

## Chemical Equilibria: Reversible Reactions & Dynamic Equilibrium

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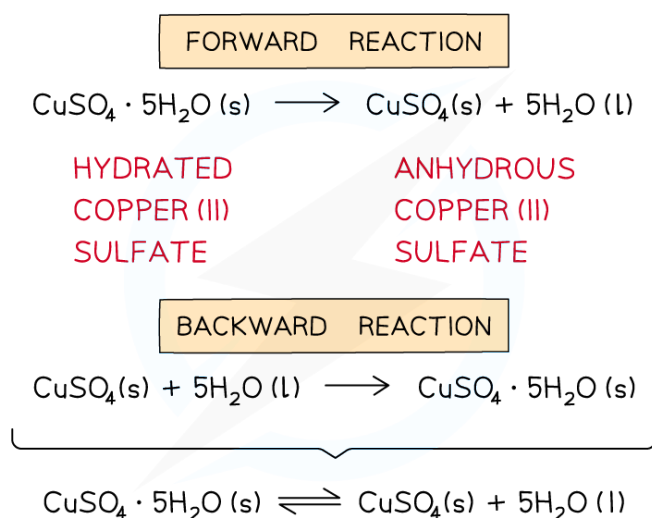


# Reversible Reactions & Dynamic Equilibrium

## Reversible reaction

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

## How reactions can be reversible

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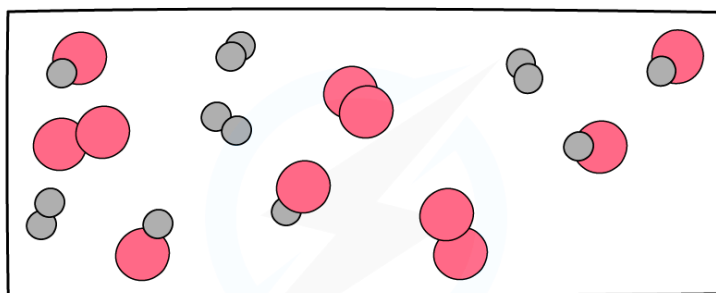
*The diagram shows an example of a forward and backward reaction that can be written as one equation using two half arrows*

## 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**
  - The **concentrations** of the **reactants** and **products** are **constant**



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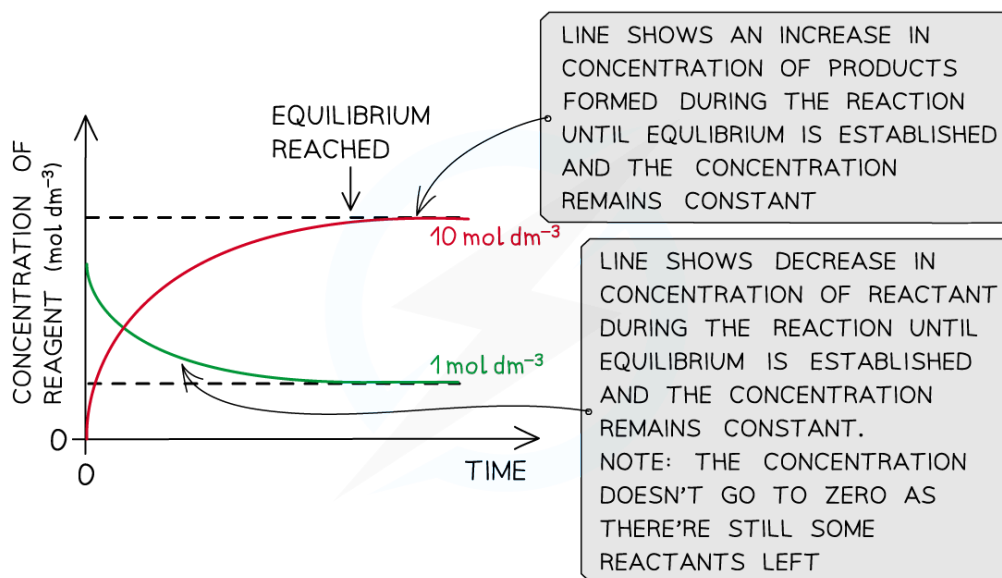
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○ = HYDROGEN ATOM    ● = IODINE ATOM

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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

## Diagrams showing reactant and product concentration as a reaction approaches equilibrium

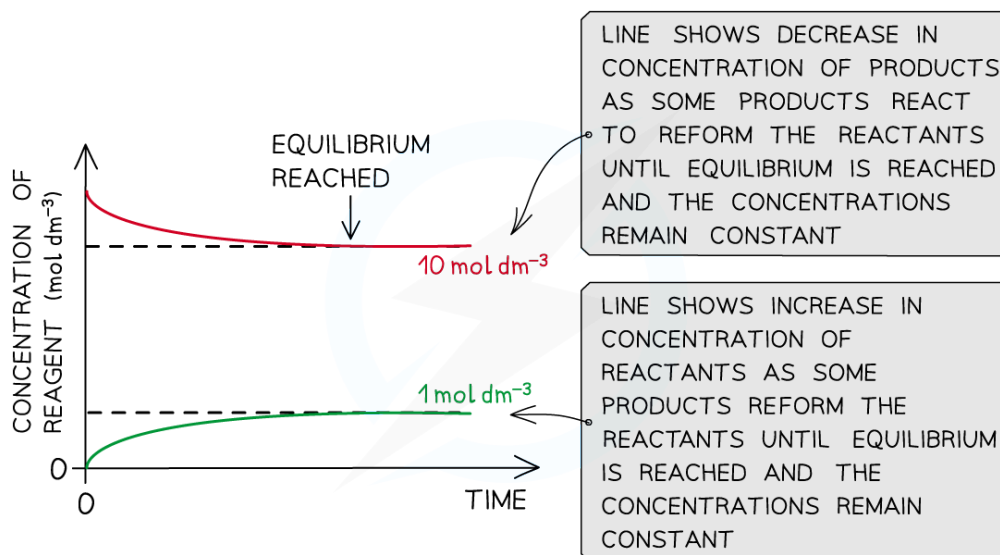


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The diagram shows that the concentration of the reactants and products does not change anymore once equilibrium has been reached (equilibrium was approached using reactants)



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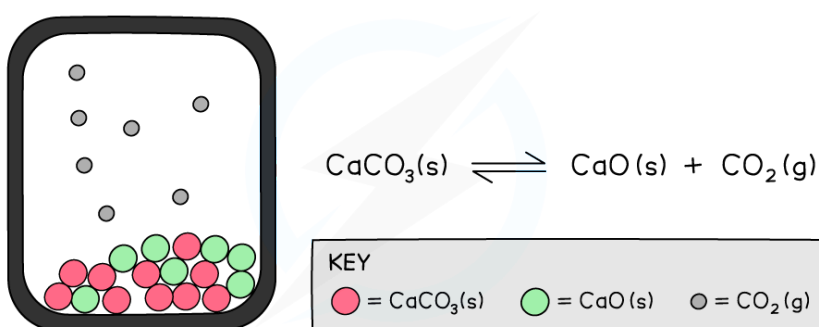


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The diagram shows that the concentration of the reactants and products does not change anymore once equilibrium has been reached (equilibrium was approached using products)

- A **closed system** is one in which none of the reactants or products escape from the reaction mixture
- In an **open system**, matter and energy can be lost to the surroundings
- When a reaction takes place entirely in solution, equilibrium can be reached in open flasks as a negligible amount of material is lost through evaporation
- If the reaction involves gases, equilibrium can only be reached in a closed system

## Thermal decomposition of calcium carbonate in a closed system



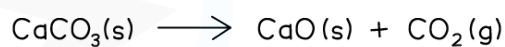
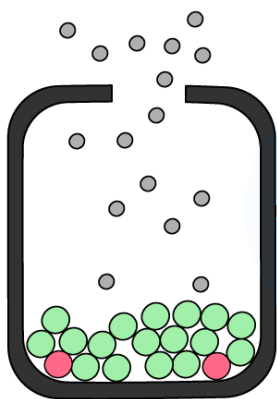
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The diagram shows a closed system in which no carbon dioxide gas can escape and the calcium carbonate is in equilibrium with the calcium oxide and carbon dioxide

## Thermal decomposition of calcium carbonate in an open system



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*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 Tips and Tricks

A common misconception is to think that the concentrations of the reactants and products are **equal**.

However, they are **not equal**, but they **remain constant** at dynamic equilibrium (i.e. the concentrations are not changing).

The concentrations will change as the reaction progresses, only **until the equilibrium** is reached.



# 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 concentration of **reactants** increases, the position of equilibrium shifts to the **right**
- When the concentration of **products** increases, the position of equilibrium shifts to the **left**

## 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

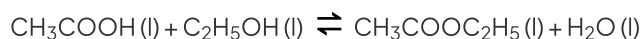
- If the concentration of a reactant is increased:
  - Equilibrium shifts to the right
- If the concentration of a reactant is decreased:
  - Equilibrium shifts to the left
- If the concentration of a product is increased:
  - Equilibrium shifts to the left
- If the concentration of a product is decreased:
  - Equilibrium shifts to the right



### Worked Example

#### Changes in equilibrium position

Use the reaction below:



Explain what happens to the position of equilibrium when:

1. More  $\text{CH}_3\text{COOC}_2\text{H}_5 \text{ (l)}$  is added

2. Some  $\text{C}_2\text{H}_5\text{OH}(\text{l})$  is removed

#### Answer

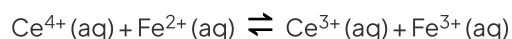
- **Answer 1:** More  $\text{CH}_3\text{COOC}_2\text{H}_5(\text{l})$  is added
  - The position of the equilibrium moves **to the left** and more ethanoic acid and ethanol are formed
  - The reaction moves in this direction to oppose the effect of added ethyl ethanoate, so the ethyl ethanoate decreases in concentration
- **Answer 2:** Some  $\text{C}_2\text{H}_5\text{OH}(\text{l})$  is removed
  - 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



### Worked Example

#### Changes in equilibrium position

Use the reaction below:



Explain what happens to the position of equilibrium when:

1. Water is added to the equilibrium mixture.

#### Answer

- 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

- If the pressure is increased
  - Equilibrium shifts in the direction that produces a smaller number of molecules of gas to decrease the pressure again
- If the pressure is decreased
  - Equilibrium shifts in the direction that produces a larger number of molecules of gas to increase the pressure again



### Worked Example



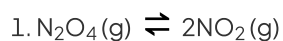
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### Changes in pressure

Predict the effect of increasing pressure on the following reactions:



#### 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  $\text{CO}_2$  on the right
- This causes a decrease in pressure



### Worked Example

#### Changes in pressure

Predict the effect of decreasing pressure on the following reaction:



#### Answer

- 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

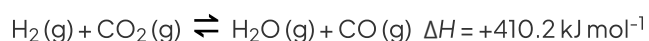
- If temperature is increased
  - Equilibrium moves in the **endothermic** direction to reverse the change
- If temperature is decreased
  - Equilibrium moves in the **exothermic** direction to reverse the change



### Worked Example

#### Changes in temperature

Predict the effect of increasing the temperature on the following reaction:





### Answer

- The reaction will absorb the excess energy
- Since the forward reaction is endothermic, the **equilibrium will shift to the right**



### Worked Example

#### Changes in temperature

For the following reaction, increasing the temperature increases the amount of CO<sub>2</sub> (g) at constant pressure.



Explain whether the reaction is endothermic or exothermic.

### Answer

- The reaction absorbs the excess energy
- Since more CO<sub>2</sub> (g) is formed, the equilibrium has shifted towards the right
- Therefore, the reaction is **endothermic**
- **Remember:** Endothermic reactions favour the products



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## 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



# Equilibrium Constant: Concentrations

## 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:



- $K_c$  is defined as:

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

- Where:
  - $[A]$  and  $[B]$  are the equilibrium concentrations of **A** and **B**, in  $\text{mol dm}^{-3}$
  - $[C]$  and  $[D]$  are the equilibrium concentrations of **C** and **D**, in  $\text{mol dm}^{-3}$
  - $a$ ,  $b$ ,  $c$  and  $d$  are the respective number of moles of each reactant and product
- Solids** are ignored in equilibrium expressions
- The  $K_c$  of a reaction is specific and only changes if the **temperature** of the reaction changes



### Worked Example

Deduce the equilibrium expression for the following reactions:

- $\text{Ag}^+ (\text{aq}) + \text{Fe}^{2+} (\text{aq}) \rightleftharpoons \text{Ag} (\text{s}) + \text{Fe}^{3+} (\text{aq})$
- $\text{N}_2 (\text{g}) + 3\text{H}_2 (\text{g}) \rightleftharpoons 2\text{NH}_3 (\text{g})$
- $2\text{SO}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightleftharpoons 2\text{SO}_3 (\text{g})$

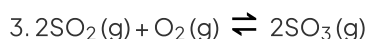
**Answer**

- $\text{Ag}^+ (\text{aq}) + \text{Fe}^{2+} (\text{aq}) \rightleftharpoons \text{Ag} (\text{s}) + \text{Fe}^{3+} (\text{aq})$

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

- $\text{N}_2 (\text{g}) + 3\text{H}_2 (\text{g}) \rightleftharpoons 2\text{NH}_3 (\text{g})$

$$K_c = \frac{[\text{NH}_3(\text{g})]^2}{[\text{N}_2(\text{g})][\text{H}_2(\text{g})]^3}$$



$$K_c = \frac{[\text{SO}_3(\text{g})]^2}{[\text{SO}_2(\text{g})]^2 [\text{O}_2(\text{g})]}$$



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# Mole Fraction & Partial Pressure

## Partial pressure

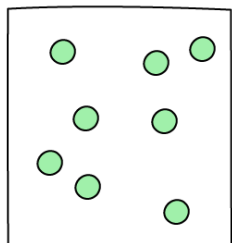
- For reactions involving mixtures of gases, the equilibrium constant  $K_p$  is used as it is easier to measure the **pressure** than the concentration for gases
- The **partial pressure** of a gas is the pressure that the gas would have if it was in the container all by itself
- The **total pressure** is the sum of the **partial pressure**:

$$P_{\text{total}} = P_A + P_B + P_C + \dots$$

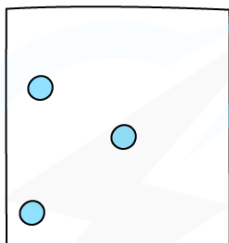
- $P_{\text{total}}$  = total pressure
  - $P_A, P_B, P_C$  = partial pressures

## How partial pressures contribute to total pressure

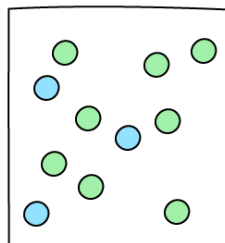
THE VOLUMES OF THE CONTAINERS ARE THE SAME



PARTIAL PRESSURE  
= 8 Pa



PARTIAL PRESSURE  
= 3 Pa



TOTAL PRESSURE  
= 11 Pa

KEY



= GAS A



= GAS B

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*Partial pressures can be added together to calculate the total pressure*

## Mole fraction

- The mole fraction of a gas is the ratio of moles of a particular gas to the total number of moles of gas present



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$$\text{Mole fraction} = \frac{\text{number of moles of a particular gas}}{\text{total number of moles of all the gases in the mixture}}$$

- To calculate the **partial pressures of each gas** the following relationship can be used:

$$\text{Partial pressure} = \text{mole fraction} \times \text{total pressure}$$

- The sum of the mole fractions should add up to 1.00, while the sum of the partial pressures should add up to the total pressure

## Equilibrium Constant: Partial Pressures

### Equilibrium expressions involving partial pressures

- Equilibrium expressions in terms of partial pressures are written similarly to those involving concentrations, with a few differences:

### Comparing $K_p$ and $K_c$ expressions

$$K_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$$

EXPRESSION CONSTANT

PARTIAL PRESSURE

NUMBER OF MOLES OF  
REACTANTS AND PRODUCTS

REACTANTS AND PRODUCTS

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

EXPRESSION CONSTANT

BRACKETS USED FOR  
CONCENTRATION

NUMBER OF MOLES OF  
REACTANTS AND PRODUCTS

REACTANTS AND PRODUCTS

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*The process of writing the expressions is similar, but there is a different presentation and different information required*



### Worked Example

#### Deducing equilibrium expressions of gaseous reactions

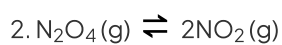
Deduce the equilibrium expression for the following reactions:

1.  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
2.  $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
3.  $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

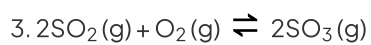
**Answer**

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

$$K_p = \frac{p^2 \text{NH}_3}{p^3 \text{H}_2 \times p \text{N}_2}$$



$$K_p = \frac{p^2 \text{NO}_2}{p \text{N}_2\text{O}_4}$$



$$K_p = \frac{p^2 \text{SO}_3}{p^2 \text{SO}_2 \times p \text{O}_2}$$



Your notes



# Equilibrium Constant: Calculations

## Calculations involving $K_c$

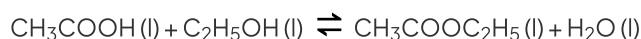
- In the equilibrium expression, each figure within a square bracket represents the concentration in  $\text{mol dm}^{-3}$
- The **units** of  $K_c$  therefore depend on the form of the equilibrium expression
- Some questions give the **number of moles** of each of the reactants and products at equilibrium 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:

$$\text{concentration (mol dm}^{-3}\text{)} = \frac{\text{number of moles}}{\text{volume (dm}^3\text{)}}$$



### Worked Example

At equilibrium,  $500 \text{ cm}^3$  of the following reaction mixture contains 0.235 mol of ethanoic acid, 0.0350 mol of ethanol, 0.182 mol of ethyl ethanoate and 0.182 mol of water.



Use this information to calculate a value of  $K_c$  for this reaction.

#### Answer

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

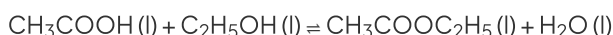
$$[\text{CH}_3\text{COOH (l)}] = 0.470 \text{ mol dm}^{-3}$$

$$[\text{C}_2\text{H}_5\text{OH (l)}] = 0.070 \text{ mol dm}^{-3}$$

$$[\text{CH}_3\text{COOC}_2\text{H}_5 \text{ (l)}] = 0.364 \text{ mol dm}^{-3}$$

$$[\text{H}_2\text{O (l)}] = 0.364 \text{ mol dm}^{-3}$$

- **Step 2:** Write out the balanced chemical equation with the calculated concentrations beneath each substance:



$$0.470 \text{ mol dm}^{-3} \quad 0.070 \text{ mol dm}^{-3} \quad 0.364 \text{ mol dm}^{-3} \quad 0.364 \text{ mol dm}^{-3}$$

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

$$K_c = \frac{[\text{H}_2\text{O}] [\text{CH}_3\text{COOC}_2\text{H}_5]}{[\text{C}_2\text{H}_5\text{OH}] [\text{CH}_3\text{COOH}]}$$



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

$$K_c = \frac{0.364 \times 0.364}{0.070 \times 0.470}$$

$$K_c = 4.03$$

- **Step 5:** Deduce the correct units for  $K_c$ :

$$K_c = \frac{(\text{mol dm}^{-3})(\text{mol dm}^{-3})}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})}$$

All units cancel out

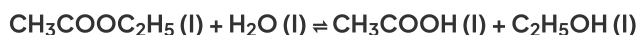
Therefore,  $K_c = 4.03$

- Note that the smallest number of significant figures used in the question is 3, so the final answer should also be given to 3 significant figures
- Some questions give the **initial and equilibrium concentrations** of the reactants but products
- An initial, change and equilibrium table should be used to determine the equilibrium concentration of the products **using the molar ratio of reactants and products in the stoichiometric equation**



### Worked Example

Ethyl ethanoate is hydrolysed by water:



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<sup>3</sup>. 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
    - $0.0654 = 0.100 + \text{Change in amount}$
    - 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<sub>2</sub>O and all other reactants/products
    - As H<sub>2</sub>O has **decreased** by **0.0346 mol**, the other reactant CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> will **decrease** by **0.0346 mol**



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- Since  $\text{CH}_3\text{COOH}$  and  $\text{C}_2\text{H}_5\text{OH}$  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  $\text{CH}_3\text{COOC}_2\text{H}_5 = 0.100 + (-0.0346) = \mathbf{0.0654 \text{ mol}}$
  - Equilibrium amount of  $\text{CH}_3\text{COOH} = 0.000 + 0.0346 = \mathbf{0.0346 \text{ mol}}$
  - Equilibrium amount of  $\text{C}_2\text{H}_5\text{OH} = 0.000 + 0.0346 = \mathbf{0.0346 \text{ mol}}$

	$\text{CH}_3\text{COOC}_2\text{H}_5 (\text{l})$ +	$\text{H}_2\text{O} (\text{l})$ $\rightleftharpoons$	$\text{CH}_3\text{COOH} (\text{l})$ +	$\text{C}_2\text{H}_5\text{OH} (\text{l})$
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:

$$[\text{CH}_3\text{COOH} (\text{l})] = \frac{0.0346}{1.0} = 0.0346 \text{ mol dm}^{-3}$$

$$[\text{C}_2\text{H}_5\text{OH} (\text{l})] = \frac{0.0346}{1.0} = 0.0346 \text{ mol dm}^{-3}$$

$$[\text{CH}_3\text{COOC}_2\text{H}_5 (\text{l})] = \frac{0.0654}{1.0} = 0.0654 \text{ mol dm}^{-3}$$

$$[\text{H}_2\text{O} (\text{l})] = \frac{0.0654}{1.0} = 0.0654 \text{ mol dm}^{-3}$$

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

$$K_c = \frac{[\text{C}_2\text{H}_5\text{OH}][\text{CH}_3\text{COOH}]}{[\text{H}_2\text{O}][\text{CH}_3\text{COOC}_2\text{H}_5]}$$

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

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

- Step 5:** Deduce the correct units for  $K_c$ :

$$K_c = \frac{[\text{C}_2\text{H}_5\text{OH}][\text{CH}_3\text{COOH}]}{[\text{H}_2\text{O}][\text{CH}_3\text{COOC}_2\text{H}_5]}$$

All units cancel out

Therefore,  $K_c = 0.280$  (**no units**)

## Calculations involving $K_p$



- In the equilibrium expression the  $p$  represent the partial pressure of the reactants and products in **Pa**
- The **units** of  $K_p$  therefore depend on the form of the equilibrium expression

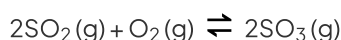


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### Worked Example

The equilibrium between sulfur dioxide, oxygen and sulfur trioxide is as follows:



At constant temperature, the equilibrium partial pressures are:

- $\text{SO}_2 = 1.0 \times 10^6 \text{ Pa}$
- $\text{O}_2 = 7.0 \times 10^6 \text{ Pa}$
- $\text{SO}_3 = 8.0 \times 10^6 \text{ Pa}$

Calculate the value of  $K_p$  for this reaction.

#### Answer

- **Step 1:** Write the equilibrium constant for the reaction in terms of partial pressures:

$$K_p = \frac{p^2 \text{ SO}_3}{p^2 \text{ SO}_2 \times p \text{ O}_2}$$

- **Step 2:** Substitute the equilibrium concentrations into the expression:

$$K_p = \frac{(8.0 \times 10^6)^2}{(1.0 \times 10^6)^2 \times (7.0 \times 10^6)}$$

$$K_p = 9.1 \times 10^{-6}$$

- **Step 3:** Deduce the correct units of  $K_p$ :

$$K_p = \frac{\text{Pa}^2}{\text{Pa}^2 \times \text{Pa}}$$

So, the units of  $K_p$  are  $\text{Pa}^{-1}$

Therefore,  $K_p = 9.1 \times 10^{-6} \text{ Pa}^{-1}$

- Some questions only give the **number of moles** of gases present and the total pressure
- The number of moles of each gas should be used to first calculate the **mole fractions**
- The mole fractions are then used to calculate the **partial pressures**
- The values of the partial pressures are then substituted in the **equilibrium expression**



### Worked Example

The equilibrium between hydrogen, iodine and hydrogen bromide is as follows:



At constant temperature, the equilibrium moles are:

- $\text{H}_2 = 1.71 \times 10^{-3}$
- $\text{I}_2 = 2.91 \times 10^{-3}$
- $\text{HI} = 1.65 \times 10^{-2}$

The total pressure is 100 kPa.

Calculate the value of  $K_p$  for this reaction.

#### Answer

- **Step 1:** Calculate the total number of moles:

$$\text{Total number of moles} = 1.71 \times 10^{-3} + 2.91 \times 10^{-3} + 1.65 \times 10^{-2}$$

$$\text{Total number of moles} = 2.112 \times 10^{-2}$$

1. **Step 2:** Calculate the mole fraction of each gas:

$$\text{H}_2 = \frac{1.71 \times 10^{-3}}{2.112 \times 10^{-2}} = 0.0810$$

$$\text{I}_2 = \frac{2.91 \times 10^{-3}}{2.112 \times 10^{-2}} = 0.1378$$

$$\text{HI} = \frac{1.65 \times 10^{-2}}{2.112 \times 10^{-2}} = 0.7813$$

- **Step 3:** Calculate the partial pressure of each gas:

$$\text{H}_2 = 0.0810 \times 100 = 8.10 \text{ kPa}$$

$$\text{I}_2 = 0.1378 \times 100 = 13.78 \text{ kPa}$$

$$\text{HI} = 0.7813 \times 100 = 78.13 \text{ kPa}$$

- **Step 4:** Write the equilibrium constant in terms of partial pressure:

$$K_p = \frac{p^2 \text{ HI}}{p \text{ H}_2 \times p \text{ I}_2}$$

- **Step 5:** Substitute the values into the equilibrium expression:

$$K_p = \frac{78.13^2}{8.10 \times 13.78}$$

$$K_p = 54.7$$

- **Step 6:** Deduce the correct units for  $K_p$ :

$$K_p = \frac{\text{Pa}^2}{\text{Pa} \times \text{Pa}}$$

All units cancel out

Therefore,  $K_p = 54.7$



Your notes

- Other questions related to equilibrium expressions may involve calculating quantities present at equilibrium given appropriate data

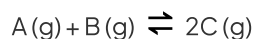


Your notes



### Worked Example

An equilibrium is set up in a closed container between equal volumes of gaseous reactants **A** and **B** to form a gaseous product **C**.



The total pressure within the container, at 50 °C, is 3 atm.

The equilibrium partial pressure of **A**, at 50 °C, is 0.5 atm.

What is the equilibrium partial pressure of **C** at this temperature?

#### Answer

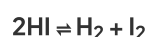
- There are equal volumes of reactants **A** and **B** in a 1 : 1 molar ratio
  - This means their partial pressures will be the same.
  - B** therefore also has an equilibrium partial pressure of 0.5 atm
- Total pressure = Σ (equilibrium partial pressures)**
  - Therefore, the sum of all the partial pressures must equal to 3 atm
  - $0.5 + 0.5 + p_{\text{C}} = 3 \text{ atm}$
  - $p_{\text{C}} = 2 \text{ atm}$



# Changes that Affect the Equilibrium Constant

## 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:



- The equilibrium expression is:

$$K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = 6.25 \times 10^{-3}$$

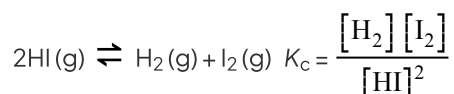
- Adding more HI makes the ratio of [products] to [reactants] smaller
- To restore equilibrium,  $[\text{H}_2]$  and  $[\text{I}_2]$  increase and  $[\text{HI}]$  decreases
- Equilibrium is restored when the ratio is  $6.25 \times 10^{-3}$  again

## Changes in pressure

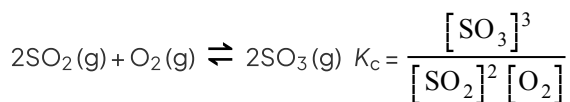
- A change in pressure **only** changes the **position of the equilibrium** (see [Le Chatelier's principle](#))
- If all other conditions stay the same, the equilibrium constant  $K_c$  is **not affected** by any changes in the pressure of the reactants and products

## Changes in temperature

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



- With an increase in temperature:
  - $[\text{H}_2]$  and  $[\text{I}_2]$  **increases**
  - $[\text{HI}]$  **decreases**
  - Because  $[\text{H}_2]$  and  $[\text{I}_2]$  **increase** and  $[\text{HI}]$  **decreases**, the equilibrium constant  $K_c$  **increases**
- For an exothermic reaction such as:



Your notes

- With an increase in temperature:
  - $[\text{SO}_3]$  **decreases**
  - $[\text{SO}_2]$  and  $[\text{O}_2]$  **increases**
  - Because  $[\text{SO}_3]$  **decreases** and  $[\text{SO}_2]$  and  $[\text{O}_2]$  **increase**, the equilibrium constant  $K_c$  **decreases**

## Presence of a catalyst

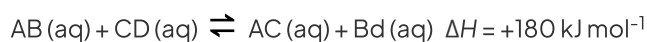
- If all other conditions stay the same, the equilibrium constant  $K_c$  is **not affected** by the presence of a catalyst
- A catalyst speeds up both the forward and reverse reactions at the same rate so the ratio of [products] to [reactants] remains unchanged



### Worked Example

#### Factors affecting $K_c$

An equilibrium is established in the following reaction:



Which factors would affect the value of  $K_c$  in this equilibrium?

#### Answer

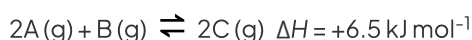
- Only a change in temperature will affect the value of  $K_c$
- Any other changes in conditions would result in the position of the equilibrium moving to oppose this change
- Adding a catalyst increases the rate of reaction meaning the state of equilibrium will be reached faster but has no effect on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



### Worked Example

#### Factors which increase $K_p$ value

What will increase the value of  $K_p$  for the following equilibrium?



#### Answer

- Only temperature changes permanently affect the value of  $K_p$

- An increase in temperature shifts the reaction in favour of the products
- The [products] increases and [reactants] decreases, therefore, the  $K_p$  value increases



Your notes

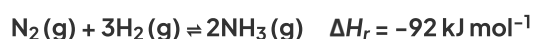


# Haber & Contact Processes

- Equilibrium reactions are involved in some stages of large-scale production of certain chemicals
- An understanding of equilibrium and Le Chatelier's principle is therefore very important in the chemical industry

## Haber process

- The Haber process involves the synthesis of ammonia according to:



- Le Chatelier's principle is used to get the best yield of ammonia

## Maximising the ammonia yield

### Pressure

- The forward reaction produces fewer moles of gas
  - 4 moles on the left and 2 on the right
- **Increasing pressure** shifts equilibrium **to the right**, increasing ammonia yield
- Higher pressure also increases **collision frequency**, enhancing the reaction rate
- However, **very high pressures** are costly and require strong containment
- **Compromise pressure** used
  - $\approx 200 \text{ atm}$

### Temperature

- The forward reaction is **exothermic**
- Lowering temperature shifts equilibrium **to the right**, favouring ammonia formation
- But too low a temperature would **slow the reaction rate**, delaying equilibrium
- **Compromise temperature:**
  - $400-450^\circ\text{C}$

## Removing ammonia

- **Ammonia is removed by cooling and condensing it** to a liquid
- This shifts the equilibrium **further to the right**, producing more ammonia
- Stored ammonia is kept at low temperatures where decomposition is **very slow**, especially in the **absence of a catalyst**

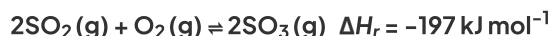


## Catalysts

- An **iron catalyst** is used to **increase the rate of reaction** without affecting equilibrium position
- Without it, the reaction would be too slow to be commercially viable

## Contact process

- The Contact process involves the synthesis of sulfuric acid according to:



- Le Chatelier's principle is used to get the best yield of sulfuric acid

## Maximising the sulfuric acid yield

### Pressure

- Fewer moles of gas on the right-hand side
  - 3 moles on the left and 2 on the right
- **Increasing pressure** shifts equilibrium to the right, favouring  $\text{SO}_3$  formation
- However, the **equilibrium constant ( $K_p$ )** is already very large at low pressures
- **Industrial pressure used:**
  - **~1 atm** to save cost, as higher pressure gives little extra benefit

### Temperature

- Reaction is **exothermic**
- Lower temperatures would favour  $\text{SO}_3$  production, but also **reduce the rate**
- **Compromise temperature:**
  - **$\approx 450^\circ\text{C}$**

## Removing sulfuric acid

- $\text{SO}_3$  is **removed by absorbing it into 98%  $\text{H}_2\text{SO}_4$** , forming **oleum**:



- This removal shifts the equilibrium to the right, driving the reaction forward

## Catalysts

- The Contact process uses vanadium(V) oxide as a catalyst to increase the rate of reaction