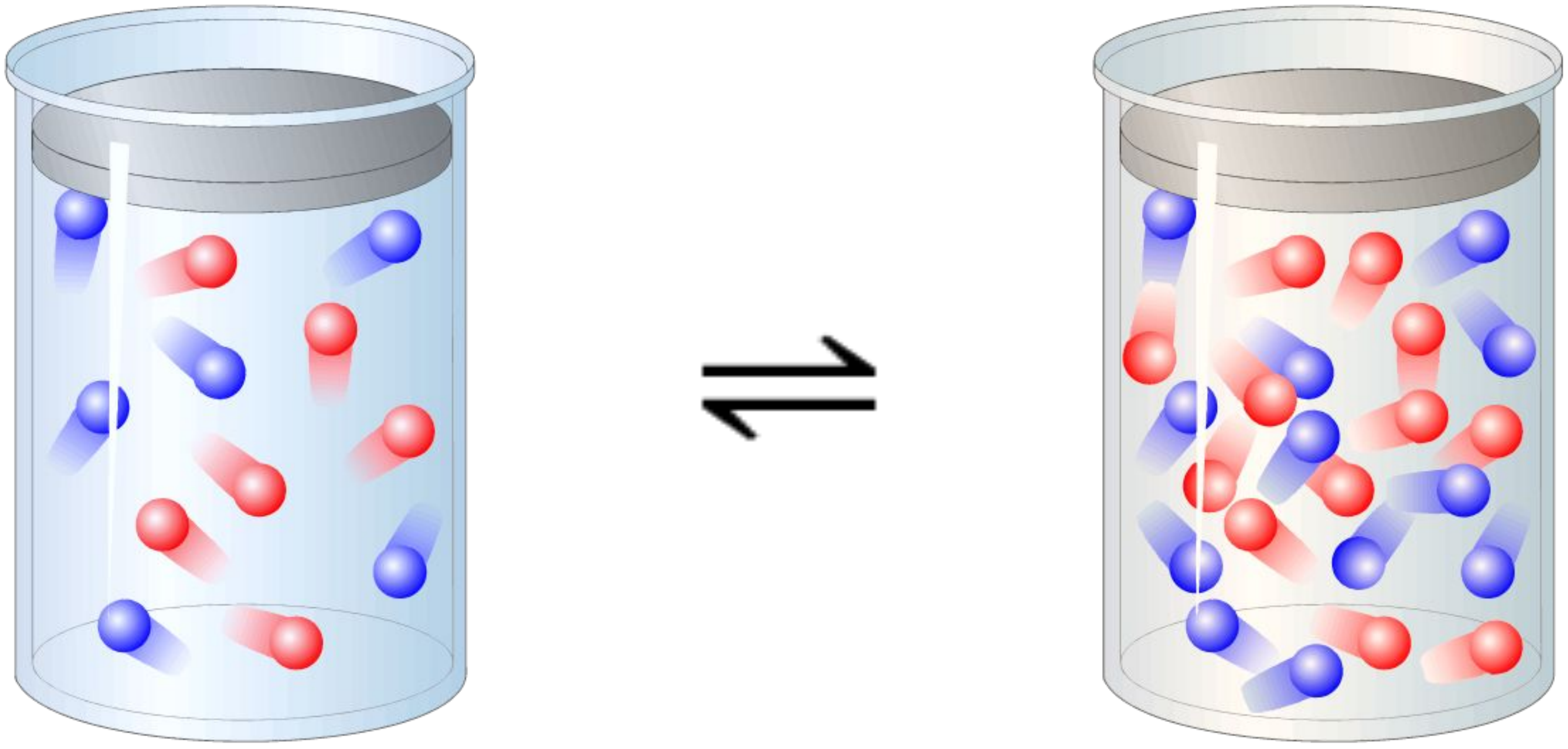
Equilibria and Energetics



Material Covered

Equilibria

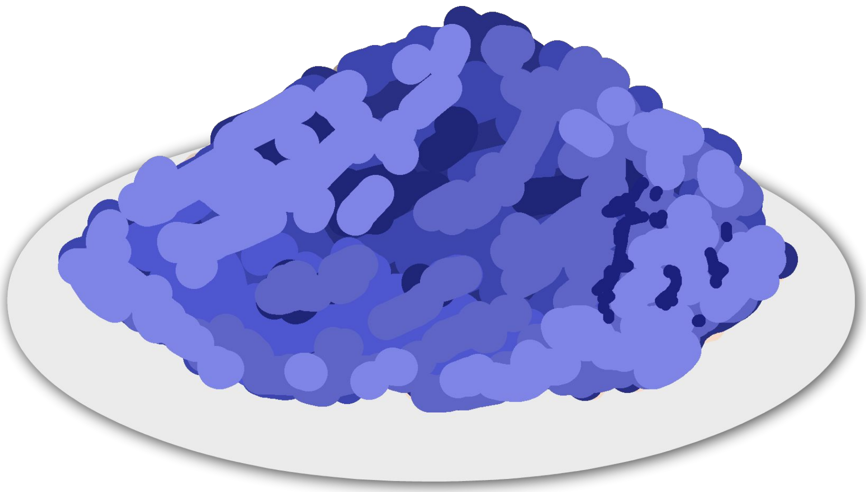
1. Reversible Reactions and K_c
2. Le Chatelier's Principle

Energetics

1. Optimising Conditions

Equilibria

$CuSO_4.5H_2O$



$\rightleftharpoons$

$CuSO_4 + 5H_2O$

Edexcel

1.	know that many reactions are readily reversible and that they can reach a state of dynamic equilibrium in which: i the rate of the forward reaction is equal to the rate of the backward reaction ii the concentrations of reactants and products remain constant
2.	be able to predict and justify the qualitative effect of a change in temperature, concentration or pressure on a homogeneous system in equilibrium
3.	evaluate data to explain the necessity, for many industrial processes, to reach a compromise between the yield and the rate of reaction
4.	be able to deduce an expression for K_c, for homogeneous and heterogeneous systems, in terms of equilibrium concentrations

AQA

Content

Many chemical reactions are reversible.

In a reversible reaction at equilibrium:

- forward and reverse reactions proceed at equal rates
- the concentrations of reactants and products remain constant.

Le Chatelier's principle.

Le Chatelier's principle can be used to predict the effects of changes in temperature, pressure and concentration on the position of equilibrium in homogeneous reactions.

A catalyst does not affect the position of equilibrium.

Students should be able to:

- use Le Chatelier's principle to predict qualitatively the effect of changes in temperature, pressure and concentration on the position of equilibrium
- explain why, for a reversible reaction used in an industrial process, a compromise temperature and pressure may be used.

Content

The equilibrium constant K_c is deduced from the equation for a reversible reaction.

The concentration, in mol dm^{-3}, of a species X involved in the expression for K_c is represented by [X]

The value of the equilibrium constant is not affected either by changes in concentration or addition of a catalyst.

Students should be able to:

- construct an expression for K_c for a homogeneous system in equilibrium
- calculate a value for K_c from the equilibrium concentrations for a homogeneous system at constant temperature
- perform calculations involving K_c
- predict the qualitative effects of changes of temperature on the value of K_c

OCR

Dynamic equilibrium and le Chatelier's principle

(a) explanation that a dynamic equilibrium exists in a closed system when the rate of the forward reaction is equal to the rate of the reverse reaction and the concentrations of reactants and products do not change

(b) le Chatelier's principle and its application for homogeneous equilibria to deduce qualitatively the effect of a change in temperature, pressure or concentration on the position of equilibrium

(c) explanation that a catalyst increases the rate of both forward and reverse reactions in an equilibrium by the same amount resulting in an unchanged position of equilibrium

(d) the techniques and procedures used to investigate changes to the position of equilibrium for changes in concentration and temperature.

(e) explanation of the importance to the chemical industry of a compromise between chemical equilibrium and reaction rate in deciding the operational conditions

The equilibrium constant, K_c

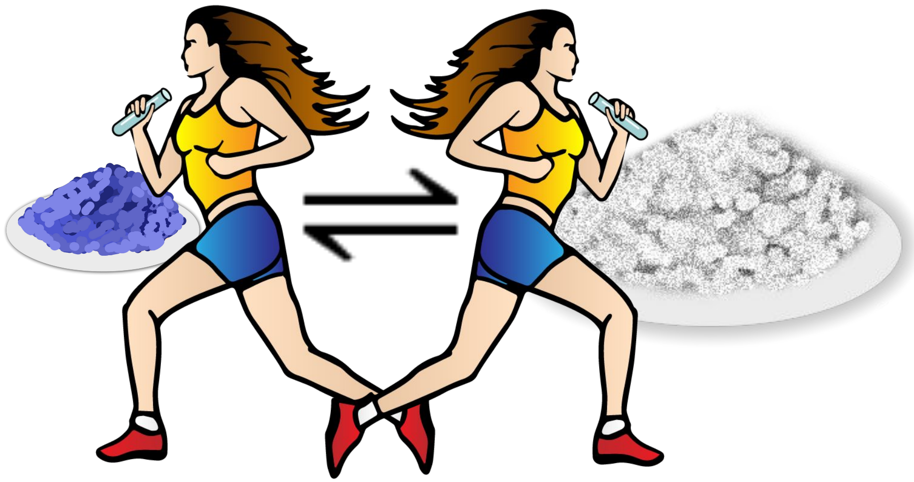
(f) expressions for the equilibrium constant, K_c, for homogeneous reactions and calculations of the equilibrium constant, K_c, from provided equilibrium concentrations

(g) estimation of the position of equilibrium from the magnitude of K_c.

Reversible Reactions

Reversible reactions taking place in **closed systems** will settle at **dynamic equilibrium**

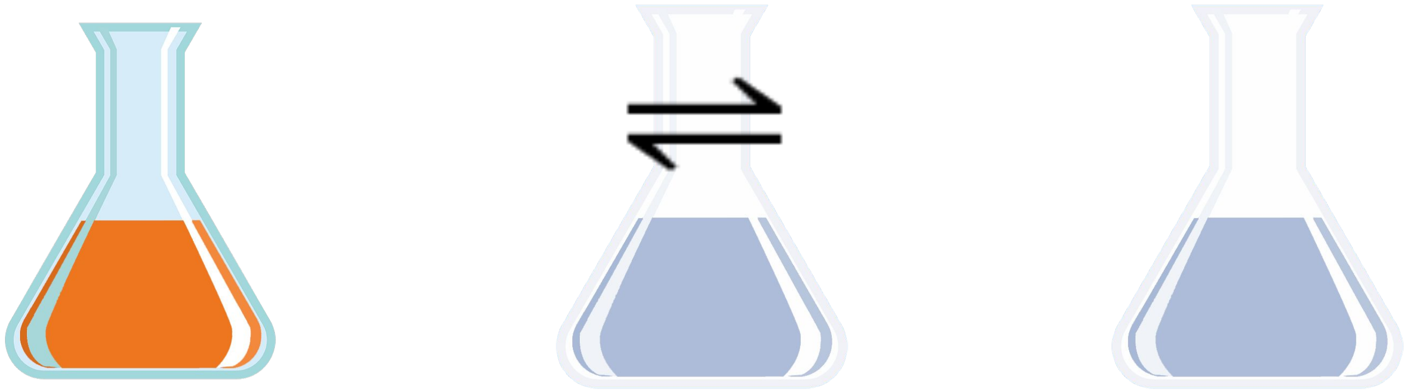
At dynamic equilibrium, the reactions **haven't stopped**



Therefore the **concentrations** of all of the reactants and products will remain **constant**

K_c

- Any reversible reaction will have an associated **K_c (equilibrium constant)**



- K_c tells you the **ratio** of the **concentration of the reactants** to the **concentration of the products at dynamic equilibrium**

K_c

The magnitude of $\mathbf{K_c}$ indicates the **position of equilibrium**

This is the **ratio** of the concentration of products to the concentration of reactants

K_c > 1 indicates products are favoured
- Reactions where $\mathbf{K_c} > 10^{10}$: regarded as going to completion

K_c < 1 indicates reactants are favoured
- Reactions where $\mathbf{K_c} < 10^{-10}$: regarded as not taking place at all

Constructing an Equilibrium Expression

General form :

$$2A\ (aq) + 2B\ (aq) \rightleftharpoons 3C\ (aq) + D\ (aq)$$

$$K_c = \frac{[\mathrm{C\ (aq)}]^3{}_{\mathrm{eqm}}[\mathrm{D\ (aq)}]_{\mathrm{eqm}}}{[\mathrm{A\ (aq)}]^2{}_{\mathrm{eqm}}[\mathrm{B\ (aq)}]^2{}_{\mathrm{eqm}}}$$

$$\mathrm{Units} = \frac{(\mathrm{mol\ dm^{-3}})^3\ \ (\mathrm{mol\ dm^{-3}})}{(\mathrm{mol\ dm^{-3}})^2\ \ (\mathrm{mol\ dm^{-3}})^2} = \frac{(\mathrm{mol\ dm^{-3}})^4}{(\mathrm{mol\ dm^{-3}})^4} = \mathrm{no\ units}$$

Constructing an Equilibrium Expression with Gases and Solids

- In the previous example, we looked at a **homogenous** reaction

- We can also write K_c expressions for reactions involving **gases**

$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$

$K_c =$ units = =

Heterogenous Kc required in:
Year 12 Edexcel
Year 13 AQA, OCR

- Solids are **not included** in the expression for K_c :

Exemplar Exam Question – Statement

1) At high temperatures, steam will react in a reversible reaction with carbon in order to produce hydrogen and carbon monoxide.

Write an expression for K_c for this equilibrium, noting what units K_c will have.

[3 marks]

Command: write the balanced equation, remembering standard states

Direction: Balance equation with correct products and include what units of K_c

Context: Reversible reaction at high temperature and K_c

1. Write a **balanced equation** for the chemical reaction we're considering:

"steam will react in a reversible reaction with carbon in order to produce hydrogen and carbon monoxide"

balanced, includes state symbols, shows reaction is **reversible**

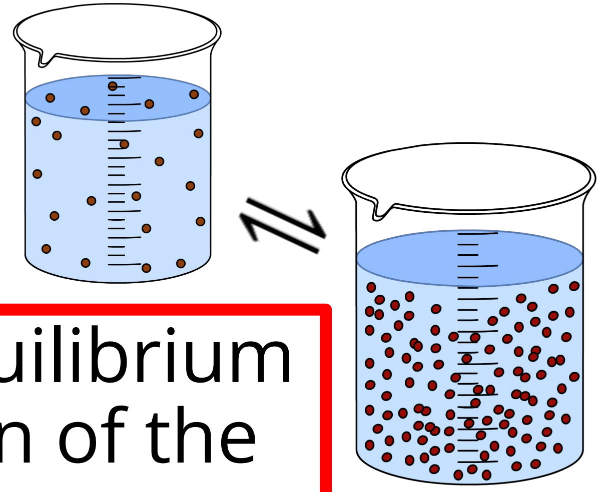
2. Write out a $\mathbf{K_c}$ expression:

$K_c =$

Units=

[3 marks]

Le Chatelier's Principle

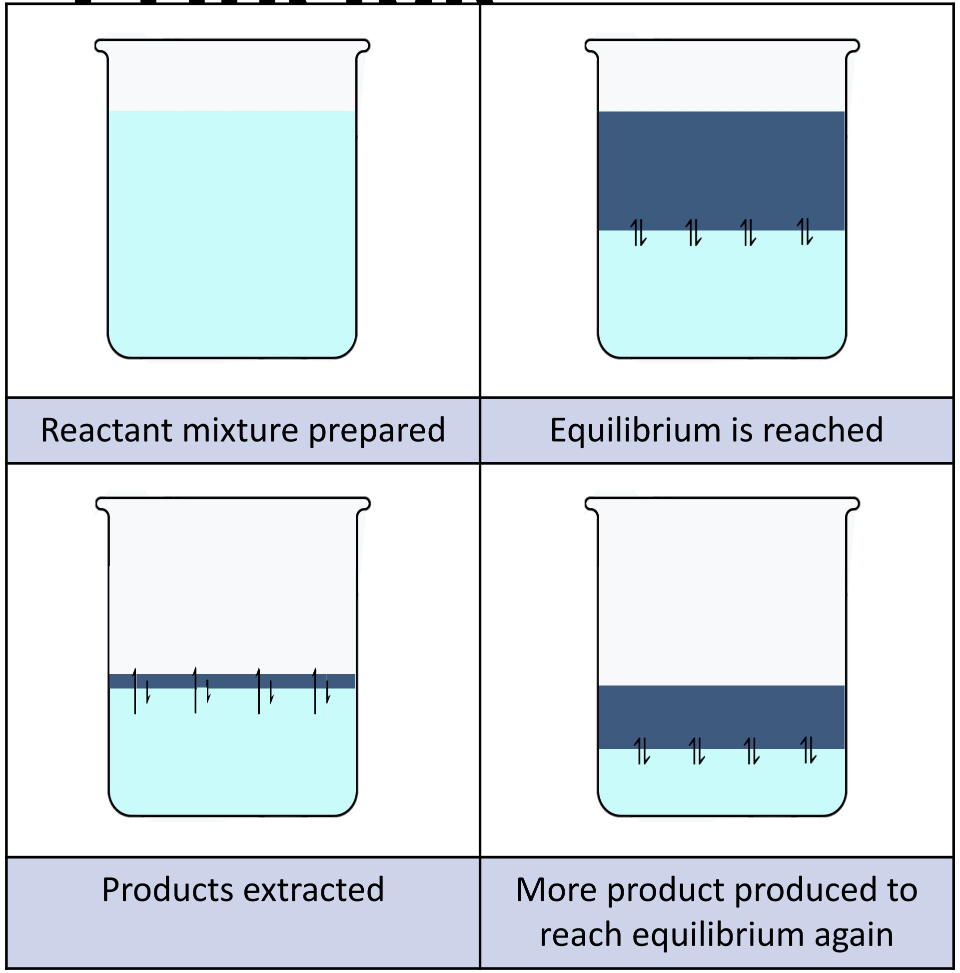


Le Chatelier's principle: If a system at dynamic equilibrium is **disturbed** by a change in conditions, the position of the equilibrium will move to **counteract the change**

At **constant temperature** (and **pressure**) **K_c doesn't change** so the **position of equilibrium** changes to keep **K_c constant**

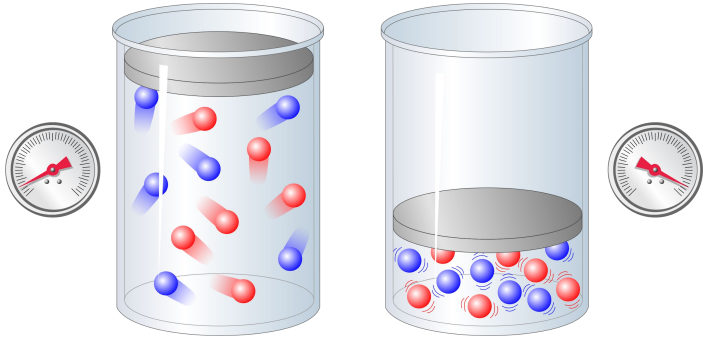
If **temperature changes**, **K_c changes**, so the **ratio of concentrations** of reactants and products **at equilibrium** will also change

Le Chatelier's Principle



- If we **increase** the **concentration** of one of the reactants, it will react more producing more product. We describe this as equilibrium moving in the direction of the products.
- Likewise, if we **increase** the **concentration** of one of the products, it will react more producing more reactants.
- A consequence is that if we **remove** a **product** from a system at equilibrium, the position of equilibrium will **shift** to produce **more**

Le Chatelier's Principle



Increasing the **pressure** of a specific **gas** is **equivalent** to increasing its **concentration**

Changing the **overall pressure** may affect the **position of equilibrium**

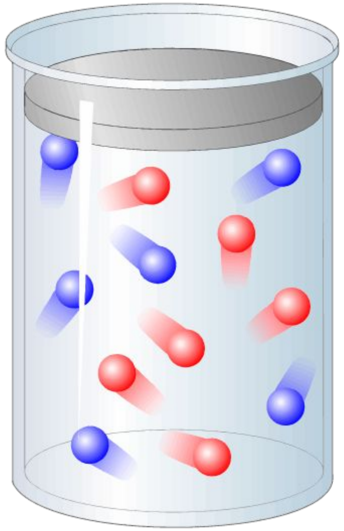
The effect of this can be **predicted** with Le Chatelier's principle

Le Chatelier’s Principle

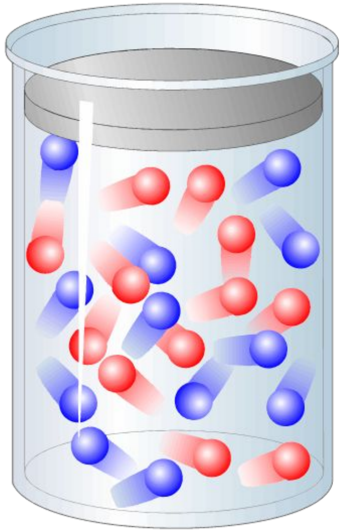
For a system at dynamic equilibrium, if the **overall pressure** is **increased**, gaseous molecules

The position of equilibrium will **move** in order to favour the reaction which produces **fewer total moles of gas**

p / 2



$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$



p

Exemplar Exam Question – Short Answer

2) Carbon monoxide and hydrogen gas react to form methanol in a sealed container under standard conditions.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

State and explain how the conc. of methanol at equilibrium will be affected if the pressure in the reaction vessel is doubled.

[2 marks]

Command: simple answer followed by reasoning

Context: equilibrium and the effects of changing pressure

Direction: how does the conc. of product change?

2) Carbon monoxide and hydrogen gas react to form methanol in a sealed container under standard conditions.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

State and explain how the conc. of methanol at equilibrium will be affected if the pressure in the reaction vessel is doubled.

[2 marks]

$[CH_3OH(g)]$ increases. Product is favoured at high pressure as there are 3 moles of gas of reactants, forming one mole of product- in order to lower the pressure.

Exemplar Exam Question – Calculation

$\rightleftharpoons$

[6 marks]

Command:
Numerical answer with full working out and to correct number of sf

Context: K_c and reversible reactions

Direction:
Mass/moles calc using relevant values given

$$CH_3COCH_3(aq) + HCN\ (aq) \rightleftharpoons CH_3C(CN)(OH)CH_3\ (aq)$$

1. Write out a K_c expression

$$K_c = \_\_\_\_\_\_\_\_\_\_ = 25.0\ mol^{-1}\ dm^3$$

2. Find Concentrations

$$c = \frac{n}{V}$$

$$[CH_3C(CN)(OH)CH_3\ (aq)] = c = \frac{\quad}{\quad} =$$

Hydrogen cyanide is in **excess**, meaning the **limiting reagent** is propanone

$$CH_3COCH_3 + HCN \rightleftharpoons CH_3C(CN)(OH)CH_3$$

Initial amount (**mol**)			
amount at equilibrium (**mol**)			
Concentration at equilibrium (**mol dm^{-3}**)			

x = number of moles of propanone required

$$K_c = \frac{}{} = 25.0 \text{ mol}^{-1} \text{ dm}^3$$

$$K_c = 25.0 = \frac{0.2}{(\frac{x-1}{5})(\frac{x-1}{5})}$$

$$0.2 = 25.0 * (\frac{x-1}{5})(\frac{x-1}{5})$$

$$0.2 = 25.0 * \frac{(x-1)(x-1)}{25}$$

$$0.2 = (x-1)^2$$

$$\pm\sqrt{0.2} = x - 1$$

$$x = 1.45 \text{ or } 0.553 \text{ mol} (3 \text{ s.f.})$$

x = 1.45 (3 s.f.) = number of **moles** of propanone needed

The question asked us: "how many **grams** of propanone are needed"

$$n = \frac{\mathrm{m}}{\mathrm{M}_r}$$

Propanone = CH_3COCH_3: C= 12.0 H=1.0 O=16.0

- molar mass = = **58.0 g mol^{-1}**
- mass = = **84.1g**

Energetics

Edexcel

1.	understand, in terms of collision theory, the effect of a change in concentration, temperature, pressure and surface area on the rate of a chemical reaction
2.	understand that reactions only take place when collisions take place with sufficient energy, known as activation energy
3.	be able to calculate the rate of a reaction from: i data showing the time taken for reaction ii the gradient of a suitable graph, by drawing a tangent, either for initial rate, or at a time, *t*
4.	understand qualitatively, in terms of the Maxwell-Boltzmann distribution of molecular energies, how changes in temperature affect the rate of a reaction
5.	understand the role of catalysts in providing alternative reaction routes of lower activation energy
6.	be able to draw the reaction profiles for uncatalysed and catalysed reactions
7.	be able to interpret the action of a catalyst in terms of a qualitative understanding of the Maxwell-Boltzmann distribution of molecular energies
8.	understand the use of a solid (heterogeneous) catalyst for industrial reactions, in the gas phase, in terms of providing a surface for the reaction
9.	understand the economic benefits of the use of catalysts in industrial reactions

AQA

The qualitative effect of changes in concentration on collision frequency.

The qualitative effect of a change in the pressure of a gas on collision frequency.

Students should be able to explain how a change in concentration or a change in pressure influences the rate of a reaction.

Meaning of the term rate of reaction.

The qualitative effect of temperature changes on the rate of reaction.

Students should be able to use the Maxwell–Boltzmann distribution to explain why a small temperature increase can lead to a large increase in rate.

OCR

Catalysts

(c) explanation of the role of a catalyst:

- **(i)** in increasing reaction rate without being used up by the overall reaction
- **(ii)** in allowing a reaction to proceed via a different route with lower activation energy, as shown by enthalpy profile diagrams

(d)

- **(i)** explanation of the terms *homogeneous* and *heterogeneous* catalysts
- **(ii)** explanation that catalysts have great economic importance and benefits for increased sustainability by lowering temperatures and reducing energy demand from combustion of fossil fuels with resulting reduction in CO_2 emissions

(e) the techniques and procedures used to investigate reaction rates including the measurement of mass, gas volumes and time

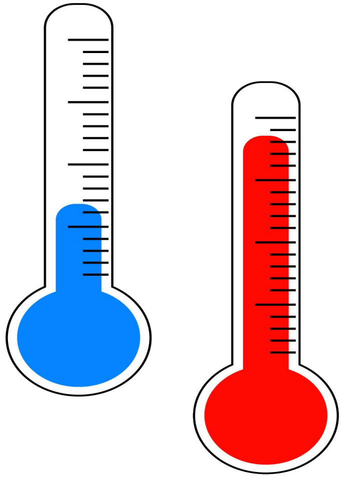
The Boltzmann distribution

(f) qualitative explanation of the Boltzmann distribution and its relationship with activation energy **(see also 3.2.1 c)**

(g) explanation, using Boltzmann distributions, of the qualitative effect on the proportion of molecules exceeding the activation energy and hence the reaction rate, for:

- **(i)** temperature changes
- **(ii)** catalytic behaviour **(see also 3.2.2 c)**.

Optimising Conditions



Changing the temperature can **change the value of K_c**

Whether K_c will increase or decrease with a change in temperature depends on whether the forward reaction is **exothermic** or **endothermic**

The effect of this can be **predicted** with Le Chatelier's principle

Optimising

Change in Temperature	Forward Reaction is...	ΔH	Change in K_c	Which means....
Increase	exothermic			
	endothermic			
Decrease	exothermic	-ve	increased	Products favoured
	endothermic	+ve	reduced	Reactants favoured

Optimising Conditions

High pressure/High temperature:

-
-
-

Low temperature:

- **Low rates** of reaction (**fewer collisions**, and fewer collisions are **successful**)
  - Therefore takes **more time** to produce a fixed amount of product from a fixed amount of reactant

Catalysts

- Equilibrium is reached **faster**, but the position of equilibrium is **unchanged**

Exemplar Exam Question – Long Answer

4) The reaction between ethene and steam can be used to produce ethanol on an industrial scale.

$$H_2C{=}CH_2\,(g) + H_2O\,(g) \rightleftharpoons CH_3CH_2OH\,(g)$$

$$\Delta H = -46\ kJ\ mol^{-1}$$

a) Explain the optimum temperature and pressure conditions needed to maximise the yield of ethanol, stating one disadvantage for each condition you identify. Exact details are not required.

[4 marks]

Command: State and explain – 4 short points with no calculation required

Direction: Identify temperature and pressure conditions and a disadvantage for each

Context: Optimising conditions to increase yield

Low temperature favours the exothermic forward reaction, but lowers the rate of reaction- therefore may be slower to produce ethanol. High pressure favours the pressure reducing forward reaction, but may be difficult and potentially dangerous to achieve

Exemplar Exam Question – Statement

4) The reaction between ethene and steam can be used to produce ethanol on an industrial scale.

$$H_2C{=}CH_2\ (g) + H_2O\ (g) \rightleftharpoons CH_3CH_2OH\ (g)$$

$$\Delta H = -46\ kJ\ mol^{-1}$$

b) Describe the effect the addition of a catalyst will have on this reaction

[2 marks]

Command: identify effects on this reaction

Direction: what will happen to the equilibrium?

Context: catalysts and their effects on reversible reactions

The reaction between ethene and steam can be used to produce ethanol on an industrial scale.

$$H_2C{=}CH_2\,(g) + H_2O\,(g) \rightleftharpoons CH_3CH_2OH\,(g)$$

b) Describe the effect the addition of a catalyst will have on this reaction
[2 marks]

Equilibrium will be reached faster (rate of reaction in both directions increased, as more collisions will have an energy greater than the activation energy) but not shifted in position

MINI MOCK PAPER

1) At high temperatures, steam will react in a reversible reaction with carbon in order to produce hydrogen and carbon monoxide.

In a sealed container of volume 2 dm^3 held at 1000°C , how many moles of steam are required to produce 1 mole of hydrogen at equilibrium?

At 1000 ° C, $K_c = 3 \times 10^{-2}\ mol^{-1}\ dm^3$

[4 marks]

2) Ammonium chloride is held in a sealed container under standard conditions

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

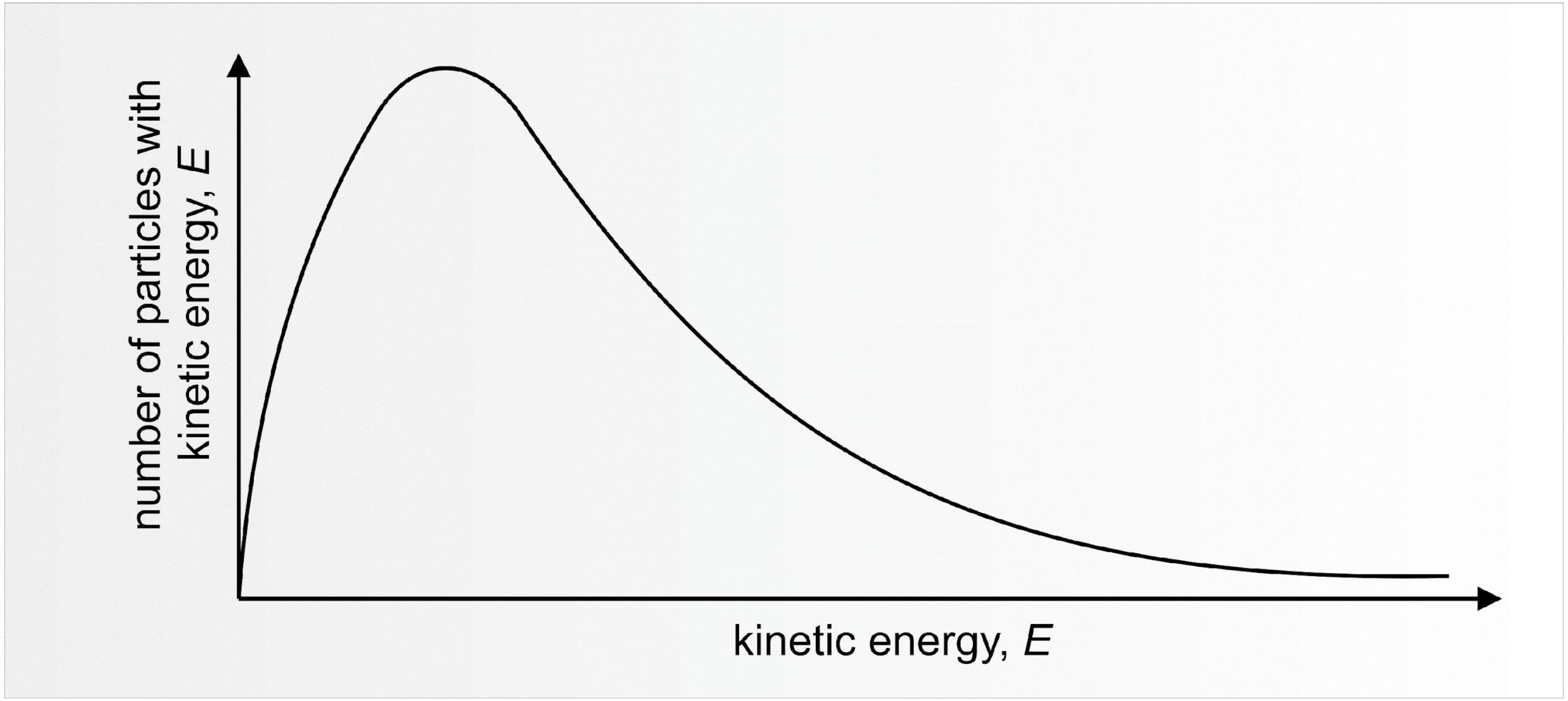
State what will happen to the conc. of HCl(g) :

a) If the concentration of ammonia gas is tripled. **[1 mark]**

b) If the pressure in the reaction vessel is doubled. **[1 mark]**

3) On the graph, draw the Maxwell Boltzmann distribution for a higher temperature. **[2 marks]**

Maxwell Boltzmann Distribution



Mini Mock Paper Answers

Mini Mock Paper

- In a sealed container of volume 2 dm^3 held at 1000°C , how many moles of steam are required to produce 1 mole of hydrogen at equilibrium?

at 1000 ° C K_c = 3×10^{-2} mol^{-1} dm^3

[3 marks]

Mini Mock Paper

Mini Mock Paper

Ammonium chloride is held in a sealed container under standard conditions

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

a)

____

b)

____

[2 marks]