Edexcel

AS - Level

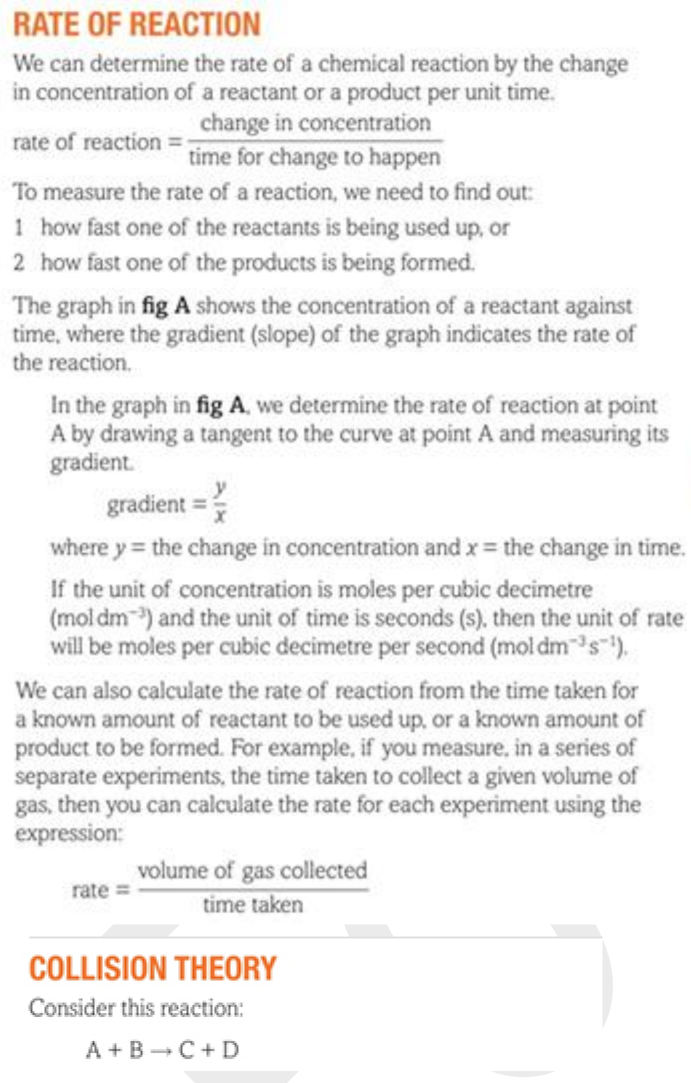
Chemistry

CODE: (WCH11)

Topic 9

Introduction to kinetics and equilibria

9A Reaction rate, conclusion theory and activation energy



RATE OF REACTION

We can determine the rate of a chemical reaction by the change in concentration of a reactant or a product per unit time.

$$\text{rate of reaction} = \frac{\text{change in concentration}}{\text{time for change to happen}}$$

To measure the rate of a reaction, we need to find out:

1 how fast one of the reactants is being used up, or
2 how fast one of the products is being formed.

The graph in **fig A** shows the concentration of a reactant against time, where the gradient (slope) of the graph indicates the rate of the reaction.

In the graph in **fig A**, we determine the rate of reaction at point A by drawing a tangent to the curve at point A and measuring its gradient.

$$\text{gradient} = \frac{y}{x}$$

where y = the change in concentration and x = the change in time.

If the unit of concentration is moles per cubic decimetre (mol dm^{-3}) and the unit of time is seconds (s), then the unit of rate will be moles per cubic decimetre per second (mol dm^{-3} s^{-1}).

We can also calculate the rate of reaction from the time taken for a known amount of reactant to be used up, or a known amount of product to be formed. For example, if you measure, in a series of separate experiments, the time taken to collect a given volume of gas, then you can calculate the rate for each experiment using the expression:

$$\text{rate} = \frac{\text{volume of gas collected}}{\text{time taken}}$$

COLLISION THEORY

Consider this reaction:

$$A + B \rightarrow C + D$$

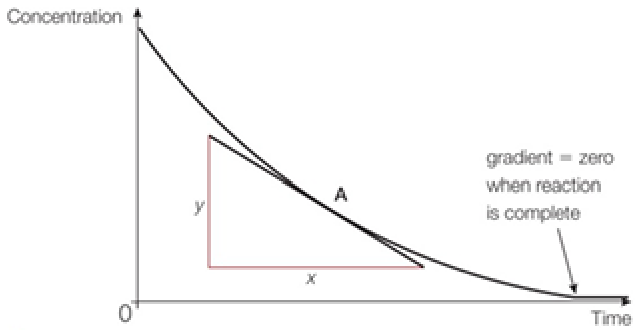


fig A A graph showing the concentration of a reactant against time.

The graph in **fig B** shows a plot of concentration against time, with tangents drawn to obtain the initial rate of reaction and the rate at time, *t*.

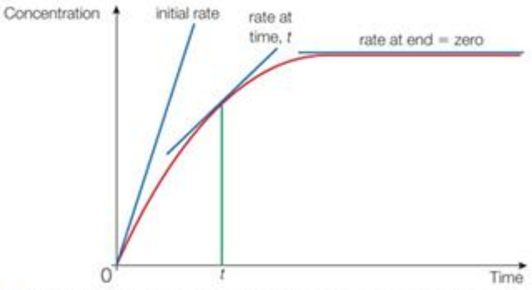


fig B A graph showing the concentration of a product against time.

In order for molecule A to react with molecule B, the two molecules must first of all collide with each other. If they collide they may react.

Why is there a possibility that the molecules may not react? This is because not all collisions between reactant molecules will result in a reaction. There are two requirements for a reaction to occur.

- The two molecules must collide with sufficient energy to cause a reaction - the activation energy E_a
- The two molecules must collide in the correct orientation.

ACTIVATION ENERGY, E_a

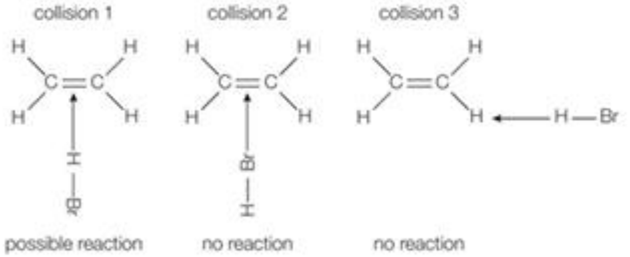
The activation energy is the minimum energy required for a reaction to occur. If particles collide with less energy than this, no reaction occurs. Activation energy acts as a barrier to the reaction, preventing collisions with energies equal to or greater than this.

ORIENTATION

Consider the reaction between ethene and hydrogen bromide, which you met in Topic 5:

The reaction can only happen if the hydrogen end of the H—Br molecule approaches the C=C of the ethene molecule. Any other collision between the two molecules will result in the molecules simply bouncing off each other.

Of the collisions shown in the figure below, only collision 1 may possibly lead to a reaction.



SUBJECT VOCABULARY

activation energy, E_a the minimum energy that colliding particles must possess for a reaction to occur

steric hindrance the slowing of a chemical reaction due to large groups within a molecule getting in the way of the attacking species

9A 2 Effect of concentration, pressure and surface area on rate of reaction

According to the collision theory, reactant particles have to collide with sufficient energy before they can react. It is sensible, therefore, to suggest that we can increase the rate of a reaction by increasing the frequency of collisions with sufficient energy between reactant particles.

THE EFFECT OF CONCENTRATION

For reactions in solution, an increase in concentration often causes an increase in reaction rate. For many reactions, if the concentration of a solution is increased, then the frequency of collisions between reacting solute particles also increases. This is because they are closer together as there are more of them in a volume of solution. The frequency of successful collisions increases (i.e. there are more successful collisions per second), which in turn produces an increase in the rate of reaction.

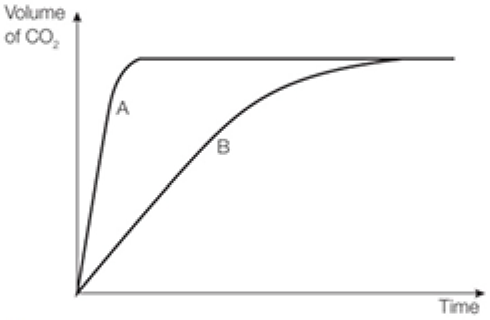


fig A A concentration-time graph showing the effect of the change in volume of carbon dioxide given off with time for the reaction between calcium carbonate and excess dilute hydrochloric acid.

Curve A represents the higher concentration of acid. You will notice that the gradient of curve A is always greater than the gradient of curve B. You will also notice that curve A levels off before curve B. Both factors indicate that the rate of reaction is greater for the higher concentration of acid.

THE EFFECT OF PRESSURE

For a reaction in which molecules collide and react in the gas phase, an increase in pressure will cause an increase in the rate of reaction.

The explanation is similar to that for concentration of solution. If the pressure of the gaseous mixture is increased, there will be more reactant molecules in a given volume of mixture. The frequency of collisions will increase. This will result in an increase in the rate of reaction.

Changing the pressure has almost no effect on reactions in the solid or liquid phase. This is because the volume of solids and liquids changes very little when they are put under pressure, so their particles do not move closer together.

THE EFFECT OF SURFACE AREA

For heterogeneous reactions involving a solid, a larger surface area of the solid will result in a faster reaction.

The reaction between magnesium and dilute hydrochloric acid is represented by this ionic equation:

$$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$$

Only collisions between the hydrogen ions and magnesium atoms on the *surface* of the magnesium can result in reaction. If the magnesium is powdered, the surface area is increased and hydrogen is given off more quickly.

The effectiveness of solid catalysts is also improved if they are finely divided. For example, the rate of the catalysed decomposition of hydrogen peroxide by manganese(IV) oxide is increased significantly if the catalyst is a powder rather than lumps. Here is the equation for the reaction:

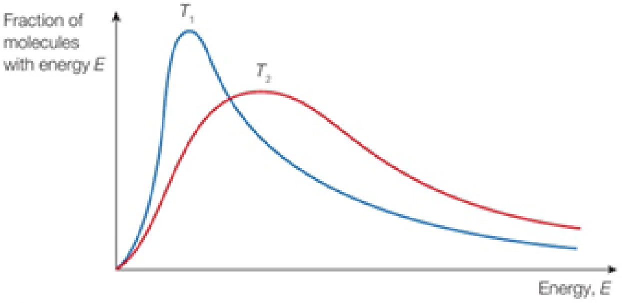
$$H_2O_2(aq) \xrightarrow{MnO_2(s)\text{ catalyst}} H_2O(l) + \tfrac{1}{2}O_2(g)$$

9A 3 Effect of temperature on rate of reaction

MAXWELL–BOLTZMANN DISTRIBUTION CURVES

The molecules in a sample of gas have a wide range of energies. To estimate what fraction of collisions will have the required activation energy, we need to know the energy distribution of the molecules.

This was first calculated in 1860 by James Clerk Maxwell and verified in 1872 by Ludwig Boltzmann. **Fig A** shows the distribution of molecular energies at two temperatures: T_1 (in blue) and T_2 (in red). T_2 is a higher temperature than T_1.



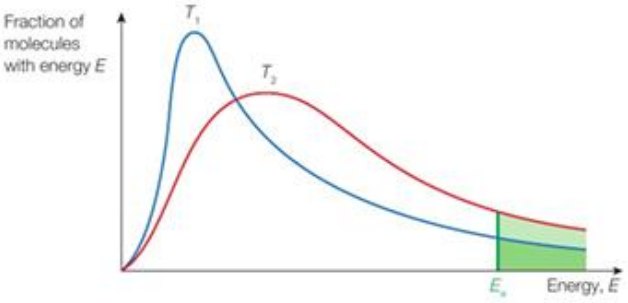
EXAM HINT

Make sure that you label the axes correctly if you are asked to reproduce this graph in an exam.

▲ **fig A** A graph showing the distribution of molecular energies at two temperatures. T_2 is a higher temperature than T_1.

There are four important points to note about the curves:

- Neither curve is symmetrical.
- Both curves start at the origin and finish by approaching the *x*-axis asymptotically.
- The area under each curve is the same, since the number of molecules has not changed.
- The peak of T_2 is displaced to the right and is lower than the peak of T_1.



▲ **fig B** A graph showing the distribution of molecular energies at two temperatures, $T_2 > T_1$

HOW CHANGES IN TEMPERATURE CAN AFFECT THE RATE OF A REACTION

Temperature changes affect the rate of a reaction by increasing the fraction of molecules with the required activation energy. This increase in successful collisions per second increases the reaction rate. However, the difference is small at high energies, making molecular energy distribution curves more appropriate.

COLLISIONS IN SOLUTION

In the gas phase, molecules move at high speeds, causing collisions between them. In solution, molecules are tightly packed, with solute molecules trapped in a solvent cage. Collisions between solute molecules are less frequent in solution due to solvent molecules getting in the way. However, trapped solute molecules can increase collision rates and react energetically, similar to gas phase collisions.

There are, therefore, two distinct stages to a reaction in solution:

- Firstly, the molecules have to come together, by a process of diffusion, in the same solvent cage.
- Secondly, they have to react.

There may, of course, be some reactions between solute molecules that have 'jumped out' of their cage and just happen to meet each other.

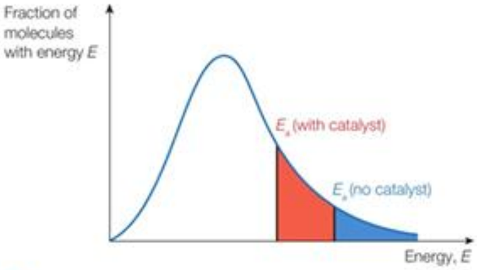
Although what is happening in a solution phase reaction is different from what is happening in the gas phase, the resulting kinetics are the same. For simple reactions involving two species, the chance of them meeting each other in solution is proportional to their concentrations, just as in the gas phase.

9A 4 Effect of catalysts on rate reaction

THE EFFECT OF CATALYSTS

A catalyst works by providing an alternative route for the reaction. This alternative route has a lower activation energy than the original route.

Fig A shows the effect on the fraction of molecules that have the required energy to react when a route of lower activation energy is available.



▲ **fig A** A graph showing the effect on the fraction of molecules that have the required energy to react when a catalyst is present.

The blue shaded area represents the fraction of molecules that have $E > E_a$ when no catalyst is present.

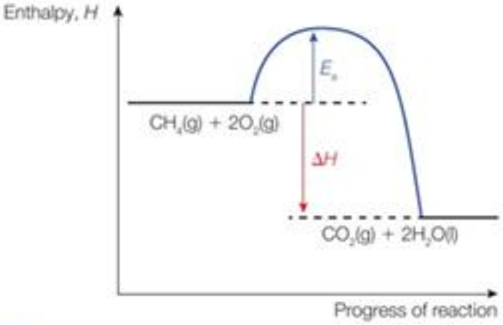
The combined blue and red shaded areas represent the fraction of molecules that have $E > E_a$ when a catalyst is present.

REACTION PROFILE DIAGRAMS

A reaction profile diagram is an extension of an enthalpy level diagram (see Topic 6B). In addition to showing the relative

enthalpy levels of reactants and products, it includes the activation energy for the reaction.

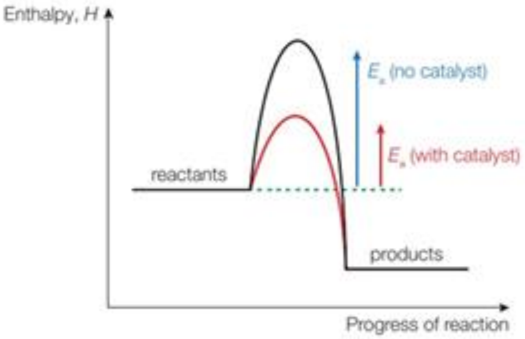
A typical reaction profile, not to scale, for the combustion of methane is shown in fig B.



▲ **fig B** A reaction profile for the combustion of methane.

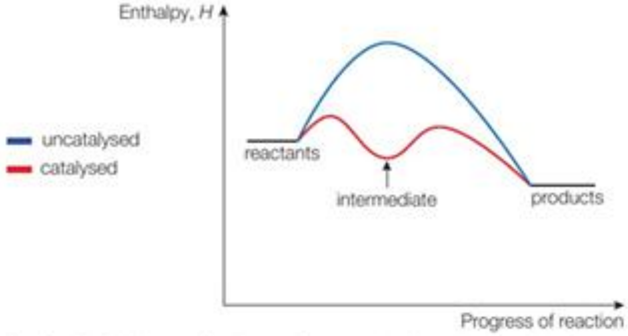
For an endothermic reaction, the enthalpy level of the products is above the enthalpy level of the reactants, but otherwise the profile is the same.

Fig C shows the simplified reaction profiles for an uncatalysed reaction and a catalysed reaction.



▲ **fig C** Simplified reaction profiles for an uncatalysed and a catalysed reaction.

If the catalysed reaction involves the formation of an intermediate, then the reaction profile is more complicated, as shown by the example in **fig D**.



▲ **fig D** Enthalpy profile diagram for a catalysed reaction involving the formation of an intermediate.

An example of a reaction that falls into this category is the reaction between peroxydisulfate ions and iodide ions, catalysed by Fe^{2+} ions.

The equation for the uncatalysed reaction is

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

The catalysed reaction occurs in two steps:

Step 1: $S_2O_8^{2-}(aq) + 2Fe^{2+}(aq) \rightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)$

Step 2: $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

The species present at the intermediate stage are $SO_4^{2-}(aq)$ and $Fe^{3+}(aq)$

N.B. The reaction can also be catalysed by Fe^{3+} ions. In this case the two steps will occur in reverse order.

CATALYSTS IN INDUSTRY

The first recorded use of a catalyst in industry was in 1746, when John Roebuck developed the lead chamber process for manufacturing sulfuric acid. Since then, catalysts have been increasingly used in the chemical industry. The development of catalysts has been mostly for economic reasons. However, more recently the development of catalysts has been for political and environmental reasons as well.

The two major economic advantages of the use of catalysts are:

- they increase the rate of a chemical reaction, meaning that more of the desired product can be made in a given time period
- reactions can take place at lower temperatures, resulting in a decrease in the energy costs to the manufacturer.

Most catalysts used in industry are **heterogeneous catalysts**. A heterogeneous catalyst is one that is in a different phase to that of the reactants. Solids are commonly used as heterogeneous catalysts for reactions involving gases. The most well-known examples are the use of iron in the Haber process and of vanadium(V) oxide in the Contact process (see Topic 17 (Book 2: IAL)).

CATALYSTS AND ATOM ECONOMY IN INDUSTRY

Chemical manufacturing often produces waste due to the formation of products with little commercial value. Using catalysts can lead to reactions with minimal co-products and reduce unwanted side reactions, making product separation easier. For example, zeolite catalysts have improved phenol production by reducing benzene oxidation to phenol using dinitrogen monoxide, while ibuprofen production uses hydrogen fluoride and Raney nickel, resulting in improved atom economy and reduced steps from six to three.

Some other considerations are:

- With fewer steps the energy costs are likely to be less.
- The percentage yield for each step may be higher (and fewer steps).
- There may be less product lost in separation after each step or separation may not be required until the end.

.

- The whole process may be quicker so that you get more product in a given time.

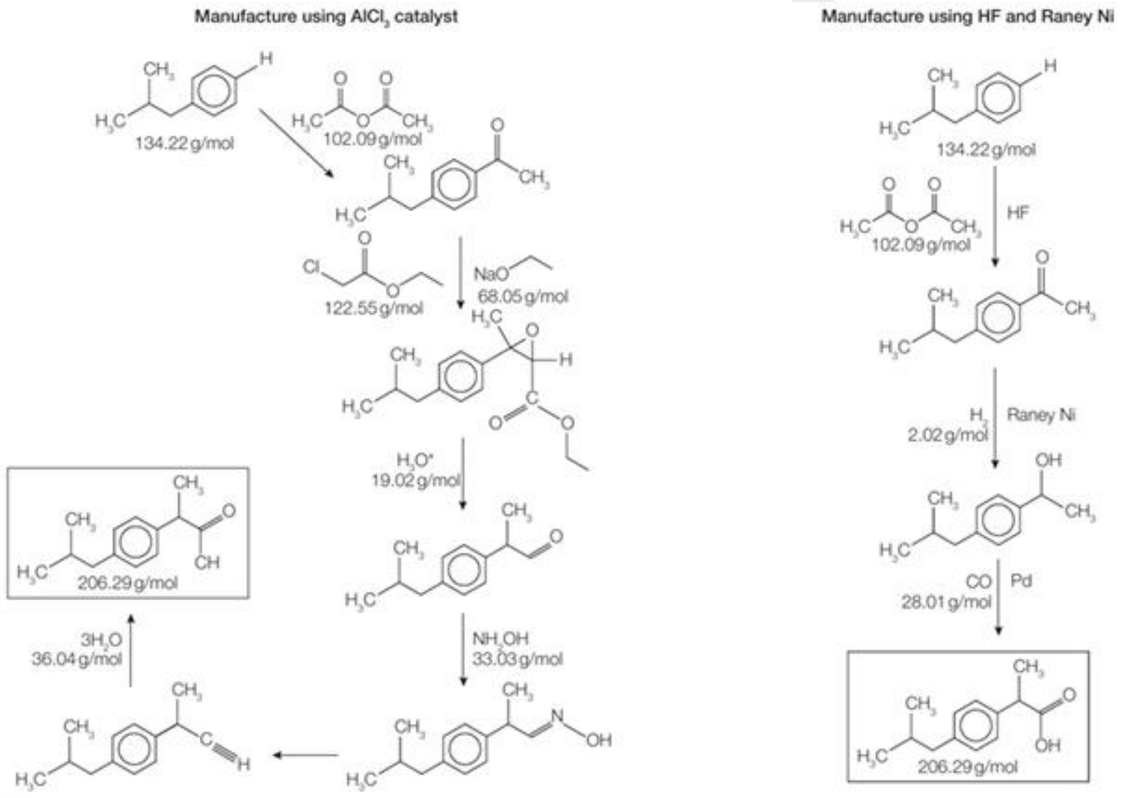
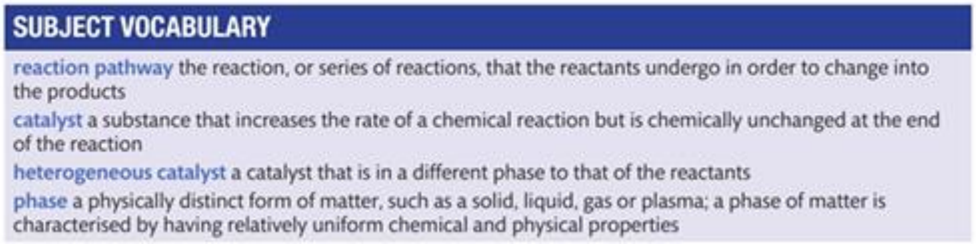


fig E Reaction pathways for two methods of manufacturing ibuprofen.



SUBJECT VOCABULARY

reaction pathway the reaction, or series of reactions, that the reactants undergo in order to change into the products

catalyst a substance that increases the rate of a chemical reaction but is chemically unchanged at the end of the reaction

heterogeneous catalyst a catalyst that is in a different phase to that of the reactants

phase a physically distinct form of matter, such as a solid, liquid, gas or plasma; a phase of matter is characterised by having relatively uniform chemical and physical properties

9B 1 Reversible reactions and dynamic equilibrium

IRREVERSIBLE AND REVERSIBLE REACTIONS

When a mixture of hydrogen and oxygen in a 2:1 molar ratio is ignited, water is produced. There is very little, if any, uncombined hydrogen or oxygen remaining at the end of the reaction. We often describe such reactions as 'irreversible'.

HOW TO DECIDE WHETHER A REACTION IS REVERSIBLE

Deciding whether a reaction is reversible or not depends on how carefully we measure the concentrations of reactants and products. For example, the reaction between dilute hydrochloric acid and aqueous sodium hydroxide appears to go to completion. Both acid and alkali are almost completely ionised in water, so the equation for the reaction is:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

Pure water has a slight electrical conductivity. This results from the ionisation of water molecules:

$$H_2O(l) \rightarrow H^+(aq) + OH^-(aq)$$

This indicates that the reverse reaction is taking place to a small extent. Since only one molecule in approximately 550 million is ionised, we usually ignore this small extent of ionisation. However, it becomes important when we study the pH scale of acidity.

In practical terms, if a reaction is more than 99% complete, we usually consider it to have gone to completion.

THE REACTION BETWEEN HYDROGEN AND IODINE

If a sample of hydrogen iodide is heated to 573 K in a closed container, it partially decomposes. The mixture formed is identical to that produced when starting with an equimolar mixture of hydrogen and iodine. The reaction is clearly reversible, and when there is no further change in the concentrations of the reactants and products, the system is said to be in 'equilibrium'.

The symbol $\rightleftharpoons$ is used in an equation to represent a reversible reaction. The equation for the reaction between hydrogen and iodine is therefore written as follows:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

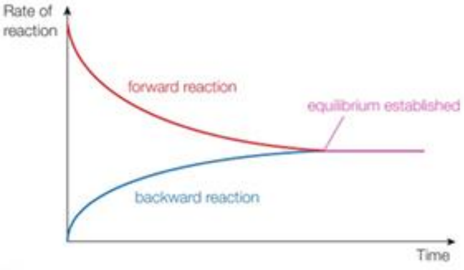
When the equation is written in this way, the reaction between hydrogen and iodine is called the *forward* reaction. The decomposition of hydrogen iodide into hydrogen and iodine is called the *backward* reaction.

HOW IS EQUILIBRIUM ESTABLISHED?

When hydrogen and iodine are heated, they react to form hydrogen iodide. As time goes on, the concentrations decrease, causing a decrease in forward reactions. As time goes on, the concentration of hydrogen iodide increases, causing a rise in backward reactions. This system reaches equilibrium, known as 'dynamic' equilibrium.

DYNAMIC EQUILIBRIUM

Fig A shows dynamic equilibrium.



▲ **fig A** Dynamic equilibrium.

Two conditions must be met for dynamic equilibrium to be established:

1 the reaction must be reversible
2 the reaction mixture must be in a closed container.
Three important features define a system that is in dynamic equilibrium:

- Both forward and backward reactions are continuously occurring.
- The rate of the forward reaction is equal to the rate of the backward reaction.
- The concentrations of reactants and products remain constant.

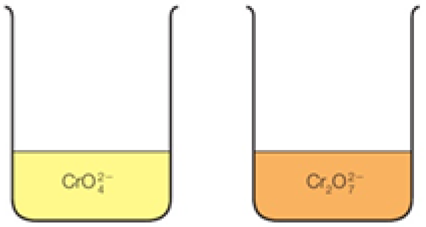
9B 2 Effect of changes in conditions on equilibrium composition

CHANGING THE COMPOSITION OF AN EQUILIBRIUM MIXTURE

When a reaction mixture reaches a position of equilibrium, the composition of the equilibrium mixture (i.e. the concentration of each component) will not alter as long as the conditions remain the same.

However, if we change a condition (i.e. add some more of, or remove one of, the components, or change the temperature of the system) then the composition may change. This is often referred to as 'changing the position of equilibrium', and we refer to the position being moved to the right, to the left or not changed.

For example, if acid is added to a yellow solution containing chromate(VI) ions, CrO_4^{2-}, the solution turns orange. This is because of an increase in the amount of dichromate(VI) ions, $Cr_2O_7^{2-}$.



$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$
yellow orange

fig A Beakers containing solutions of chromate(VI) ions and dichromate(VI) ions.

The equilibrium position moves to the right when the acid (H^+) is added. If sufficient alkali is added to the orange solution, it will turn yellow as the amount of CrO_4^{2-} ions increases and exceeds the amount of $Cr_2O_7^{2-}$ ions. The equilibrium position moves to the left when alkali (OH^-) is added.

We will consider four factors that may affect the position of equilibrium of a reaction mixture. These are:

1. concentration of a component
2. pressure of the system
3. temperature of the system
4. addition of a catalyst.

EFFECT OF A CHANGE IN CONCENTRATION

If we increase the concentration of one of the reactants in a system in equilibrium, the rate of the forward reaction will increase and more products will form. As the concentration of the products increases, the rate of the backward reaction increases and eventually a new equilibrium is established. The equilibrium position has moved to the right, with slightly more product being present than at the original position of equilibrium.

If the concentration of one of the reactants is *decreased*, the position of equilibrium moves to the left. Similar changes occur if the concentration of the product is increased or decreased.

The changes that occur are summarised in the **table A**.

CONCENTRATION OF REACTANTS	CONCENTRATION OF PRODUCTS	CHANGE IN POSITION OF EQUILIBRIUM
increased		to the right
decreased		to the left
	increased	to the left
	decreased	to the right

table A The change in the position of equilibrium when the concentration of reactants or products is increased or decreased.

EFFECT OF A CHANGE IN PRESSURE

The effect of pressure only applies to reversible reactions involving gases. At a given temperature, the pressure of a gaseous mixture depends only on the number of gas molecules in a given volume. So, the pressure of a gaseous mixture may be increased by reducing the volume and reduced by increasing the volume.

Alternatively, the pressure at which the reaction is carried out can be:

- increased by initially using more moles of the reactants in the same volume
- decreased by using fewer moles of the reactants in the same volume.

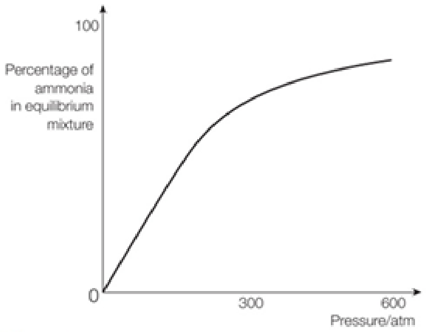
The effect of a change in pressure (at constant temperature) caused by changing the volume of the reaction mixture can be studied using a gas syringe and pushing in, or pulling out, the plunger. The effect depends on the total number of moles of gas on each side of the balanced equation, and is summarised in table B.

NUMBER OF MOLES OF REACTANTS	NUMBER OF MOLES OF PRODUCTS	CHANGE IN POSITION OF EQUILIBRIUM WHEN THE PRESSURE IS INCREASED
more	fewer	to the right
fewer	more	to the left
same	same	no change

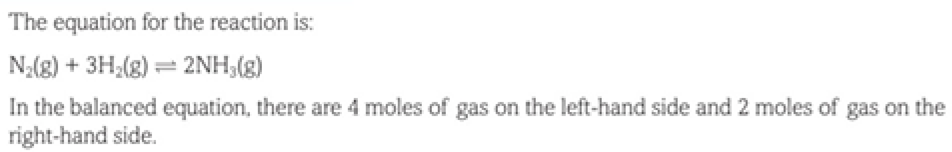
table B The change in the position of equilibrium when the pressure is increased and the number of moles of reactants or products is increased, decreased or not changed.

The reverse changes are true for a decrease in pressure.

The effect of changes in pressure as a result of using different amounts of gaseous reactants in a fixed volume container is shown in **fig B**. The reaction is between nitrogen and hydrogen, forming ammonia.



▲ **fig B** The effect of pressure changes using different amounts of nitrogen and hydrogen to form ammonia.



The equation for the reaction is:

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

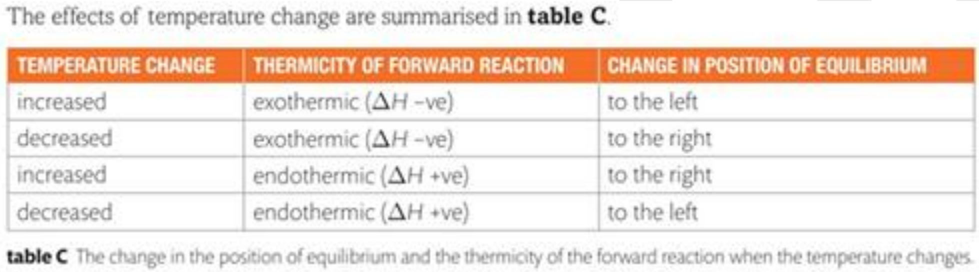
In the balanced equation, there are 4 moles of gas on the left-hand side and 2 moles of gas on the right-hand side.

The graph in fig B shows that the higher the pressure, the more ammonia there is in the equilibrium mixture formed. This agrees with the prediction in table B which states that an increase in pressure shifts the position of equilibrium to the side that has fewer moles of gas.

EFFECT OF A CHANGE IN TEMPERATURE

If the temperature of an equilibrium mixture is raised, the rates of both the forward and the backward reactions will increase. However, the increase in the rate of the endothermic reaction will be greater than the increase in the rate of the exothermic reaction.

Therefore, an increase in temperature will shift the position of equilibrium in the direction of the endothermic reaction. So, the change in position of equilibrium will depend on whether the forward reaction is exothermic or endothermic.
The effects of temperature change are summarised in table C.



The effects of temperature change are summarised in **table C**.

TEMPERATURE CHANGE	THERMICITY OF FORWARD REACTION	CHANGE IN POSITION OF EQUILIBRIUM
increased	exothermic (ΔH –ve)	to the left
decreased	exothermic (ΔH –ve)	to the right
increased	endothermic (ΔH +ve)	to the right
decreased	endothermic (ΔH +ve)	to the left

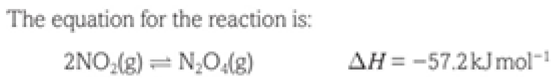
table C The change in the position of equilibrium and the thermicity of the forward reaction when the temperature changes.

EFFECT OF THE ADDITION OF A CATALYST

If a catalyst is added to a reaction mixture that is in equilibrium, the rate of both the forward and the backward reactions will increase. However, unlike the effect of increasing the temperature, the increase in rate will be the same for both reactions. So, the position of equilibrium is not altered. The advantage of adding a catalyst at the beginning of the reaction is that it will reduce the time required to establish equilibrium.

LIMITATIONS OF MAKING QUALITATIVE PREDICTIONS

Qualitative predictions about concentration, pressure, and temperature's impact on equilibrium position are predictions, not explanations for changes. Sometimes, it's impossible to predict the direction of change or the prediction is incorrect. For example, a gaseous mixture's temperature and pressure will rise when placed in hot water.



The equation for the reaction is:

$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H = -57.2\,kJ\,mol^{-1}$

The forward reaction is exothermic, causing an equilibrium shift to the left. An increase in temperature shifts it to the right, while an increase in pressure shifts it to the right. The temperature effect is greater, as the mixture becomes darker.

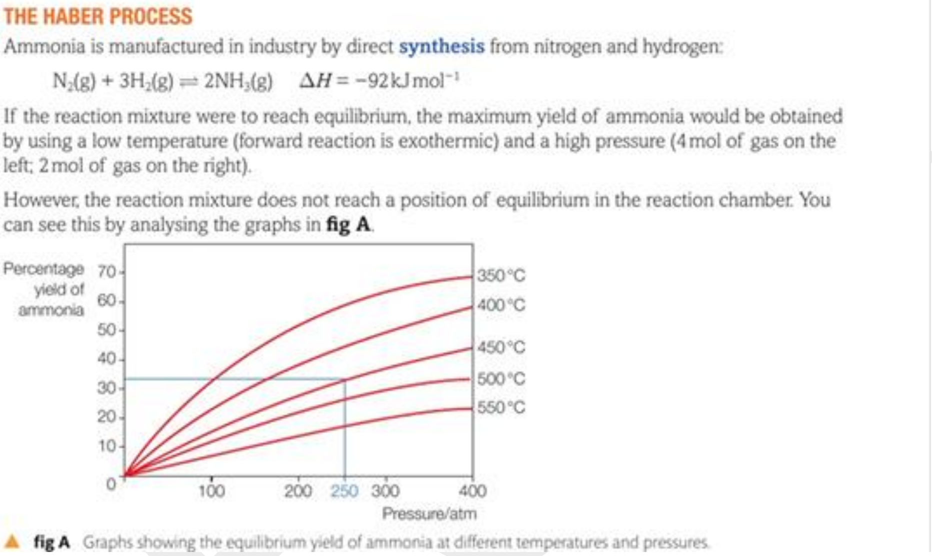
9B 3 Reversible reactions in industry

APPLYING THE PRINCIPLES OF REACTION RATES AND REVERSIBILITY TO INDUSTRIAL PROCESSES

The principles of reaction rates and reversibility play an important role in the design and conditions for many industrial processes. In order to maximise profits, the major problems chemists face are to convert the reactants into the products:

- as quickly as possible
- as completely as possible.

The first problem relates to kinetics (rate of reaction) and the second problem relates to reversibility.
The solution to each of these problems requires a careful choice of reaction conditions. This is easily demonstrated by considering the Haber process for the manufacture of ammonia.



THE HABER PROCESS

Ammonia is manufactured in industry by direct **synthesis** from nitrogen and hydrogen:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92\,kJ\,mol^{-1}$$

If the reaction mixture were to reach equilibrium, the maximum yield of ammonia would be obtained by using a low temperature (forward reaction is exothermic) and a high pressure (4 mol of gas on the left; 2 mol of gas on the right).

However, the reaction mixture does not reach a position of equilibrium in the reaction chamber. You can see this by analysing the graphs in **fig A**.

fig A Graphs showing the equilibrium yield of ammonia at different temperatures and pressures.

WHY ARE CONDITIONS OF 450°C AND 250 ATM USED?

The reaction between nitrogen and hydrogen is extremely slow at room temperature. This is mainly because of the very strong nitrogen to nitrogen triple bond [E(N=N) = 945 kJ mol-'] producing a high activation energy for the reaction. Even at high temperatures, the rate of reaction is slow in the absence of a suitable catalyst.

THE CONTACT PROCESS

Sulfuric acid is manufactured by the Contact process. The name of this process comes from the stage of the process that involves the reaction between sulfur dioxide and oxygen at the surface of a solid vanadium(V) oxide, V2Os, catalyst, to form sulfur trioxide.

$$SO_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons SO_3(g) \quad \Delta H = -96\,kJ\,mol^{-1}$$

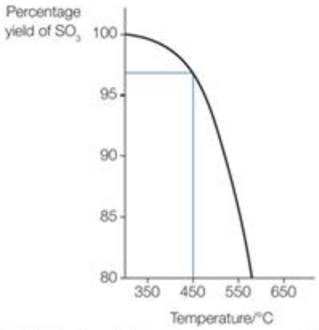


fig B A graph showing the percentage yield of sulfur trioxide against temperature at a pressure of 1 atm.

The forward reaction is exothermic, requiring a high temperature for high yield of SO(g). A moderately high temperature of 450°C is used, with a 97% yield at 1 atm pressure. Higher pressures increase yield.

The pressure employed in the Contact process is about 2 atm. This is high enough to maintain a constant flow of gases through the reaction chamber. Pressures higher than this are unnecessary since the yield is already very high. It is interesting to look at the mechanism of action of the vanadium(V) oxide. Unlike the iron in the Haber process, the vanadium changes its oxidation state during the reaction, but it then converts back to its original oxidation state at the end.

The mechanism for the reaction is:

$$SO_2(g) + V_2O_5(s) \rightleftharpoons SO_3(g) + V_2O_4(s)$$

$$V_2O_4(s) + \frac{1}{2}O_2(g) \rightleftharpoons V_2O_5(s)$$

SUBJECT VOCABULARY

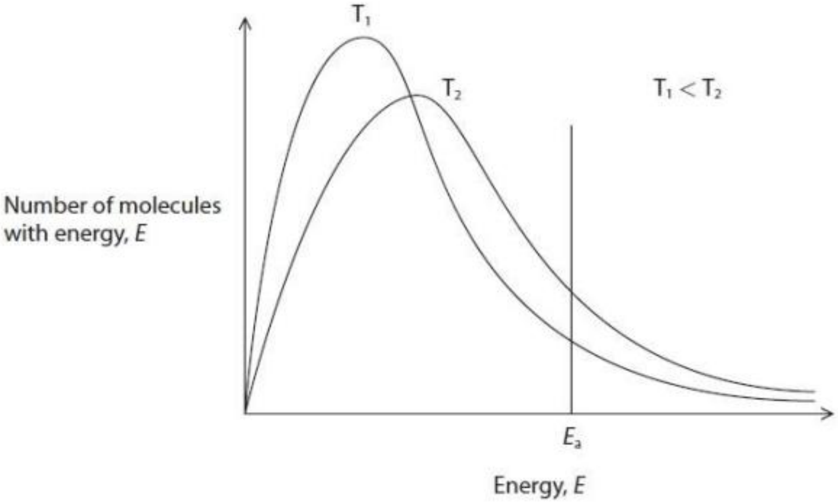
synthesis the production of chemical compounds by reaction from simpler substances

Revision questions

1.

This question is about reaction kinetics.

Maxwell-Boltzmann distributions of the molecular energies of particles in a gas are shown at two different temperatures.
The activation energy for the reaction, E_a, is labelled.



(i) The activation energy is the minimum energy required

(1)

☒ **A** for a reaction to take place when reactant molecules collide
☒ **B** for reactant molecules to collide
☒ **C** for all collisions to result in a reaction
☒ **D** for the particles to collide with the appropriate orientation

(ii) Explain, with reference to the gaseous particles, the differences in the two distributions.

(2)

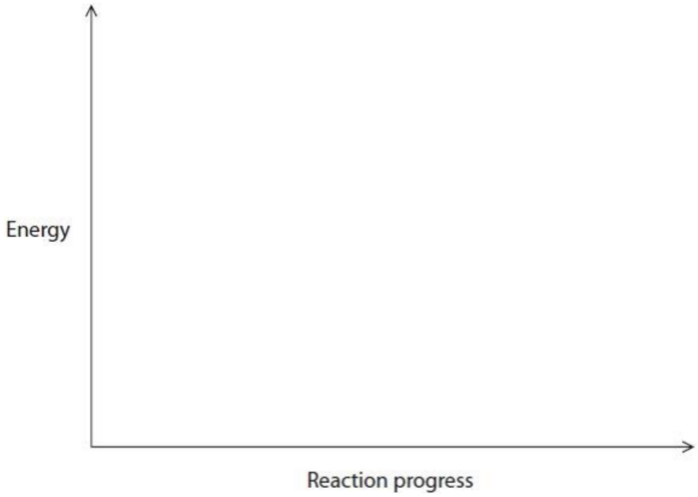
2.

This question is about reaction kinetics.

Reaction profiles can be used to show the effect of the addition of a catalyst on the energy changes during the course of a reaction.

(i) Draw fully labelled reaction profiles for the reaction both with and without a catalyst for an exothermic reaction.

(4)



(ii) State how a catalyst increases the rate of a chemical reaction.

(1)

3.

The progress of the reaction between iodine and propanone with an acid catalyst can be followed in an experiment using a titrimetric method.

Procedure

Step **1** Mix 25 cm^3 of 1 mol dm^{-3} aqueous propanone with 25 cm^3 of 1 mol dm^{-3} sulfuric acid in a beaker. Both these reactants are in excess.

Step **2** Start the stop clock as 50 cm^3 of 0.02 mol dm^{-3} iodine solution is added to the beaker. Mix the reactants thoroughly.

Step **3** Withdraw a 10.0 cm^3 sample of the reaction mixture, using a pipette, and transfer it to a conical flask.

Step **4** Add a spatula measure of sodium hydrogencarbonate, noting the exact time.

Step **5** Titrate the iodine present in the 10.0 cm^3 sample with 0.01 mol dm^{-3} sodium thiosulfate solution, using starch indicator.

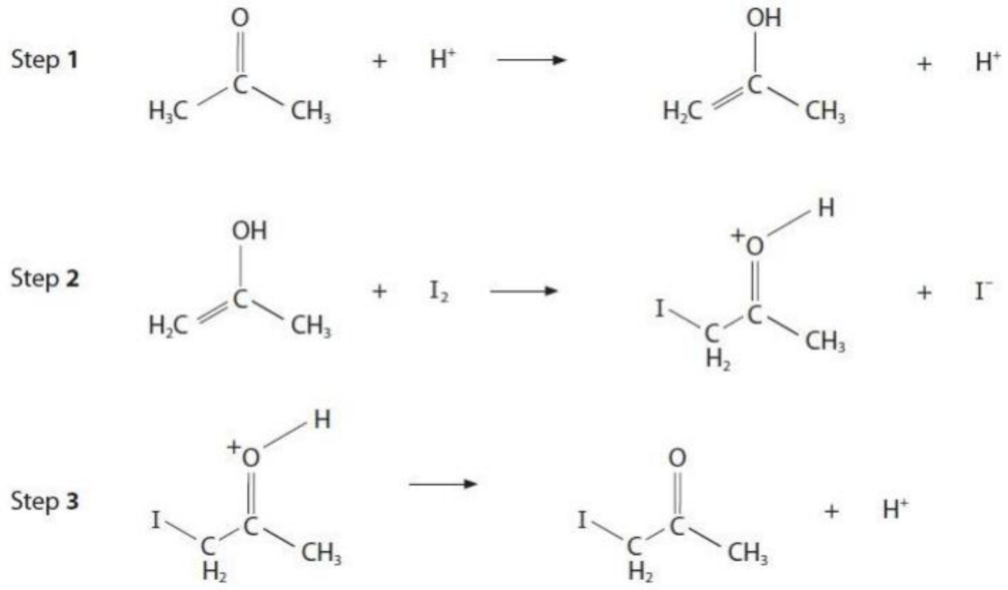
Step **6** Continue to withdraw 10.0 cm^3 samples about every two minutes, repeating Steps **4** and **5** with each sample.

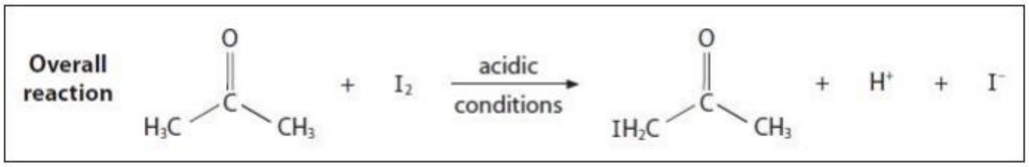
Some data from the experiment are shown.

Time sodium hydrogencarbonate is added / min	2.0	5.0	6.5	8.0	10.5	12.0
Volume of sodium thiosulfate / cm^3	19.2	15.5	14.0	12.1	9.5	7.2

The overall rate equation for the reaction is rate = $k[H^+(aq)][CH_3COCH_3(aq)]$.

A student researching the mechanism for the reaction found this example.





(i) Predict which of the three steps is the rate-determining step. Justify your answer.

(2)

(ii) The student stated that
'The hydrogen ions cannot be acting as a catalyst.
One hydrogen ion is a reactant in Step **1** but two hydrogen ions are formed as products in Steps **1** and **3**.'
Explain whether or not this statement is valid.

(2)

4.

Methanol is manufactured from a mixture of carbon monoxide and hydrogen.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \quad \Delta H = -90.8\ \text{kJ mol}^{-1}$$

Explain why, in the industrial process involving this reaction, a catalyst is used.

(2)

5.

One of the stages in the production of sulfuric acid from sulfide ores involves the oxidation of sulfur dioxide to sulfur trioxide. The equation for the reaction is

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta rH = -197\ \text{kJ mol}^{-1}$$

The conditions used in one industrial process are: 420°C and a pressure of 1.7 atm together with a vanadium(V) oxide catalyst.

It is proposed to change the conditions to 600°C and 10 atm pressure, while still using the same catalyst.

* Evaluate the feasibility of each of these changes in terms of their effect on the rate, yield and economics of the reaction.

(6)

6.

This question is about transition metals.

Manganate(VII) ions, MnO_4^-, react with ethanedioate ions in acid solution.

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

The reaction starts slowly, the rate of reaction then increases, before it decreases again.

Explain this sequence.

(3)

7.

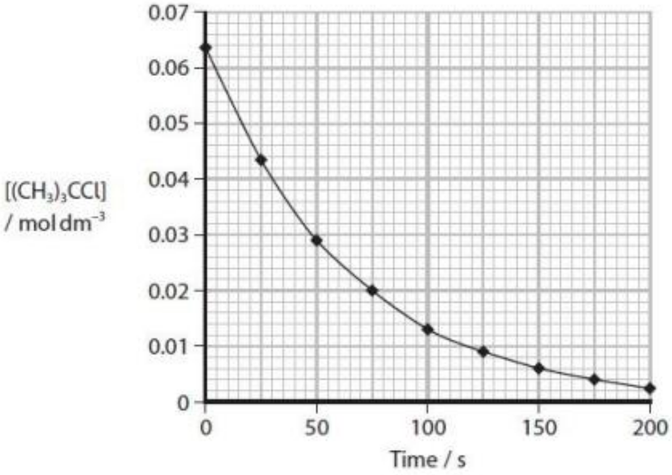
This question is about halogenoalkanes.

2-chloro-2-methylpropane can be hydrolysed by water.

The equation for this reaction is

$$(CH_3)_3CCl + H_2O \rightarrow (CH_3)_3COH + H^+ + Cl^-$$

The graph shows how the concentration of 2-chloro-2-methylpropane changes with time during an investigation of this reaction.



Calculate the rate of reaction at 50 s. Show your working on the graph. Include units with your final answer.

(3)

Rate of reaction at 50 s = ...

8.

Aqueous hydrogen peroxide decomposes according to the following equation.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

The decomposition is catalysed by manganese(IV) oxide.

This can be investigated by measuring the volume of oxygen produced at various times as the reaction proceeds.

Catalysts are not used up during a reaction. Manganese(IV) oxide acts as a heterogeneous catalyst.

Describe in outline a method to show that the manganese(IV) oxide is not used up in the decomposition of hydrogen peroxide **and** that it still functions as a catalyst.

(4)