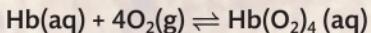


TOPIC 9 INTRODUCTION TO KINETICS AND EQUILIBRIA

A KINETICS | B EQUILIBRIA

Reaction kinetics is the study of rates of reactions. Some reactions in everyday life take place very quickly, while other reactions are very slow. The combustion of petrol in the engine of a racing car is very rapid and allows the car to travel at very fast speeds. The formation of stalactites and stalagmites by the decomposition of dissolved calcium hydrogencarbonate into solid calcium carbonate is very slow. It has taken hundreds of years for these to form in limestone caves, such as the one shown from central Saudi Arabia. Some types of food are kept in a refrigerator or a freezer to slow down the rate at which they go bad.

Haemoglobin is the substance in red blood cells responsible for transporting oxygen around the body. Each haemoglobin molecule attaches to four oxygen molecules in a reversible reaction:

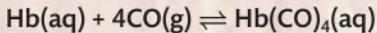


where 'Hb' stands for haemoglobin.

As long as there is sufficient oxygen in the air, a healthy equilibrium is maintained. However, at high altitudes, changes occur. The concentration of oxygen is lowered and this produces a shift in equilibrium to the left.

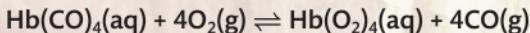
Without an adequate oxygen supply to the body's cells and tissues, you may feel light-headed. If you are not physically prepared for the change, you may need to breathe pressurised oxygen from an oxygen tank. This shifts the equilibrium to the right. For people born and raised at high altitudes, however, the body's chemistry performs the equilibrium shift to the right by producing more haemoglobin.

If you are exposed to carbon monoxide, it bonds to haemoglobin in preference to oxygen and sets up the following reversible reaction:



Carboxyhaemoglobin is formed, which is even redder than haemoglobin, so one sign of carbon monoxide poisoning is a flushed face.

Carbon monoxide in small quantities can cause headaches and dizziness, but larger concentrations can be fatal. To reverse the effects of the carbon monoxide, pure oxygen must be introduced to the body. It will react with the carboxyhaemoglobin to produce oxygenated haemoglobin, along with carbon monoxide:



The gaseous carbon monoxide thus produced is removed from the body when the person exhales.

MATHS SKILLS FOR THIS TOPIC

- Recognise and make use of appropriate units in calculations
- Recognise and use expressions in decimal and ordinary form
- Use an appropriate number of significant figures
- Plot two variables from experimental or other data
- Construct and/or balance equations using ratios

What prior knowledge do I need?

- The effect of changes in concentration of solutions, pressure of gases, temperature, surface area of solids and the use of a catalyst on the rate of a reaction
- Simple experiments to demonstrate these effects
- Explanations of these effects using the collision theory
- Examples of reversible reactions such as the action of heat on ammonium chloride
- The concept of dynamic equilibrium
- Predicting the effect of changing the temperature and pressure of the equilibrium position

What will I study in this topic?

- The concept of activation energy
- The Maxwell-Boltzmann model of distribution of molecular energies
- The role of catalysts in increasing the rate of chemical reactions
- Reaction profiles for both uncatalysed and catalysed reactions
- The effect of concentration of a reactant on the position of equilibrium
- Reversible reactions in industry

What will I study later?

Topic 11 (Book 2: IAL)

- Order of reaction and rate equations
- Experimental methods of determining rate of reaction
- Experimental method of determining activation energy
- The importance of reaction rate data in determining mechanisms for organic reactions

Topics 11 and 17 (Book 2: IAL)

- Homogeneous and heterogeneous catalysis

Topic 12 (Book 2: IAL)

- The relationship between total entropy change and equilibrium constant

Topic 13 (Book 2: IAL)

- The equilibrium constant in terms of concentrations, K_c and in terms of partial pressures, K_p
- Calculating values for K_c and K_p
- The effect of changing the temperature on the value of K_c and K_p

Topic 14 (Book 2: IAL)

- Acid-base equilibria

9A 1 REACTION RATE, COLLISION THEORY AND ACTIVATION ENERGY

LEARNING OBJECTIVES

- Know what is meant by the term 'rate of reaction'.
- Calculate the rate of a reaction from:
 - (i) the gradient of a suitable graph, by drawing a tangent, either for initial rate or at a time t
 - (ii) data showing the time taken for a reaction, using

$$\text{rate} = \frac{1}{\text{time}}$$

- Understand that reactions take place only when collisions have sufficient energy, known as the 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.

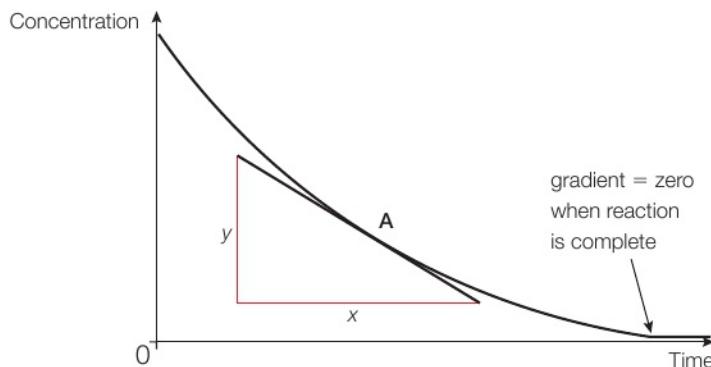


fig A A graph showing the concentration of a reactant against time.

The gradient decreases as the rate decreases, and becomes zero when all of the reactant is used up.

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 ($\text{mol dm}^{-3} \text{s}^{-1}$).

Sometimes it is more convenient to measure the concentration of the product formed over a period of 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 .

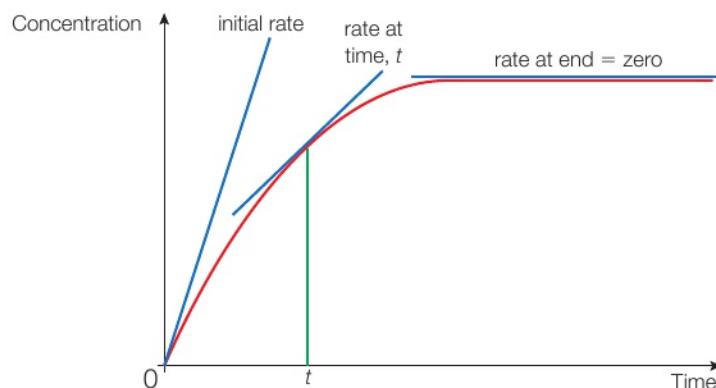


fig B A graph showing the concentration of a product against time.

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:

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

This is illustrated in **table A**.

TIME TAKEN TO COLLECT 20.0 cm^3 OF GAS / s	RATE OF REACTION / $\text{cm}^3 \text{s}^{-1}$
10.0	2.00
20.0	1.00
40.0	0.50
80.0	0.25

table A The rate of reaction can be calculated from the time taken for a known amount of product to be formed.

COLLISION THEORY

Consider this reaction:



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 that colliding particles must possess for a reaction to occur. If the particles collide with less energy than the activation energy, they simply bounce apart and no reaction occurs. Think of the activation energy as a barrier to the reaction. Only those collisions that have energies equal to or greater than the activation energy result in a reaction.

Any chemical reaction results in the breaking of some bonds (needing energy) and the making of new ones (releasing energy). Obviously, some bonds have to be broken before new ones can be made. Activation energy is involved in breaking some of the original bonds.

Where collisions are relatively gentle, there is not enough energy available to start the bond-breaking process, and so the particles do not react.

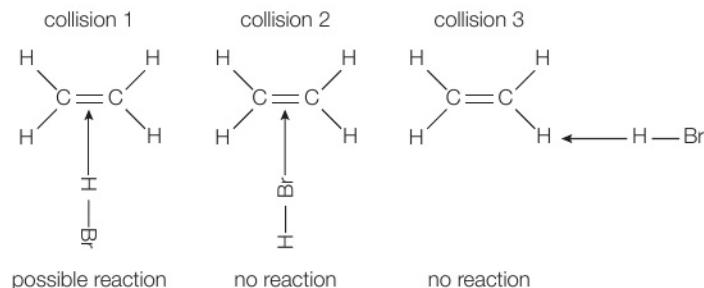
ORIENTATION

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.



DID YOU KNOW?

When the shapes of molecules influence reactions, we say that there is a ‘steric factor’ involved in the reaction. In some cases, the atoms (or groups of atoms) in a molecule can hinder (interfere with) the course of a reaction. If an atom or group of atoms is particularly large, then it can get in the way of an attacking species. If this happens, we say that the reaction suffers from ‘steric hindrance’.

For example, the halogenoalkane 2-bromomethylpropane, $(\text{CH}_3)_3\text{CBr}$, is hydrolysed rapidly when added to water. However, the mechanism of the reaction does not involve attack by the water molecule on the $\delta+$ carbon atom attached to the bromine, as it does with bromomethane, CH_3Br .

This is because the three methyl groups are so large that they prevent the water molecule approaching the carbon atom sufficiently close to interact with it. The mechanism for the reaction is totally different.

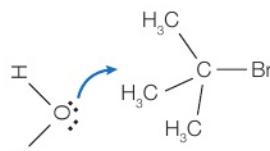


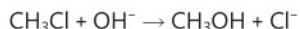
fig C The three methyl groups do not allow the water molecule to approach the carbon atom of the C–Br bond.

ADDITIONAL READING

If you would like to find out more, you can research S_N1 and S_N2 mechanisms for the hydrolysis of halogenoalkanes on the internet.

CHECKPOINT

1. At room temperature and pressure, in each cubic decimetre of gas there are about 1×10^{32} collisions every second. Why, therefore, are reactions between gases not completed in a fraction of a second?
2. Why do many reactions involving organic compounds have to be heated or refluxed for long periods of time?
3. Chloroalkanes, such as chloromethane (CH_3Cl), can be hydrolysed to alcohols by heating with aqueous sodium hydroxide. The hydroxide ion acts as a nucleophile attacking the $\delta+$ carbon atom and replacing the chlorine:



When tetrachloromethane (CCl_4) is heated under reflux with aqueous sodium hydroxide, no reaction takes place. Suggest a reason why.

4. What will happen if a hydrogen atom and a chlorine atom collide and their combined energy of collision is $1.0 \times 10^{-18}\text{ J}$? [$E(\text{H}-\text{Cl}) = 431\text{ kJ mol}^{-1}$].

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

LEARNING OBJECTIVES

- Understand, in terms of the collision theory, the effect of changes in concentration of solution, pressure of a gas and surface area of a solid on the rate of a chemical reaction.

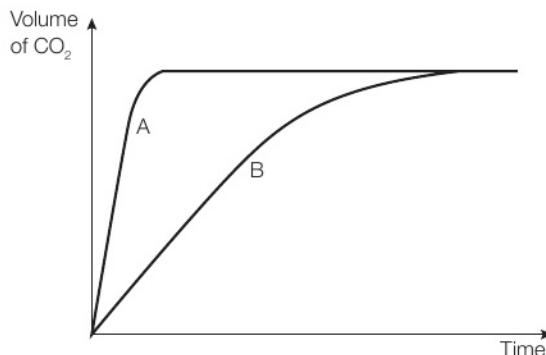
According to the collision theory, reactant particles have to collide with sufficient energy before they can react. It is sensible, therefore, to suggest that we can increase the rate of a reaction by increasing the frequency of collisions with sufficient energy between reactant particles. This is often true, but as in so many situations in chemistry, there are exceptions. You will learn about these in **Topic 11 (Book 2: IAL)**.

Collisions that result in a reaction are called *successful* collisions.

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.

The graph in **fig A** shows 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.



▲ **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

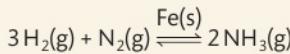
For a reaction in which molecules collide and react in the gas phase, an increase in pressure will cause an increase in the rate of reaction.

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.

ADDITIONAL READING**THE HABER PROCESS**

It is interesting to look at the situation that exists when a reaction between two gases takes place on the surface of a solid that is in contact with the reaction mixture. This is the case with the catalytic conversion of hydrogen gas and nitrogen gas to make ammonia in the Haber process.



The reaction between the hydrogen and nitrogen molecules takes place at the surface of the iron catalyst, but only at selected sites called 'active' sites. At the high pressures used in the Haber process, there are always more reactant molecules than there are active sites. For this particular reaction, an increase in pressure will not increase the rate of reaction, since all of the active sites are already occupied.

LEARNING TIP

A heterogeneous reaction is one in which the reactants are in more than one phase; for example, a solid and a gas, or a solid and a solution.

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:



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.

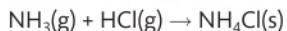
The effectiveness of solid catalysts is also improved if they are finely divided. For example, the rate of the catalysed decomposition of hydrogen peroxide by manganese(IV) oxide is increased significantly if the catalyst is a powder rather than lumps. Here is the equation for the reaction:

**EXAM HINT**

It is important to remember that for a reaction at a position of equilibrium between reactants and products, a catalyst does not affect the position of equilibrium. It only speeds up the rate at which the system achieves equilibrium.

CHECKPOINT**SKILLS** → **REASONING**

1. Ammonia and hydrogen chloride react in the gas phase to form ammonium chloride.



State and explain the effect, if any, on the rate of reaction of:

- (a) halving the volume of the container at constant temperature
- (b) increasing the pressure by adding more ammonia at constant volume and temperature.

2. (a) Draw a concentration-time graph for the reaction between marble chips (calcium carbonate) and excess dilute hydrochloric acid. Place the concentration of the hydrochloric acid on the vertical axis.
- (b) On the same axes, draw the curve that would be obtained if the reaction was repeated at the same temperature, with the same mass of powdered marble.
- (c) Explain the reason for the different-shaped curves obtained.

9A 3 EFFECT OF TEMPERATURE ON RATE OF REACTION

LEARNING OBJECTIVES

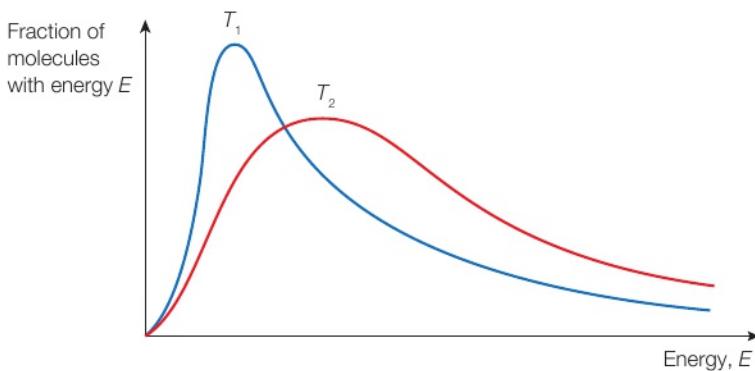
- Understand qualitatively, in terms of the Maxwell-Boltzmann distribution of molecular energies, how changes in temperature can affect the rate of a reaction.

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

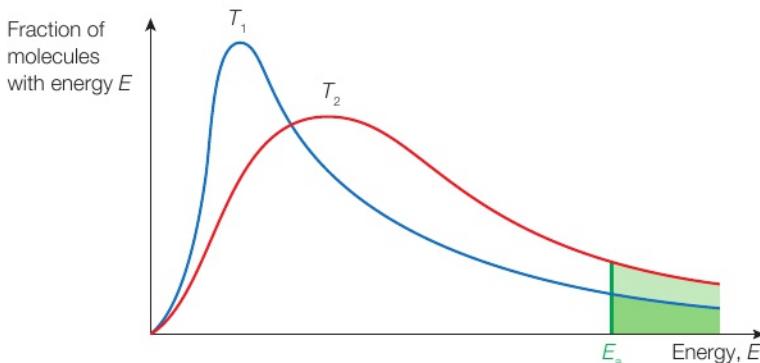
Make sure that you label the axes correctly if you are asked to reproduce this graph in an exam.

▲ **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 .

The curves in the graph in **fig B**, show, once again, the molecular distribution of energies at two temperatures, T_1 and T_2 , where $T_2 > T_1$. E_a is the activation energy for the reaction.



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

The area shaded dark green represents the fraction of molecules that have the required energy to react at T_1 .

The combined area shaded in dark green and light green represents the fraction of molecules that have the required energy to react at T_2 .

It is easy to see that the fraction of molecules that can react at the higher temperature is greater.

LEARNING TIP

The Maxwell-Boltzmann diagram showing the effect of temperature consists of two curves and *one* activation energy line.

If you are asked to use the Maxwell-Boltzmann distribution curves as part of your explanation, you must make it clear that the area under the curve to the right of the activation energy line represents the fraction of molecules that has enough energy for the collisions to be successful.

HOW CHANGES IN TEMPERATURE CAN AFFECT THE RATE OF A REACTION

We can now explain the effect of an increase in temperature on the rate of a reaction.

An increase in temperature increases the fraction of molecules that possess the required activation energy. The rate of the reaction increases because the number of successful collisions per second increases.

The argument used above assumes that the fraction of collisions with energy greater than or equal to E_a is the same as the fraction of molecules with this energy. This is not exactly true. However, the difference is very small at high energies when the fraction is very small. Under these circumstances, it is reasonable to draw and use the molecular energy distribution curve instead of the collision distribution curve.

LEARNING TIP

When explaining the increase in reaction rate owing to an increase in temperature, it is important to mention that the number of *successful* collisions per second increases, and not just that the *overall* number of collisions per second increases.

Although there is an increase in the overall collision frequency, the effect of this is negligible (very small) compared to the increase in frequency of collisions that have energy equal to or greater than the activation energy.

COLLISIONS IN SOLUTION

In the gas phase, molecules are moving around at high speeds so they frequently collide with one another. At a pressure of 100 kPa and a temperature of 298 K, a single molecule might have somewhere between 10^9 and 10^{10} collisions per second, depending on its size.

In solution, the situation is different. The molecules are much more closely packed together so there is not a lot of 'space' between them. In low-to-medium concentrations, most of the solution is solvent, so solute molecules tend to be entirely surrounded by solvent molecules. These solute molecules are said to be trapped in a 'solvent cage'.

You may think that collisions between solute molecules would be far less frequent than similar collisions in the gas phase because the solvent molecules will get in the way. However, there are situations in which a number of solute molecules become trapped in the same solvent cage. This increases the collision rate between the solute molecules and, if the collisions are sufficiently energetic, they may react, just as in the gas phase.

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.

CHECKPOINT

1. State the effect of increasing the temperature on the rate of:
 - (a) an exothermic reaction
 - (b) an endothermic reaction.
2. (a) Draw Maxwell-Boltzmann distribution curves for a gas at two temperatures, T_c and T_h , where $T_c < T_h$.
 - (b) Indicate a suitable value for the activation energy of the reaction and use the curves to explain the effect of lowering the temperature on the rate of reaction.

9A 4 EFFECT OF CATALYSTS ON RATE OF REACTION

LEARNING OBJECTIVES

- Be able to interpret the action of a catalyst in terms of a qualitative understanding of the Maxwell–Boltzmann distribution of molecular energies.
- Understand the role of catalysts in providing alternative reaction routes of lower activation energy.
- Be able to draw the reaction profiles of both uncatalysed and catalysed reactions including the energy level of the intermediate formed with the catalyst.
- Understand the use of catalysts in industry to make processes more sustainable by using less energy and/or higher atom economy.
- Understand the use of a solid (heterogeneous) catalyst for industrial reactions involving gases, in terms of providing a surface for the reaction.

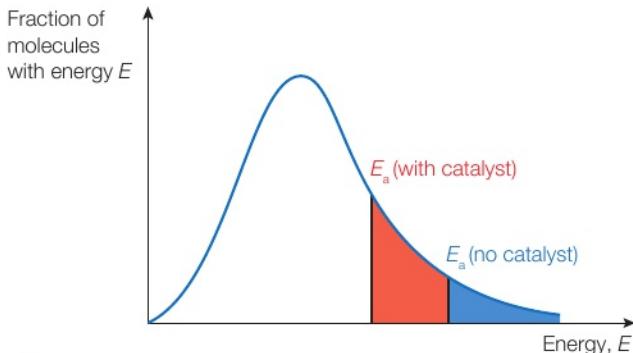
THE EFFECT OF CATALYSTS

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

EXAM HINT

It is wrong to say that a catalyst lowers the activation energy for a particular **reaction pathway**. It provides a *different* pathway with a lower activation energy.

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.

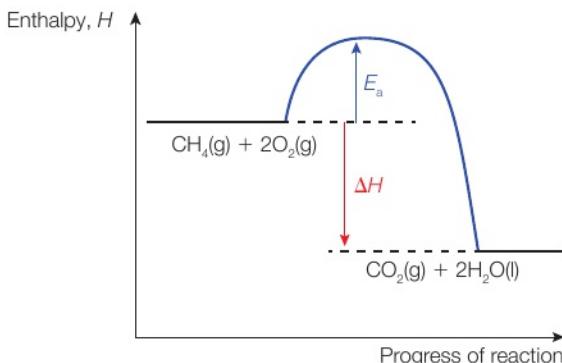
LEARNING TIP

The Maxwell–Boltzmann diagram showing the effect of a catalyst consists of one curve and two activation energy lines. Do not confuse this with the diagram used to show the effect of temperature.

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.

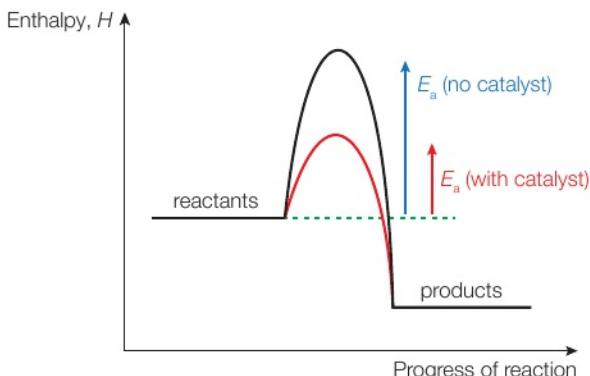
A typical reaction profile, not to scale, for the combustion of methane is shown in **fig B**.



▲ **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**.

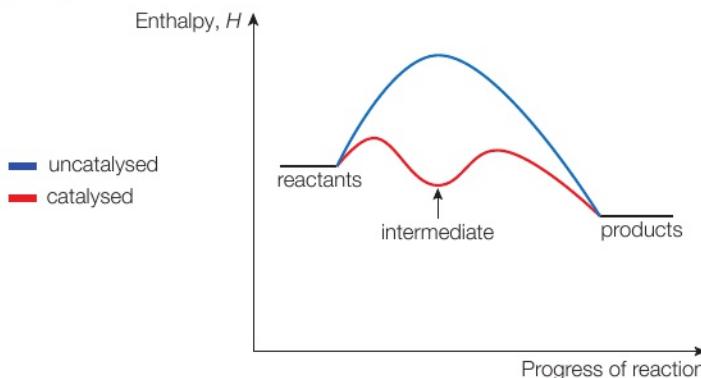
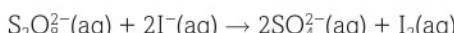


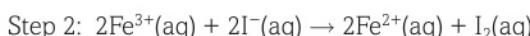
fig D Enthalpy profile diagram for a catalysed reaction involving the formation of an intermediate.

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



The catalysed reaction occurs in two steps:



The species present at the intermediate stage are $\text{SO}_4^{2-}(\text{aq})$ and $\text{Fe}^{3+}(\text{aq})$

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.

EXAM HINT

Longer exam questions may ask you to compare different industrial processes. Remember to include ideas about yield and atom economy as well as issues of energy and broader environmental issues.

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)**).

A solid catalyst provides a surface on which the gas molecules can adsorb and then react. The product molecules then desorb from the surface and more reactant molecules take their place. This process is described in more detail in **Topic 11 (Book 2: IAL)**.

DID YOU KNOW?

Environmental catalysts have also been developed to remove toxic products from industrial waste materials. Do some research to identify these catalysts.

CATALYSTS AND ATOM ECONOMY IN INDUSTRY

In the manufacture of chemicals, waste is produced when products are formed that are of little or no commercial value.

Using catalysts can lead to reactions being developed that make the desired product with little or no co-product. They may also reduce side reactions producing other unwanted products, making product separation easier.

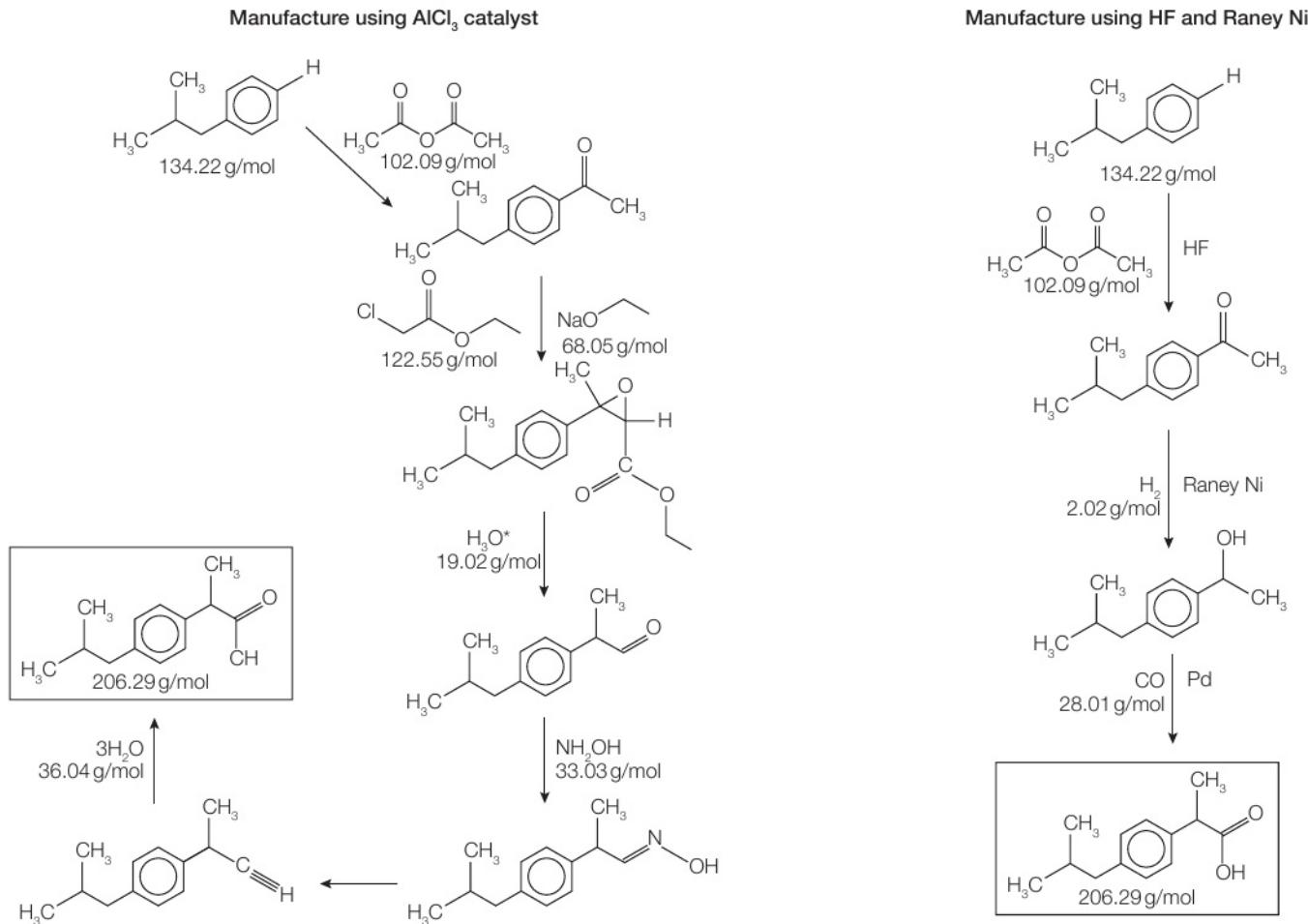
A good example is the manufacture of phenol. The development of zeolite catalysts has meant that benzene can be oxidised to phenol using dinitrogen monoxide (N_2O), with nitrogen as the only other product. The alternative manufacture from benzene via cumene has a much lower atom economy.

The manufacture of ibuprofen is another example. The original method for making it used six steps with aluminium chloride as a catalyst, and several other reagents. Although behaving as a catalyst, the aluminium chloride cannot be recovered.

A newer method uses two catalysts, hydrogen fluoride and Raney nickel (an alloy of nickel and aluminium). These can be recovered and reused many times. The effect of using better catalysts has been to improve the atom economy of the process and to reduce the number of steps needed from six to three. You can see this in **fig E**, but you don't need to know these steps.

Some other considerations are:

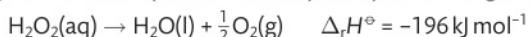
- With fewer steps the energy costs are likely to be less.
- The percentage yield for each step may be higher (and fewer steps).
- There may be less product lost in separation after each step or separation may not be required until the end.
- The whole process may be quicker so that you get more product in a given time.



▲ **fig E** Reaction pathways for two methods of manufacturing ibuprofen.

CHECKPOINT

1. An aqueous solution of hydrogen peroxide decomposes very slowly at room temperature into water and oxygen. The decomposition is catalysed by solid manganese(IV) oxide.



- Using the same axes, draw labelled reaction profiles for the reaction both with and without manganese(IV) oxide.
- Explain the change in rate of reaction that occurs when manganese(IV) oxide is added to the hydrogen peroxide solution.

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

1 REVERSIBLE REACTIONS AND DYNAMIC EQUILIBRIUM

LEARNING OBJECTIVES

- Know that many reactions are readily reversible.
- Know that reversible reactions can reach a state of dynamic equilibrium in which:
 - (i) both forward and backward reactions are still occurring
 - (ii) the rate of the forward reaction is equal to the rate of the backward reaction
 - (iii) the concentrations of reactants and products remain constant.

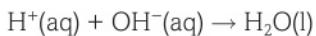
IRREVERSIBLE AND REVERSIBLE REACTIONS

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'.

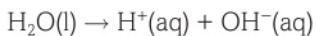
Most combustion reactions are in this category since they are highly exothermic. That is, ΔH is large and negative. However, ΔH is small for many reactions, especially in organic chemistry. These reactions may not go to completion. At the end of the reaction, detectable amounts of the reactants remain, mixed with the product. These reactions are called 'reversible' reactions.

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:



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



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.

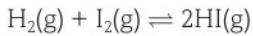
In practical terms, if a reaction is more than 99% complete, we usually consider it to have gone to completion.

THE REACTION BETWEEN HYDROGEN AND IODINE

If a mixture of hydrogen and iodine vapour in a 1:1 molar ratio is heated to 573 K in a closed container, about 90% of the hydrogen and iodine react to form hydrogen iodide. Provided the reaction mixture remains in the closed container at 573 K, 10% of the hydrogen and iodine will remain unreacted even if you leave the reaction mixture for a long time.

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:



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?

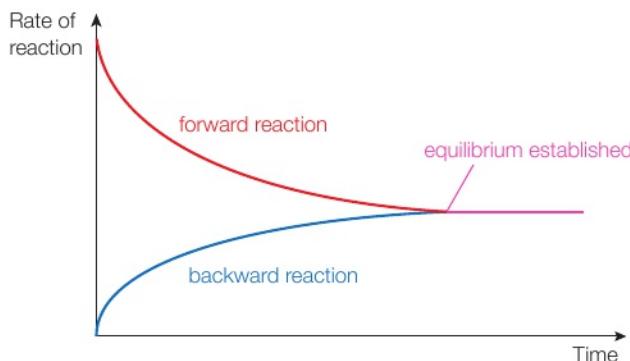
When the mixture of hydrogen and iodine is heated, the two gases start to react and form hydrogen iodide. With increasing time, the concentrations of hydrogen and iodine decrease, so the rate of the forward reaction decreases.

As soon as some hydrogen iodide is formed, it starts to slowly decompose. With increasing time, however, the concentration of hydrogen iodide increases, so the rate of the backward reaction increases.

Eventually, the rates of the forward and the backward reactions become equal. After this point there is no further change in concentrations of reactants and products. The system is now in equilibrium. It is referred to as a 'dynamic' equilibrium since both forward and backward reactions are taking place at the same time, and also at the same rate.

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:

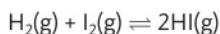
- Both forward and backward reactions are continuously occurring.
- The rate of the forward reaction is equal to the rate of the backward reaction.
- The concentrations of reactants and products remain constant.

LEARNING TIP

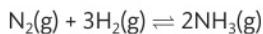
Remember these features!

CHECKPOINT

1. Explain what is meant by the term 'dynamic equilibrium' with reference to the following reaction:



2. Nitrogen and hydrogen react reversibly to form ammonia:



1 mol of nitrogen and 3 mol of hydrogen were mixed in a closed container and allowed to reach equilibrium. Twenty per cent of the nitrogen and hydrogen were converted into ammonia.

Draw three graphs, using a single set of axes, to show how the number of moles of nitrogen, hydrogen and ammonia vary with time.

9B

2 EFFECT OF CHANGES IN CONDITIONS ON EQUILIBRIUM COMPOSITION

LEARNING OBJECTIVES

- Predict and justify the qualitative effect of a change in concentration, pressure or temperature, or the addition of a catalyst, on the composition of an equilibrium mixture.

CHANGING THE COMPOSITION OF AN EQUILIBRIUM MIXTURE

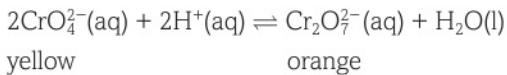
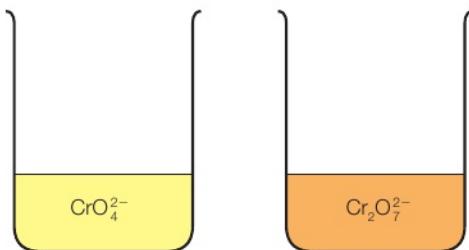
When a reaction mixture reaches a position of equilibrium, the composition of the equilibrium mixture (i.e. the concentration of each component) will not alter as long as the conditions remain the same.

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, $\text{Cr}_2\text{O}_7^{2-}$.

EXAM HINT

Note that there is no change in the oxidation number of the chromium in this reaction.



▲ **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 $\text{Cr}_2\text{O}_7^{2-}$ 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:

- concentration of a component
- pressure of the system
- temperature of the system
- 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.

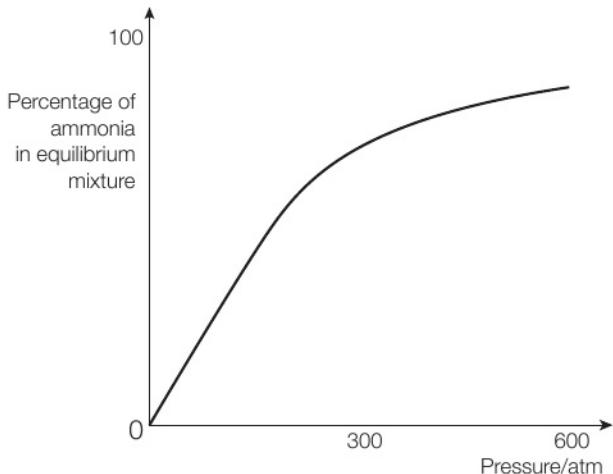
The effect of a change in pressure (at constant temperature) caused by changing the volume of the reaction mixture can be studied using a gas syringe and pushing in, or pulling out, the plunger. The effect depends on the total number of moles of gas on each side of the balanced equation, and is summarised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

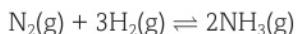
The reverse changes are true for a decrease in pressure.

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:



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.

EXAM HINT

When you answer questions dealing with the effect of temperature change, avoid phrases such as 'an increase in temperature favours the endothermic direction'. An increase in temperature 'favours' (i.e. increases the rate of) *both* the endothermic and the exothermic reactions.

The important point to remember is that it increases the rate of the endothermic reaction *more than* it increases the rate of the exothermic reaction.

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**.

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

The first thing to recognise is that the qualitative predictions we have made about the effect of concentration, pressure and temperature on the position of equilibrium are just that – predictions.

The arguments we have used are *not* explanations of why changes sometimes occur. In fact, there are occasions when it is impossible to predict the direction of change, or indeed when the prediction turns out to be incorrect.

For example, if an equilibrium mixture of $\text{NO}_2(\text{g})$ (brown) and $\text{N}_2\text{O}_4(\text{g})$ (colourless) in a closed container is placed into a beaker of hot water at room temperature, both the temperature and the pressure of the gaseous mixture will rise.

The equation for the reaction is:



Because the forward reaction is exothermic, we would predict that an increase in temperature would shift the equilibrium to the left.

However, since there are fewer moles of gas on the right-hand side of the equation, we would predict that an increase in pressure would shift the equilibrium to the right.

We do not know which effect is greater, so we cannot make a prediction of which way the equilibrium will shift. In practice, the mixture becomes darker in colour, so the temperature effect must be greater than the pressure effect. This is because the equilibrium must have shifted to the left to produce more brown $\text{NO}_2(\text{g})$.

It might be interesting for you to do further research into the limitations of qualitative predictions. For example, what would you expect to happen if you add more nitrogen at constant pressure and temperature to an equilibrium mixture of nitrogen, hydrogen and ammonia? What would you expect to happen if you added an inert gas at constant volume and temperature to an equilibrium mixture of sulfur dioxide, oxygen and sulfur trioxide? The results may surprise you!

DID YOU KNOW?

A principle known as Le Chatelier's Principle is sometimes recommended as a useful way of working out the possible change in position of equilibrium when a condition is altered. There is no requirement to learn or use this principle in this course.

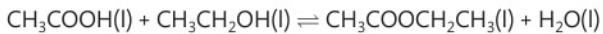
Le Chatelier's Principle does not offer an explanation as to why a position of equilibrium alters.

Explanations are only possible through the use of the equilibrium constant, K . This concept will be introduced in Topic 13 (Book 2: IAL).

CHECKPOINT

SKILLS ➤ REASONING

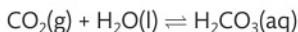
1. Ethanoic acid and ethanol react reversibly to produce ethyl ethanoate and water:



Assume $\Delta H = 0 \text{ kJ mol}^{-1}$

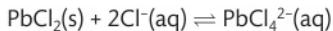
- (a) Predict the effect on the position of equilibrium of increasing the temperature. Justify your answer.
(b) Suggest why the reaction mixture is heated when used to prepare ethyl ethanoate.

2. When carbon dioxide dissolves in water, it forms a solution containing some carbonic acid:



Carbon dioxide is less soluble in hot water than in cold water. Is ΔH for the forward reaction negative or positive? Justify your answer.

3. A sample of insoluble solid lead(II) chloride, PbCl_2 , is shaken with some dilute hydrochloric acid and left until an equilibrium mixture containing some undissolved lead(II) chloride is established:



State what would be observed if concentrated hydrochloric acid was added to the mixture. Justify your answer.

4. In each case, predict whether the equilibrium position shifts to the right or the left, or is unaltered when the pressure is increased at constant temperature.

- (a) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI(g)}$
(b) $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$
(c) $2\text{O}_3(\text{g}) \rightleftharpoons 3\text{O}_2(\text{g})$
(d) $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO(g)} + 6\text{H}_2\text{O(g)}$

9B 3 REVERSIBLE REACTIONS IN INDUSTRY

LEARNING OBJECTIVES

- Evaluate data to explain the necessity, for many industrial processes, of reaching a compromise between the yield and the rate of reaction.

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:

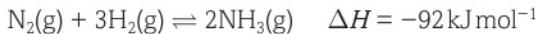
- as quickly as possible
- as completely as possible.

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.

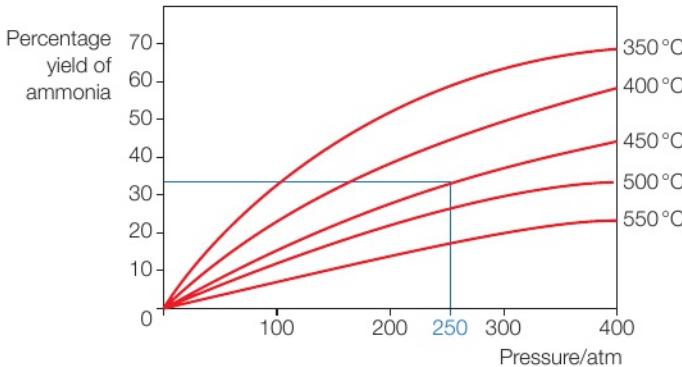
THE HABER PROCESS

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



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.

The conditions used in the Haber process are typically 450 °C and 250 atmospheres (atm) pressure. If the reaction mixture were to reach equilibrium, then the yield of ammonia would be just over 30%. In practice, the yield is approximately 15%. This is because the reaction mixture does not remain in the reaction chamber long enough for equilibrium to be established.

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 [$E(\text{N}\equiv\text{N}) = 945 \text{ kJ mol}^{-1}$] 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. Many metals will catalyse this reaction, including tungsten and platinum. However, these metals are very expensive, so iron is used in the industrial process.

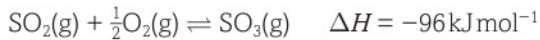
The catalyst does not function very efficiently at low temperatures, so a relatively high temperature is necessary. However, a very high temperature would be uneconomical, because of the extra energy costs involved. It might also result in a decreased yield, since the increase in rate of the backward reaction will be greater than the increase in rate of the forward reaction. This is debatable, because the reaction mixture may not be in the reaction chamber for long enough for this to make a significant difference. For these reasons, a compromise temperature of 450 °C is used.

Under these conditions, the actual yield is about 50% of the equilibrium yield. If we assume this to be true for other pressures at a temperature of 450 °C, then a pressure of 100 atm would give a yield of around 12–13%, while a pressure of 400 atm would give a yield of around 27–28%. The higher the pressure, the larger the energy costs of compressing the gases; the lower the pressure, the lower the yield. Once again, a compromise is reached between yield and cost and a pressure of 250 atm is used.

In order to increase the efficiency of the process, the unreacted nitrogen and hydrogen, after separation from the ammonia, are mixed with fresh nitrogen and hydrogen and fed into the reaction chamber.

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, V₂O₅, catalyst, to form sulfur trioxide.



The forward reaction is exothermic, so a low temperature would favour a high yield of SO₃(g). You can see this in the graph in **fig B**, which shows the percentage yield of SO₃(g) against temperature at a pressure of 1 atm.

Once again, the catalyst would not be very effective at low temperatures, so a moderately high temperature of 450 °C is used.

At 1 atm pressure, the yield of SO₃(g) is already very high at around 97%. Higher pressures would increase the yield since there are fewer moles of gas on the right-hand side of the equation.

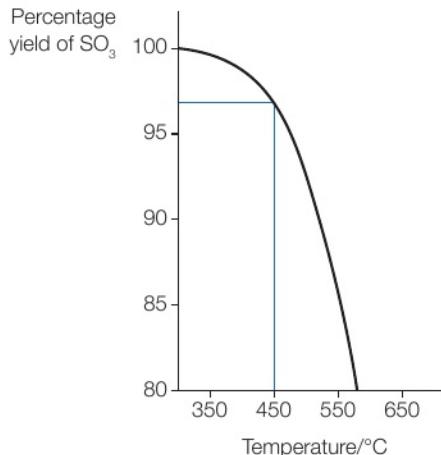
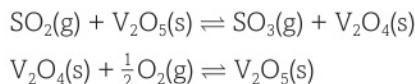


fig B A graph showing the percentage yield of sulfur trioxide against temperature at a pressure of 1 atm.

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:



CHECKPOINT

SKILLS ➤ **REASONING**

1. The first step in the manufacture of nitric acid, HNO₃(l), from ammonia involves the exothermic reaction of ammonia with oxygen gas to form nitrogen monoxide NO(g) and steam. This is a reversible reaction that can reach a position of equilibrium.
 - (a) Write an equation for the reaction between ammonia and oxygen to form nitrogen monoxide and steam.
 - (b) Assuming the reaction mixture reaches a position of equilibrium, make a qualitative prediction of the conditions of temperature and pressure that would produce the maximum yield of NO(g).
 - (c) In industry, the conditions used are high temperature and a pressure of around 7 atm. Suggest why these conditions are different to those you predicted in (b) to obtain a high yield of NO(g) in the equilibrium mixture. Again, assume that the reaction reaches a position of equilibrium.
2. ▶ The densities of diamond and graphite are 3.5 and 2.3 g cm⁻³, respectively. The change from graphite to diamond can be represented by the equation:

$$\text{C(graphite)} \rightleftharpoons \text{C(diamond)} \quad \Delta H = +2 \text{ kJ mol}^{-1}$$
 Suggest the conditions of temperature and pressure that would favour the formation of diamond from graphite. Justify your answers.

SUBJECT VOCABULARY

synthesis the production of chemical compounds by reaction from simpler substances

IN AT THE DEEP END

SKILLS ➔ CREATIVITY

In this spread we will consider the role of chlorine in the treatment of water; specifically in swimming pools. Water-borne pathogens are still responsible for millions of deaths across the world and so effective treatment is important both for drinking water and for recreation. However, this article raises some additional issues about the use of chlorine.

SOMETHING IN THE WATER...



fig A 'A better way to cut the chloroform levels would be to reduce the amount of organic matter in the water.'

Public swimming pools contain high levels of a chemical linked to miscarriage.

A team led by Mark Nieuwenhuijsen at Imperial College, London, found that the chloroform* content of eight pools in the city was on average 20 times as high as in drinking water. The chloroform is formed when chlorine disinfectants react with organic compounds in the water.

From an article in *New Scientist* magazine

Some studies in the US have suggested there's a correlation between the amount of chlorinated tap water drunk daily by pregnant women and their risk of miscarriage. Chloroform and related chemicals in the water have been blamed. Nieuwenhuijsen accepts that the studies linking chlorination and miscarriage are inconsistent. 'But pregnant women are advised to go swimming', he says. 'And there is a much higher level of chloroform in pools than in drinking water, so it could be a bigger pathway for exposure.'

Chloroform is produced when chlorine in the water reacts with flecks of skin, body-care products and other organic materials. Swimmers absorb the chemical through their skin, by swallowing water or by inhaling the gas.

Nieuwenhuijsen found an average of 113.3 micrograms of chloroform per litre in 40 samples from eight different pools. He also found that the more people using the pool and the warmer the water, the higher the concentration of chloroform.

But stopping chlorination is not the answer, says Nieuwenhuijsen, as alternative disinfectants such as ozone or ultraviolet light don't work so well. 'Chlorine is very effective', he says. 'A better way to cut the chloroform levels would be to reduce the amount of organic matter in the water by making sure people shower before a swim, and by improving filtration.'

*Chloroform = trichloromethane

DID YOU KNOW?

Chlorine gas is an irritant that causes serious damage to the eyes and respiratory system by reacting with water to form hydrochloric acid. For this reason, it was used as a chemical weapon in the First World War. The strong odour and the green colour of the gas made it easy to detect so more effective alternatives were soon developed. One of these was phosgene – a gas with the chemical formula COCl_2 . The gas was formed by the reaction of chlorine and carbon monoxide in the presence of light so it was named by combining the Greek 'phos' (meaning light) and 'genesis' (meaning birth). Since 1925, over 190 states have signed up to the Geneva Protocol, which prohibits the use of chemical and biological weapons.

SCIENCE COMMUNICATION

1. You can have some fun with this question! Imagine you are the editor of a local newspaper. It is a slow news day and you have to lead with this article and give the story maximum impact. Using some illustrations and the key parts of this article, write the most sensational article you can, using only the information given above.

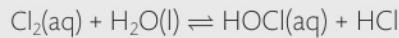
CHEMISTRY IN DETAIL

2. (a) The IUPAC name for chloroform is trichloromethane. Draw out the displayed formula for trichloromethane.

(b) Describe the shape of the trichloromethane molecule and, using diagrams, explain why the molecule has a permanent dipole.

3. Convert 113.3 µg/l into a micromolar concentration. ($1 \mu\text{g} = 1 \times 10^{-6} \text{ g}$)

4. When chlorine is added to water the following equilibrium is set up:



(a) The reaction shown is an example of a disproportionation reaction. State what 'disproportionation' means.

(b) There are two acids formed in the reaction above: HCl is a strong acid, and HOCl is a weak acid. Explain the difference between a strong and a weak acid.

5. When HOCl is dissolved in water, the following equilibria is set up:



(a) How would an increase in the pH value of this solution affect the above equilibrium? Explain your answer.

(b) How would a greater dilution of HOCl(aq) affect the above equilibrium? Explain your answer.

6. A second chloro-organic molecule detected in the analysis in the study had the molecular formula $\text{C}_2\text{H}_3\text{Cl}_3$. Draw both structural isomers of $\text{C}_2\text{H}_3\text{Cl}_3$ and name them.

WRITING SCIENTIFICALLY

When you are asked to state the meaning of a word or phrase, you'll need to describe the term clearly and concisely in your own words. There might be more than one way it can be described.

ACTIVITY

Design an experiment to investigate how a change of pH in a sample of swimming pool water might influence bacterial growth. Your plan should include:

- all the important variables that need to be considered
- how bacterial growth might be quantified experimentally
- how you would ensure experimental reliability.

It might be worth looking at other experimental protocols that you can find either in science books or on the internet. This may help you appreciate the variables that are important and how they can be controlled.

SKILLS ➔ CREATIVITY**THINKING BIGGER TIP**

Think of everything you have learned so far in the course and how it fits together to inform your understanding as a scientist. By now, you should be able to use correct terminology, analyse sources, write scientifically, and think like a scientist.

1 Look at the following statements. Which statement explains correctly why a small increase in temperature leads to a significant increase in the rate of a gas phase reaction?

- A The frequency of collisions between molecules is greater at a higher temperature.
- B The activation energy of the reaction is less when the gases are at higher temperature.
- C The frequency of collisions between molecules with kinetic energy greater than the activation energy is greater at a higher temperature.
- D The average kinetic energy of the molecules is slightly greater at a higher temperature. [1]

(Total for Question 1 = 1 mark)

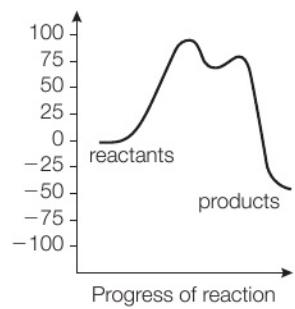
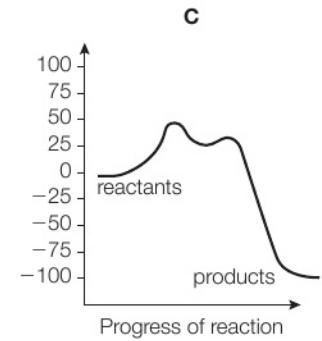
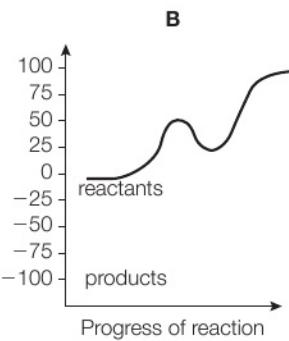
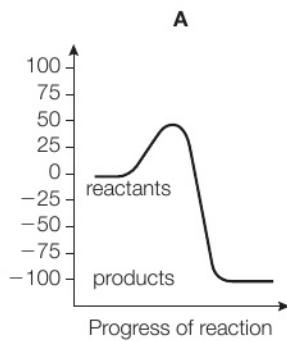
2 An exothermic reaction proceeds by two stages.



The activation energy of stage 1 is 50 kJ mol^{-1} .

The overall enthalpy change of reaction is -100 kJ mol^{-1} .

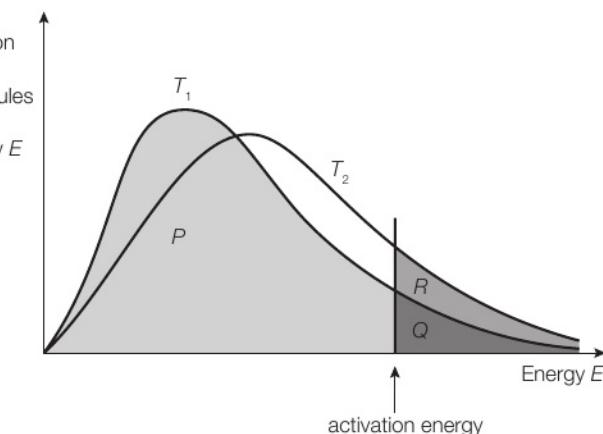
Which diagram could represent the energy profile diagram for the reaction?



(Total for Question 2 = 1 mark)

3 The distribution of the fraction of molecules with energy E is given in the diagram for two different temperatures T_1 and T_2 . T_2 is greater than T_1 .

The letters P , Q and R represent separate and different shaded areas under the curves.

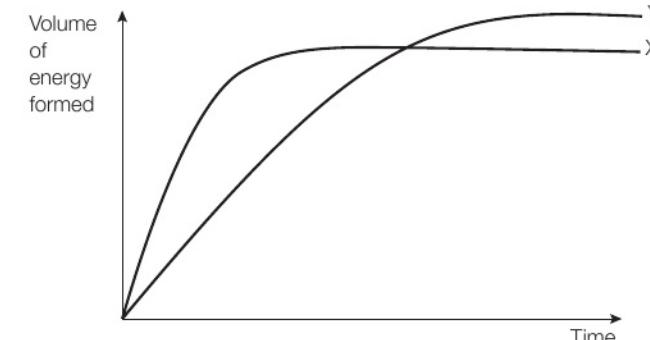


Which expression gives the fraction of molecules that have energy equal to or greater than the marked activation energy?

- A $\frac{Q}{P}$
- B $\frac{Q+P}{P}$
- C $\frac{Q+R}{P+Q}$
- D $\frac{Q+R}{P+Q-R}$ [1]

(Total for Question 3 = 1 mark)

4 Curve X in the diagram shows the volume of oxygen given off during the decomposition of 100 cm^3 of 1.0 mol dm^{-3} hydrogen peroxide, catalysed by manganese(IV) oxide.

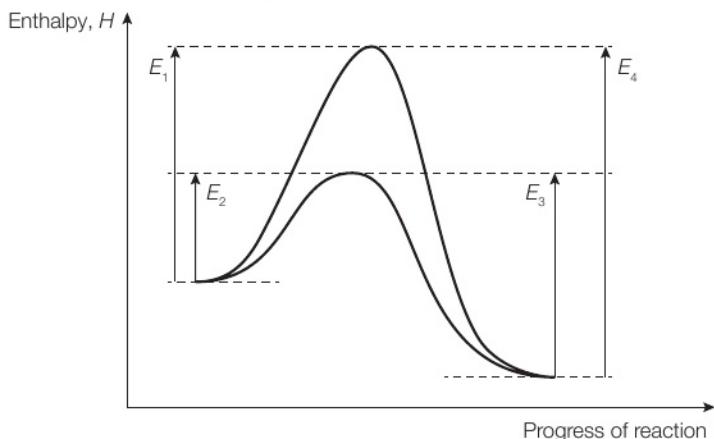


Which of the following alterations to the original experimental conditions would produce Curve Y?

- A adding water
- B adding some 0.1 mol dm^{-3} hydrogen peroxide
- C using less manganese(IV) oxide
- D lowering the temperature [1]

(Total for Question 4 = 1 mark)

- 5 The enthalpy level diagram represents a reaction occurring with and without a catalyst.



Which of the following statements is correct?

- A E_4 is the activation energy for the reverse reaction.
 B The forward reaction, with catalyst, is endothermic.
 C The enthalpy change of reaction is $(E_2 - E_3)$.
 D The enthalpy change of reaction is reduced using a catalyst.

- (b) Which statement about the effect of a catalyst on an endothermic, reversible reaction that is in dynamic equilibrium is correct?

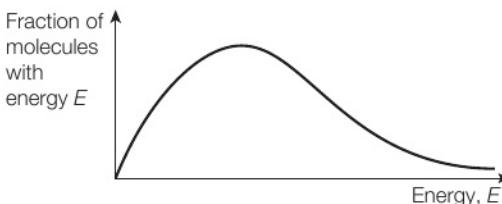
- A It increases/decreases the yield of the product.
 B It increases the rate of the forward reaction but not that of the backward reaction.
 C It increases the rate of the backward reaction but not that of the forward reaction.
 D It increases the rate of both the forward and the backward reactions.

[1]

(Total for Question 6 = 2 marks)

- 7 This question is about some graphs that you may have seen during your course.

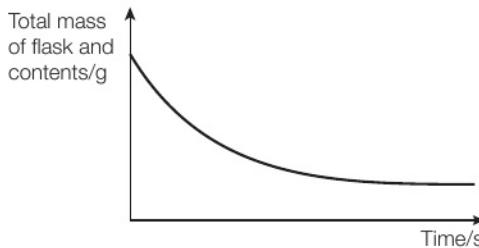
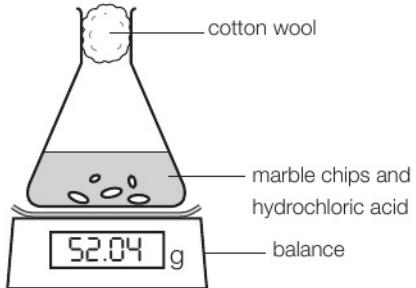
- (a) The graph below is a Maxwell-Boltzmann distribution curve.



Explain, using the graph, the effect of adding a catalyst on the rate of reaction.

[4]

- (b) The graph below shows the change in mass observed in an experiment to investigate the rate of reaction between marble chips and dilute hydrochloric acid.



- (i) State the purpose of the cotton wool in the neck of the conical flask.

[1]

- (ii) Explain why the mass of the flask and contents decreases during the course of the experiment.

[2]

- (iii) The experiment was repeated at the same temperature, with the same volume and concentration of acid and with the same mass of powdered marble.

Sketch, on the graph, the curve you would expect to obtain.

[2]

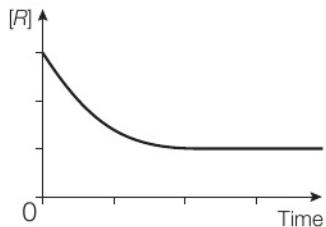
(Total for Question 7 = 9 marks)

- 6 (a) R reacts with T in a reversible, exothermic reaction.

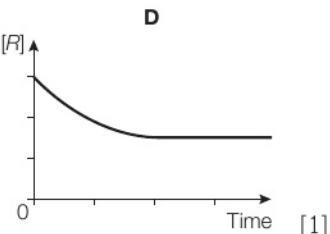
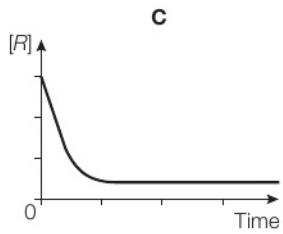
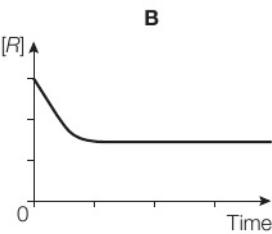
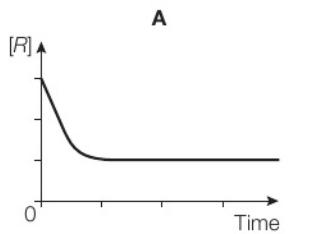
The reaction is allowed to reach equilibrium.

The concentration of one reactant, R, is plotted against time.

The graph shows the results.



Which of the graphs below could be obtained if the reaction were repeated at a higher temperature, but with the same concentrations of R and T?



[1]

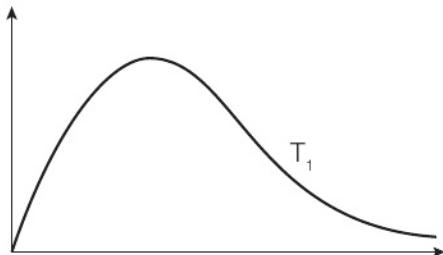
- 8** This question is about the effect that an increase in temperature has on the rate of a chemical reaction.

(a) A student found this statement in a text book:

'The rate of a chemical reaction increases as the temperature increases because the particles collide more often.'

Discuss the extent to which this statement is true. [5]

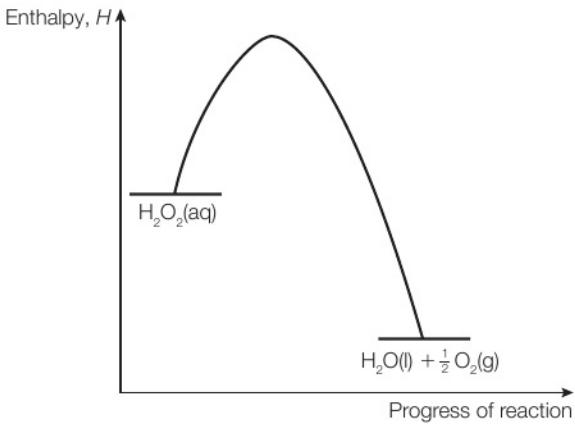
- (b) The graph below shows a Maxwell-Boltzmann distribution curve for a gas at temperature T_1 .



- (i) Label the axes on the diagram. [2]
(ii) On the graph, sketch a curve to represent the distribution at higher temperature. Label this curve T_2 . [2]

(Total for Question 8 = 9 marks)

- 9** The graph below shows the reaction profile for the uncatalysed decomposition of hydrogen peroxide (H_2O_2) into water and oxygen.



- (a) On the graph, label the activation energy (E_a) and the enthalpy change of reaction (ΔH). [2]
(b) The decomposition is catalysed by the addition of solid manganese(IV) oxide (MnO_2).
(i) Draw the curve to represent the catalysed decomposition. [2]
(ii) State, in principle, how the catalyst works in this reaction. [2]
(c) State whether the reaction is exothermic or endothermic. Justify your answer. [1]

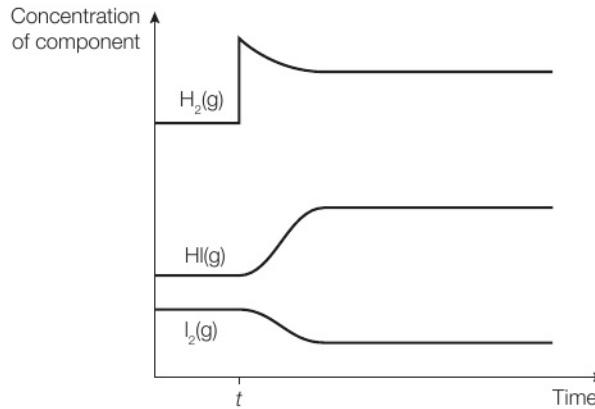
(Total for Question 9 = 7 marks)

- 10** Many chemical reactions are easily reversible and can form equilibrium mixtures. Hydrogen and iodine react together in the gaseous state to form hydrogen iodide:



Hydrogen (colourless) and iodine vapour (purple) are placed into a sealed container at 400°C and allowed to reach equilibrium with hydrogen iodide (colourless). The resulting mixture has a very pale purple colour.

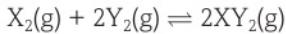
- (a) When the reaction mixture is cooled to 200°C , the reaction mixture becomes notably darker in colour. Give a reason for this observation in terms of the change to the equilibrium composition of the mixture. [2]
(b) In another experiment, all three gases were mixed together in a sealed tube and once again allowed to establish an equilibrium. The concentrations of the gases were monitored and the results were plotted on a graph. At time t , a change was made to the composition of the mixture.



- (i) State the change that was made to the reaction mixture at time t . [1]
(ii) Describe the changes that occur to the reaction mixture after time t . [3]

(Total for Question 10 = 6 marks)

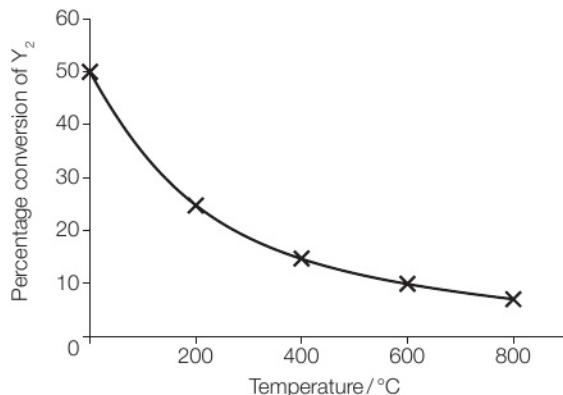
- 11** Many industrial processes involve reversible reactions. Chemists were investigating the production of a chemical XY_2 that can be formed from X_2 and Y_2 as shown in the equation



The chemists carried out a series of experiments at different temperatures, each time allowing the reaction mixture to establish equilibrium.

The chemists measured the percentage conversion of Y_2 at each temperature.

The results are shown in the graph.



- (a) Explain how the graph shows that the forward reaction is exothermic. [2]

(b) The chemists decide to use a catalyst in the process. Explain the effect of a catalyst on:

 - the rate at which equilibrium is established
 - the percentage conversion of Y_2 at equilibrium. [4]

(Total for Question 11 = 6 marks)

12 Methanol (CH_3OH) can be manufactured from carbon monoxide and hydrogen.



- (a) Predict how the composition of the equilibrium mixture is affected by:

 - (i) carrying out the reaction at a higher temperature but keeping the pressure the same
 - (ii) carrying out the reaction at a higher pressure but keeping the temperature the same.

In each case justify your answer. [4]

- (b) Assuming the reaction takes place by collision of molecules in the gas phase, explain the effect on the rate of reaction of increasing the pressure. [2]

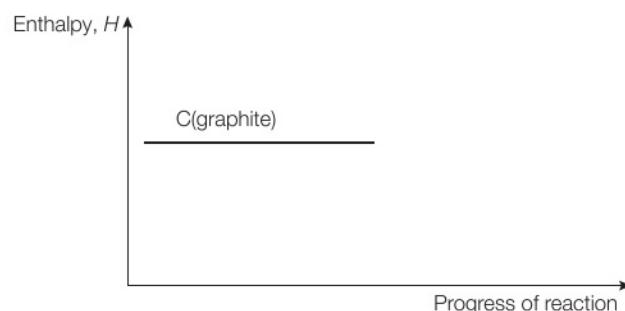
(Total for Question 12 = 6 marks)

13 Graphite and diamond are two allotropes of carbon. Artificial diamonds can be made from graphite.



Substance	Density / g cm⁻³
graphite	2.25
diamond	3.51

- (a) Complete the enthalpy profile diagram below for the conversion of graphite into diamond. Label the enthalpy change, ΔH . [2]



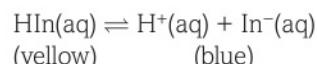
- (b) State and justify which allotrope is the more thermodynamically stable. [1]

(c) State and justify in which allotrope the atoms take up less space per mole of substance. [1]

(d) Predict the conditions of temperature and pressure that are required to convert graphite into diamond. Justify your predictions. [4]

(Total for Question 13 = 8 marks)

- 14** An acid-base indicator, HIn, dissolves in water to form a green solution. The following equilibrium is established:



The indicator appears green because it contains sufficient amounts of both the yellow and blue species.

- (a) Hydrochloric acid is added to the indicator solution. State what you would observe. Give a reason for your answer. [2]

(b) Aqueous sodium hydroxide is added dropwise to the resulting solution from (a) until no further colour change takes place. State all of the colours that would be observed. Give a reason for each colour. [4]

(Total for Question 14 = 6 marks)

- 15** The hydrogen required for the manufacture of ammonia and margarine is made by reacting methane with steam. The two gases react in a reversible reaction as shown by the equation:



- (a) State the conditions of temperature and pressure that would provide a high yield of hydrogen. Justify your answers. [4]

(b) State the conditions of temperature and pressure that would produce a fast rate of reaction. Justify your answers. Assume that the reaction takes place by molecules colliding in the gas phase. [4]

(c) Use your answers to (a) and (b) to explain why a

(c) Use your answers to (a) and (b) to explain why a temperature of $800\text{ }^{\circ}\text{C}$ and a pressure of 30 atm are used for the manufacture of hydrogen from methane. [3]

(Total for Question 15 = 11 marks)