

# KINETICS

- 6.1 Rates of reaction
- 6.2 Collision theory
- 16.1 Rate Expression (AHL)
- 16.2 Reaction mechanism (AHL)
- 16.3 Activation energy (AHL)

## 6



## 6.1 RATES OF REACTION

- 6.1.1 Define the term rate of reaction.
- 6.1.2 Describe suitable experimental procedures for measuring rates of reactions.
- 6.1.3 Analyse data from rate experiments.

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Different chemical reactions occur at different rates (i.e. speeds). Some, such as the neutralisation of a strong acid by a strong base in aqueous solution, take place very rapidly whilst others, such as the rusting of iron, take place far more slowly. Rates of reactions should not be confused with how far a reaction goes - this is determined by equilibrium.

The **rate of a chemical reaction** is a measure of the speed at which products are formed, measured as the change in concentration divided by the change in time, so reaction rate has units of  $\text{mol dm}^{-3} \text{s}^{-1}$ . This is equal to the rate at which the reactants are consumed, so for a reaction:

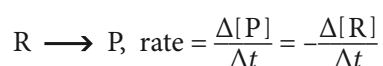


Figure 601 An explosion is a quick reaction

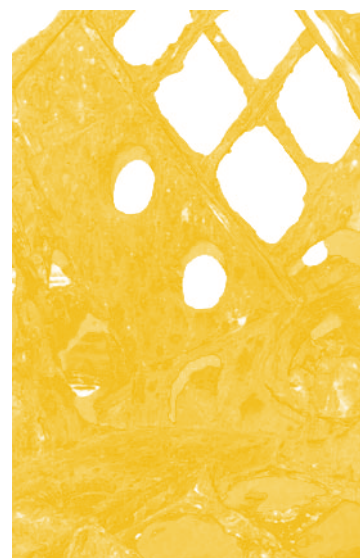
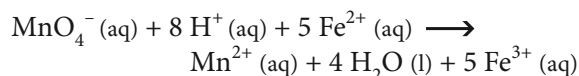


Figure 602 Corrosion is a slow reaction

Note the minus sign for the reactants, which is necessary as the concentrations of reactants decreases with time whereas the concentrations of products increases. Rate is always positive.

The numerical value will vary according to the amount of the substance involved in the stoichiometric equation, so that in the reaction:



The rate of appearance of  $\text{Fe}^{3+}$  is five times as great as the rate at which  $\text{MnO}_4^-$  is consumed. The rate is usually considered to apply to a product that has a coefficient of one as the equation is usually written:

$$\text{Rate} = -\frac{\Delta[\text{MnO}_4^-]}{\Delta t} = \frac{1}{5} \frac{\Delta[\text{Fe}^{3+}]}{\Delta t}$$

Or more simply for a reaction:  $a \text{A} \longrightarrow b \text{B}$ , then

$$\text{Rate} = \frac{1}{b} \frac{\Delta[\text{B}]}{\Delta t} = -\frac{1}{a} \frac{\Delta[\text{A}]}{\Delta t}$$

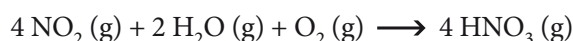
Any property that differs between the reactants and the products can be used to measure the rate of the reaction. Refer to Section 6.2. Whichever property is chosen, a graph is drawn of that property against time and the rate of reaction is proportional to the gradient of the curve or line ignoring the sign. Changes in the gradient of similar graphs illustrate the effect of changing conditions on the rate of reaction, without the need to convert the units to  $\text{mol dm}^{-3} \text{s}^{-1}$ .

In most cases the rate of reaction decreases with time because the concentration of the reactants decreases with time and the reaction rate usually depends on the reactant

concentration. It is most common to compare initial rates, that is, the gradient of the tangent to the curve at  $t = 0$ . At this time the concentrations of the reagents are accurately known, as is the temperature of the system. It is also easiest to draw tangents at this time as this section of the curve is the most linear. Typical curves obtained for the consumption of a reagent and formation of a product are shown in Figure 603.

### Exercise 6.1

- The equation for a reaction is:



Which one of the following is not numerically equal to the others?

- A  $-\frac{1}{2} \frac{\Delta[\text{NO}_2]}{\Delta t}$
- B  $-\frac{1}{2} \frac{\Delta[\text{O}_2]}{\Delta t}$
- C  $-\frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$
- D  $\frac{1}{2} \frac{\Delta[\text{HNO}_3]}{\Delta t}$

- Which of the curves on the following graph shows the greatest initial reaction rate?

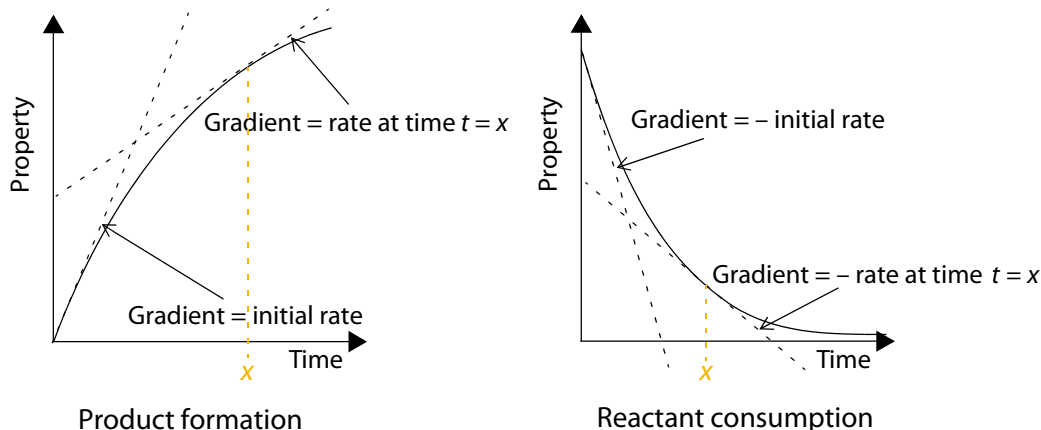
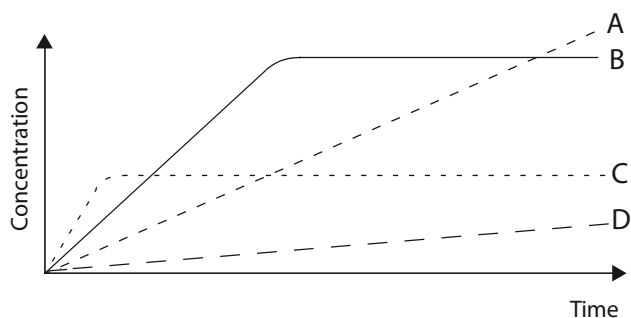
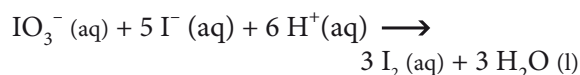


Figure 603 The variation of reaction rate with time



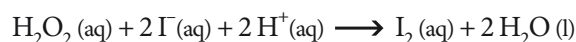
3. Iodate(V) ions oxidise iodide ions in acidic solution to form iodine and water according to the equation



If the number of moles of each reactant consumed after one minute was measured, which would have been consumed least?

- A  $\text{IO}_3^-$   
 B  $\text{I}^-$   
 C  $\text{H}^+$   
 D They would all have been consumed to the same extent.

4. The rate of reaction between hydrogen peroxide and the iodide ions was measured by monitoring the absorption of blue light by the iodine. If the equation for the reaction is



- a) If  $0.005 \text{ mol dm}^{-3}$  of iodine is produced in the first 2 minutes, what is the initial reaction rate in  $\text{mol dm}^{-3} \text{ s}^{-1}$ ?  
 b) What is the rate at which  
     i hydrogen peroxide is consumed?  
     ii iodide ions are consumed?  
 Explain why these are different.

5. The rate of reaction between zinc and sulfuric acid is measured by weighing a zinc plate, which is then placed into a beaker of the acid. Every 10 minutes it is removed, rinsed, dried and reweighed. This is continued until all of the acid is consumed.

- a) Sketch the graph you would expect for the mass of the zinc plate against time in the acid.  
 b) At what point is the reaction rate the greatest? How can you tell?  
 c) Suggest another way that the rate of this reaction could have been measured.

## SOME TECHNIQUES FOR MEASURING RATES

There are a variety of techniques that can be used to measure the rate of a chemical reaction and some of the more common are described below. Any property that changes between the start and end of the reaction can in principle be used. It is however best if this changes by a large amount compared to the limits of accuracy of its measurement. It is also simpler to use quantitatively if the characteristic is directly proportional to the concentration of one or more components. For these reasons monitoring the rate of reaction by observing a pH change is generally not to be recommended, because the pH, being a logarithmic scale, will only change by 0.30 for a change of  $[\text{H}^+]$  by a factor of 2.

In some techniques the time taken for a particular event to occur may be used to measure the reaction rate (e.g. the time taken for a piece of magnesium ribbon to dissolve in a dilute acid). In these techniques it is important to remember that the greater the time the smaller the rate of reaction, i.e. the rate of reaction is inversely proportional to the time taken:

$$\text{Rate} \propto \frac{1}{\text{Time}}$$

If the purpose of the investigation is simply to observe the effect of some variable, such as the concentration of a particular species, on the rate of reaction, then a graph of the property proportional to concentration against time, will suffice. If however the reaction rate is required in standard units ( $\text{mol dm}^{-3} \text{ s}^{-1}$ ) then it will be necessary to calibrate the system so as to produce graphs of concentration against time.

Whichever technique is being used, it is important to keep the reaction mixture at a constant temperature during the reaction, because temperature has a great effect on the rate of reaction. For this reason it is usual to immerse the reaction vessel in a water bath at the required temperature. It is also preferable to immerse the reactants in the water bath, to allow them to reach the required temperature before mixing. One reason for preferring 'initial rate' data is that the effect of an endo- or exothermic reaction on the temperature of the system is minimised.

## TOK The empirical nature of chemistry

I used to think all magpies were black and white. In both England and New Zealand (my two “home” countries – whatever that concept implies) the magpie (very different species in both countries – the New Zealand version is a lot heavier and doesn’t have the long tail) are black and white birds. Then there’s the magpie robin, a much smaller bird, and the magpie goose – both also black and white. Indeed in England Newcastle United football club are nicknamed ‘the magpies’ because of their black and white shirts. My simple world was turned on its head when I arrived in Hong Kong and encountered the blue magpie. Definitely a magpie shape, but with bright blue as the dominant colour (along with black and white) and a gorgeous long tail. I’m afraid I was another victim of the fundamental problem of inductive logic – you can never be sure. However, in case you’re thinking you will just rely on deductive techniques, reflect for a few seconds on how you establish your premises.

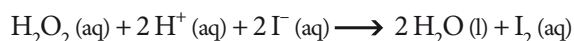
All empirical science suffers in the same way – it is quite easy to prove a theory wrong, but it is never possible to prove it correct. Tomorrow somebody might come up with a piece of evidence that contradicts your theory and then it’s back to the drawing boards. Falsification is so fundamental to science that the Austrian philosopher, *Karl Popper*, said that if you could not think of an experiment that would disprove your theory, then it was not a scientific theory.

In kinetics, the balanced equation tells us nothing about how changing the concentrations will affect the rate and we have to do experiments to determine the rate equation. We can then postulate mechanisms that would account for the empirical rate equation and certainly we can rule out some possible mechanisms, but even if we have a mechanism that explains the rate equation (and sometimes there can be more than one mechanism that does this, read this chapter) we can never be sure that tomorrow somebody will not come up with an alternative.

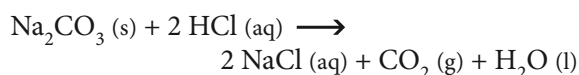
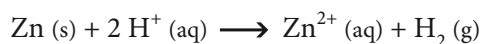
## Titration

This involves removing small samples from the reaction mixture at different times and then titrating the sample to determine the concentration of either one of the reactants or one of the products at this time. The results can then be used directly to generate a graph of concentration against time. In its simplest form this is only really suitable for quite slow reactions, in which the time taken to titrate the mixture is insignificant compared to the total time taken for the reaction. One common variant that helps to overcome this difficulty is to quench the reaction before carrying out the titration. This means altering the conditions so as to virtually stop the reaction. This can be done by rapidly cooling the reaction mixture to a very low temperature or by adding an excess of a compound that rapidly reacts with one of the reactants. If for example the reaction was that of a halogenoalkane with an alkali, it could be quenched by running the reaction mixture into an excess of a strong acid. This means that the time at which the sample of the reaction mixture was quenched is much easier to determine.

Another example of a reaction that can be readily measured by this technique is the rate of reaction of hydrogen peroxide with iodide ions in acidic solution to produce iodine and water. The amount of iodine produced can be measured by titrating the mixture with aqueous sodium thiosulfate. The reaction mixture can be quenched by adding excess of an insoluble solid base, such as powdered calcium carbonate, to neutralise the acid required for reaction.

Collection of an evolved gas/  
increase in gas pressure

The gas produced in the reaction is collected either in a gas syringe, or in a graduated vessel over water. The volume of gas collected at different times can be recorded. This technique is obviously limited to reactions that produce a gas. In addition, if the gas is to be collected over water, this gas must not be water soluble. An alternative technique is to carry out the reaction in a vessel of fixed volume and monitor the increase in the gas pressure. These techniques would be suitable for measuring the rate of reaction between a moderately reactive metal (such as zinc) and an acid (such as hydrochloric acid), or reaction of a carbonate with acid:





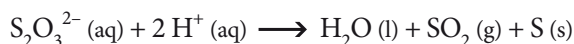
## Measurement of the mass of the reaction mixture

The total mass of the reaction mixture will only vary if a gas is evolved. To be really effective, the gas being evolved should have a high molar mass (i.e. not hydrogen), so that there is a significant change in mass, also the gas should not be significantly soluble in the solvent used. This technique would be suitable for measuring the rate of reaction between a metal carbonate (such as calcium carbonate, marble chips) and an acid (such as hydrochloric acid), by measuring the rate of mass loss resulting from the evolution of carbon dioxide.



## Light absorption

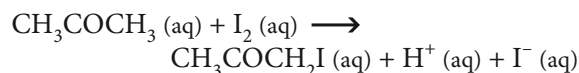
If a reaction produces a precipitate, then the time taken for the precipitate to obscure a mark made on a piece of paper under the reaction vessel can be used as a measure of reaction rate. For simple work comparison of the times, keeping the depth of the liquid constant will suffice; e.g. if the time taken doubles then the reaction rate is halved. A reaction that is often studied by this technique is the reaction between aqueous thiosulfate ions and a dilute acid which gives sulfur dioxide, water and a finely divided precipitate of sulfur.



A convenient way to follow this reaction is to place a black cross/mark on a white piece of paper under the reaction mixture and to measure the time taken for the finely suspended yellow sulfur to obscure the cross.

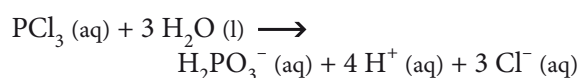
If the reaction involves a coloured reactant or product, then the intensity of the colour can be used to monitor the concentration of that species. In its simplest form this can be done by comparing the colour by eye against a set of standard solutions of known concentration. The technique is far more precise if an instrument that measures the absorbance (which is directly proportional to concentration – refer to the Beer–Lambert law in Section A8.6, Chapter 12) such as a colorimeter or spectrophotometer is available. If a colorimeter is used then a filter of the complementary colour to that of the coloured species should be chosen – an aqueous solution of a copper(II) salt is blue because it absorbs red light, so that it is the intensity of transmitted red light not blue light that will vary with its concentration. If a spectrophotometer is used, then a wavelength near to the absorption maximum of the coloured species should be selected.

A reaction that is often studied by this technique is the reaction between propanone and iodine to form iodopropanone. The yellow–brown iodine is the only coloured species involved and so the intensity of blue light (or light of wavelength  $\approx 450$  nm if a spectrophotometer is used) passing through the solution will increase with time as the concentration of the iodine falls. Most instruments, however, give a direct reading of absorbance which has an inverse relationship to the transmitted light, so that absorbance decreases with time.



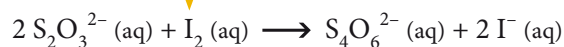
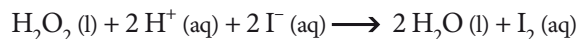
## Electrical conductivity

The presence of ions allows a solution to conduct, so if there is a significant change in the concentration of ions (especially hydrogen and hydroxide ions which have an unusually high conductivity) during the course of a reaction, then the reaction rate may be found from the change in conductivity. This is usually found by measuring the A.C. resistance between two electrodes with a fixed geometry, immersed in the solution. A reaction that is suitable for this technique would be the hydrolysis of phosphorus(III) chloride that produces dihydrogenphosphate(III) ions, hydrogen ions and chloride ions from non-ionic reactants.



## Clock techniques

There are some reactions in which the product can be consumed by further reaction with another added substance. When all of this substance is consumed then an observable change will occur. The time taken for this corresponds to the time for a certain amount of product to have been formed and so is inversely proportional to the rate of reaction. The classic reaction studied in this way is the reaction between hydrogen peroxide and iodide ions, in the presence of acid, to form iodine and water. Thiosulfate ions are added to the system and these initially react rapidly with the iodine produced. When all of the thiosulfate has been consumed, free iodine is liberated and this colours the solution yellow, or more commonly blue–black through the addition of starch solution (which forms an intensely coloured complex with iodine) to the system.



The blue colour of the iodine-starch complex suddenly appears when all of the thiosulfate has been consumed. The time taken for this to occur is inversely proportional to the rate.

### Exercise 6.1

- The rate of a chemical reaction can sometimes be determined by measuring the change in mass of the reaction flask and its contents with time. For which of the following reactions would this technique be most successful?
  - Magnesium oxide and dilute sulfuric acid.
  - Aqueous sodium chloride and aqueous silver nitrate.
  - Copper(II) carbonate and dilute hydrochloric acid.
  - Zinc and aqueous copper(II) sulfate.
- You wish to carry out an investigation that involves the use of a conductivity meter to monitor the rate of a chemical reaction. Which of the reactions below would be the least suitable for this?
  - $$\text{H}_2\text{O}_2 (\text{aq}) + 2 \text{H}^+ (\text{aq}) + 2 \text{I}^- (\text{aq}) \longrightarrow 2 \text{H}_2\text{O} (\text{l}) + \text{I}_2 (\text{aq})$$
  - $$\text{Ba}^{2+} (\text{aq}) + \text{SO}_4^{2-} (\text{aq}) \longrightarrow \text{BaSO}_4 (\text{s})$$
  - $$\text{POCl}_3 (\text{l}) + 3 \text{H}_2\text{O} (\text{l}) \longrightarrow 4 \text{H}^+ (\text{aq}) + 3 \text{Cl}^- (\text{aq}) + \text{H}_2\text{PO}_4^- (\text{aq})$$
  - $$2 \text{H}_2\text{O}_2 (\text{aq}) \longrightarrow 2 \text{H}_2\text{O} (\text{l}) + \text{O}_2 (\text{g})$$
- For which one of the following reactions would a colorimeter be most suitable for monitoring the reaction rate?
  - The reaction of acidified permanganate ions (manganate(VII)) ions with ethanedioic acid (oxalic acid) to form carbon dioxide, manganese(II) ions and water.
  - The reaction of magnesium carbonate with a dilute acid to form a soluble magnesium salt, carbon dioxide and water.
  - The reaction of bromobutane with aqueous sodium hydroxide to form butanol and aqueous sodium bromide.
  - The reaction of lithium with water to form aqueous lithium hydroxide and hydrogen.
- You wish to measure the rate of reaction of acidified dichromate(VI) ions with aqueous sulfur dioxide to produce aqueous chromium(III) ions and aqueous sulfate ions at 35 °C. This reaction involves a colour change from orange to green. Discuss how you might go about doing this, the measurements you would need to take and the precautions required.
- During your study of chemistry you will most likely have studied the way in which altering certain variables affected the rate of a chemical reaction.
  - What reaction did you study?
  - What technique did you use to study the rate of this reaction? Why do you think this method was appropriate?
  - What variable did you change? How was this carried out?
  - How could you modify the investigation to study another variable. State which variable you are now going to study and outline how you would carry this out along with any precautions you would take.

## 6.2 COLLISION THEORY

- 6.2.1 Describe the kinetic theory in terms of the movement of particles whose average energy is proportional to temperature in kelvins.
- 6.2.2 Define activation energy,  $E_a$ .
- 6.2.3 Describe the collision theory.
- 6.2.4 Predict and explain, using collision theory, the qualitative effects of particle size, temperature, concentration and pressure on the rate of a reaction.
- 6.2.5 Sketch and explain qualitatively the Maxwell–Boltzmann energy distribution curve for a fixed amount of gas at different temperatures and its consequences for changes in reaction rate.
- 6.2.6 Describe the effect of a catalyst on a chemical reaction.
- 6.2.7 Sketch and explain Maxwell–Boltzmann curves for reactions with and without catalysts.

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**Collisions** are vital for chemical change, both to provide the energy required for a particle to change (for example, a bond to break), and to bring the reactants into contact.

As particles approach each other there is repulsion between the electron clouds of the particles. In order for reaction to occur, the collision must have sufficient **kinetic energy** to overcome this repulsion. Frequently energy is also required to break some of the bonds in the particles before a reaction can take place. Hence not all collisions lead to a reaction. This minimum amount of energy required for reaction is known as the **activation energy** ( $E_a$ ) for the reaction (units of  $E_a$ :  $\text{kJ mol}^{-1}$ ). This is illustrated, for an exothermic reaction, in Figure 605.

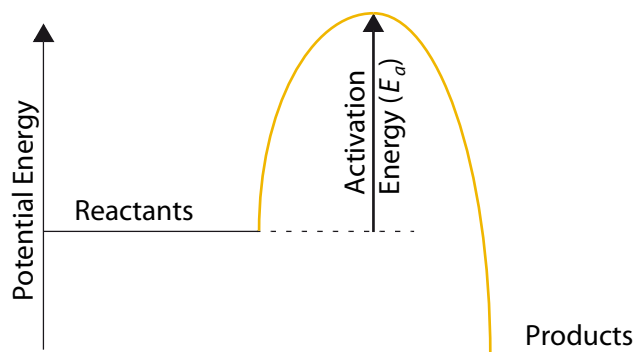


Figure 605 The principle of activation energy

The activation energy involved varies tremendously from reaction to reaction. In some cases (such as the reaction of the hydrogen ion and hydroxide ion) it is so low that reaction occurs on almost every collision even at low temperatures. In other cases (such as sugar and oxygen) it is so high that reaction at room temperature is negligible.

In order to react, the two particles involved must:

- collide with each other
- the collision must be energetic enough to overcome the activation energy of the reaction, (i.e. the collision must have  $E > E_a$ )
- the collision must occur with the correct geometrical alignment, that is it must bring the reactive parts of the molecule into contact in the correct way

This final factor, often called the **steric factor**, is particularly important with regard to reactions involving large organic molecules.

If anything increases the **collision rate**, then the rate of reaction increases. Similarly anything that increases the proportion of the collisions that have an energy equal to or greater than the activation energy will increase the rate of reaction. These factors are summarised in Figure 606.

Factors mainly affecting the collision rate	Factors mainly affecting the proportion with required $E_a$
Concentration/pressure	Temperature
Surface area	Catalyst

Figure 606 Factors affecting the rate of reaction (table)

## THE EFFECT OF CONCENTRATION

The rate at which particles collide is increased by increasing the concentration of the reactants. Thus marble chips react faster with concentrated hydrochloric acid than they do with the dilute acid. For reacting gases, increasing the pressure is equivalent to increasing the concentration. The effect of concentration on rate is illustrated in Figure 607.

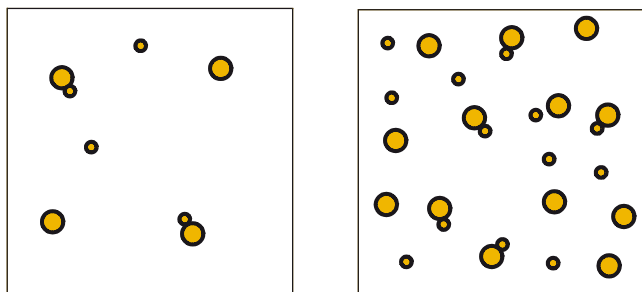


Figure 607 The effect of concentration

## THE EFFECT OF SURFACE AREA

If the reaction involves substances in phases that do not mix (e.g. a solid and a liquid, or a liquid and a gas) then an increase in the surface area in contact will increase the collision rate. As a result powdered calcium carbonate reacts faster with hydrochloric acid than lumps of the solid with the same mass. This is illustrated in Figure 608.

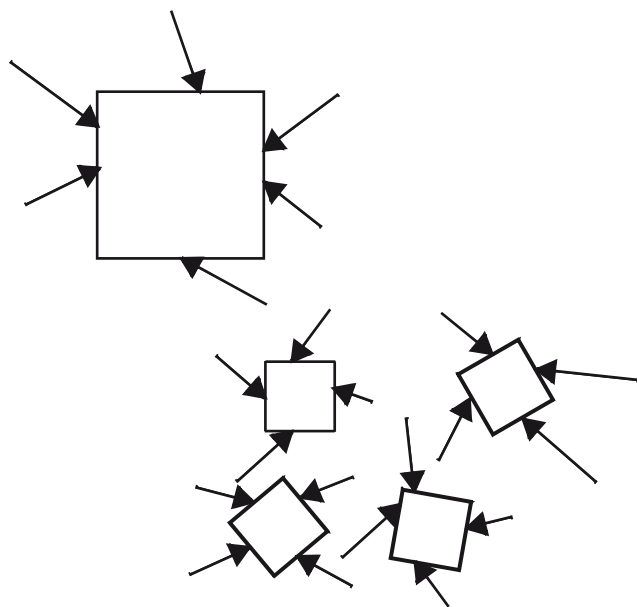


Figure 608 The effect of surface area

## THE EFFECT OF TEMPERATURE

Not all particles have the same energy so there is a distribution of kinetic energy, and hence velocity, amongst the particles of the gas, known as the **Maxwell-Boltzmann distribution**, shown in Figure 609. As with cars on a freeway, some are moving more rapidly and others more slowly. The mean speed of the particles is proportional to the absolute temperature but, because the curve is asymmetric, this does not coincide with the most probable speed. The area under the curve represents the total number of particles and hence, in a closed system, this area must remain constant.

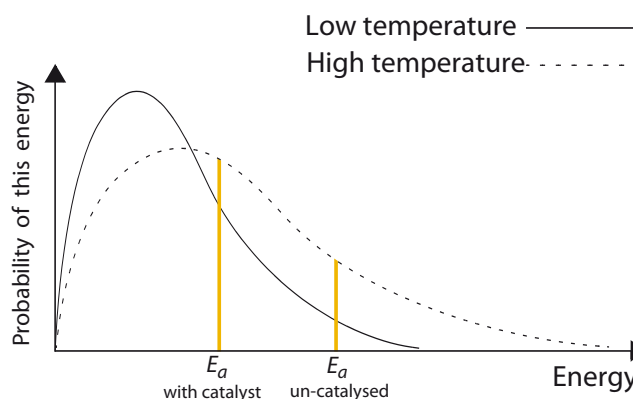


Figure 609 The effects of temperature and catalyst

As previously stated, a collision must have a certain minimum energy, the activation energy, before reaction can occur. As can be seen in Figure 609, the number of molecules with the required activation energy is much greater at a higher temperature than at a lower one. This means that marble chips react more rapidly with warm hydrochloric acid than with cold hydrochloric acid. Increasing the temperature also has a very slight effect on the collision rate, but in most cases this is insignificant compared to its effect on the proportion of collisions with the required activation energy. For many reactions an increase in temperature of  $10^\circ\text{C}$  will approximately double the rate of reaction (a crude generalization), but the increase in the collision rate that this rise in temperature causes is only  $\approx 2\%$ . To summarise, increasing the temperature increases the frequency of collisions but, more important is the increase in the proportion of molecules with  $E > E_a$ . The effect of temperature on reaction rate is discussed in much more detail in Chapter 6.6.



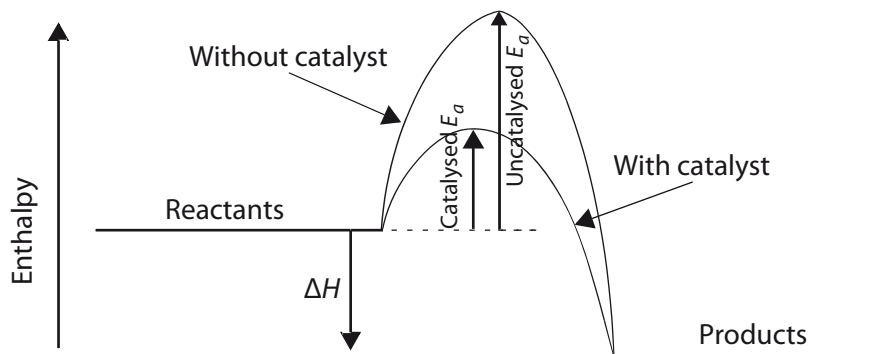


Figure 610 The effect of a catalyst

## THE EFFECT OF CATALYST

A catalyst is a substance that is usually required in small amounts and can increase the rate of a chemical reaction without undergoing any overall change. Catalysts speed up a reaction by providing an alternative reaction mechanism or pathway (like a mountain pass) with a lower activation energy by which the reaction can take place. This means that a greater proportion of collisions will have the required energy to react by the new mechanism and so the reaction rate increases. Typically, the efficiency of a catalyst decreases with time as it becomes inactive due to impurities in the reaction mixture, side reactions, or if its surface becomes coated and unavailable for activity.

The way this affects the situation in terms of the Maxwell-Boltzmann distribution and the energy diagram is shown in Figures 609 & 610.

## THE EFFECT OF LIGHT

Some chemical reactions are brought about by exposure to light. Examples would be the darkening of silver halides when exposed to sunlight (the basis of black and white photography) and the reaction of alkanes with chlorine or bromine (for example, the reaction of methane and chlorine). This is because reactant particles absorb light energy and this brings about either the excitation of one of the reactants (as is the case with the silver halides) or the breaking of a bond (such as the halogen—halogen bond in the halogenation of the alkanes) which initiates the reaction. It is for this reason that many chemicals are stored in brown glass containers.

### Exercise 6.2

- Which one of the following factors does not affect the rate of a chemical reaction?
  - The amounts of the reagents.
  - The concentration of the reagents.
  - The temperature of the reagents.
  - The presence of a catalyst.
- In most chemical reactions, the rate of reaction decreases as the reaction proceeds. The usual reason for this is that
  - The energy for the reaction is running out.
  - The concentrations of the reactants are becoming lower.
  - The temperature is falling as the reaction proceeds.
  - The activation energy becomes greater.
- In which of the following situations would you expect the rate of reaction between marble (calcium carbonate) and nitric acid to be the greatest?
  - Powdered marble and  $2 \text{ mol dm}^{-3}$  acid at  $40^\circ\text{C}$ .
  - Powdered marble and  $0.5 \text{ mol dm}^{-3}$  acid at  $40^\circ\text{C}$ .
  - Powdered marble and  $2 \text{ mol dm}^{-3}$  acid at  $20^\circ\text{C}$ .
  - Marble chips and  $0.5 \text{ mol dm}^{-3}$  acid at  $40^\circ\text{C}$ .

4. In which one of the following reactions would surface area not be a factor affecting the rate?
- Zinc and sulfuric acid.
  - Carbon dioxide gas with limewater (aqueous calcium hydroxide).
  - Vegetable oil and aqueous sodium hydroxide.
  - Aqueous ethanedioic (oxalic) acid and aqueous potassium permanganate.
5. Which one of the following reactions must occur by more than one reaction step?
- $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{H}_2\text{O}(\text{l})$
  - $2 \text{H}_2\text{O}_2(\text{aq}) \longrightarrow 2 \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$
  - $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2 \text{H}_2\text{O}(\text{l})$
  - $\text{H}_2(\text{g}) + \text{O}_3(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$
6. Explain briefly why:
- Increasing the concentration of the reagents usually increases the rate of a chemical reaction.
  - A reaction does not occur every time the reacting species collide.
  - Increasing the temperature increases the rate of reaction.
7. The rate of decomposition of an aqueous solution of hydrogen peroxide can be followed by recording the volume of gas collected over water in a measuring cylinder, against time.
- Sketch the graph of volume against time you would expect for the complete decomposition of a sample of hydrogen peroxide.
  - On the same axes, use a dotted line to sketch the curve that you would expect to find if the experiment were repeated using a smaller volume of a more concentrated solution of hydrogen peroxide so that the amount of hydrogen peroxide remains constant.
  - When lead(IV) oxide is added, the rate at which oxygen is evolved suddenly increases, even though at the end of the reaction, the lead(IV) oxide remains unchanged. Explain this.
  - In what way, apart from altering the concentration or adding another substance, could the rate at which the hydrogen peroxide decomposes be increased?

## HIGHER LEVEL

### 16.1 RATE EXPRESSION (AHL)

- 16.1.1 Distinguish between the terms rate constant, overall order of reaction and order of reaction with respect to a particular reactant.
- 16.1.2 Deduce the rate expression for a reaction from experimental data.
- 16.1.3 Solve problems involving the rate expression.
- 16.1.4 Sketch, identify and analyse graphical representations for zero-, first- and second-order reactions.

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Altering the concentration of the reactants usually affects the rate of the reaction, but the way in which the rate is affected is not the same for all substances, nor can it be predicted from the balanced equation for the reaction. The **rate expression**, which is a mathematical function expressing the dependence of the rate on the concentrations of the reactants, must be determined experimentally. This is usually done by measuring the reaction rate whilst varying the concentration of one species but holding those of the other species constant. Consider a reaction involving reactants A, B, etc. The rate expression for this reaction takes the form:

$$\text{Rate of reaction} = -\frac{d[\text{A}]}{dt} = k[\text{A}]^m[\text{B}]^n \text{ etc}$$

The **order of reaction** is said to be '*m*' in substance A, '*n*' in substance B etc. The overall order of the reaction is the sum of these powers, i.e. *m* + *n* etc. The constant '*k*' in the rate expression is known as the rate constant.

Note that '*k*' does not vary with concentration, but it varies greatly with temperature, so it is important to always state the temperature at which the rate constant was measured. Note that where a solid is involved in a reaction, '*k*' must also vary with particle size (since for example in the reaction of acid with calcium carbonate at the same concentration of acid and temperature, the rate changes as particle size changes).

Experiment	[A] mol dm <sup>-3</sup>	[B] mol dm <sup>-3</sup>	[C] mol dm <sup>-3</sup>	Initial rate mol dm <sup>-3</sup> s <sup>-1</sup>
1	0.400	1.600	0.0600	$4.86 \times 10^{-3}$
2	0.800	1.600	0.0600	$9.72 \times 10^{-3}$
3	0.400	0.800	0.0600	$4.86 \times 10^{-3}$
4	0.800	1.600	0.1800	$87.5 \times 10^{-3}$

Figure 611 The effect of concentration changes on the rate of a reaction

If doubling the concentration of one species (say A), whilst the other conditions are held constant, has no effect on the initial rate of reaction, then the reaction is zero order with respect to A (as  $2^0 = 1$ ). If doubling the concentration of A doubles the rate, then the reaction is first order with respect to A (as  $2^1 = 2$ ). If it increases by a factor of four it is second order with respect to A (as  $2^2 = 4$ ), by a factor of eight then third order with respect to A (as  $2^3 = 8$ ) etc. Similar considerations apply to altering the concentrations by other factors (for example if the concentration was decreased by a factor of 3, then the rate would also decrease by a factor of 3 if the reaction was first order with respect to this reagent).

Figure 611 gives some data about the effect of varying concentrations upon the rate of a chemical reaction involving three species – A, B and C:

Comparing experiments 1 and 2, the only change is that the concentration of A has been doubled. The data in the table indicate that the rate has been doubled, so the reaction is first order with respect to A. Comparing 1 and 3, the only change is that the concentration of B has been halved, but there is no effect on the reaction rate, indicating that the reaction is zero order with respect to B (if first order it would be  $\frac{1}{2}$  the rate in 1, if second order, then  $\frac{1}{4}$  of the rate in 1). Comparing 2 and 4 the only difference is that the concentration of C has been increased by a factor of three. The rate has increased by a factor of nine, so the reaction is second order in C (as  $3^2 = 9$  – if it had been first order in C, the rate would only have increased by a factor of 3.). This means that the rate expression for this reaction is:

$$\text{Rate} = k.[A]^1[B]^0[C]^2$$

or more simply

$$\text{Rate} = k.[A][C]^2$$

Hence the reaction is third order (1 + 2) overall.

The rate constant for a reaction may be calculated provided that the rate of reaction has been measured in standard

units of mol dm<sup>-3</sup> s<sup>-1</sup>, for known concentrations of the reagents. Consider the data in Figure 611 above. The rate constant can be calculated by substituting any set of data in the rate expression. For example using the data from experiment 1:

$$\text{Rate} = k.[A][C]^2$$

$$4.86 \times 10^{-3} = k[0.400][0.06]^2$$

$$k = \frac{4.86 \times 10^{-3}}{0.400 \times 0.06^2} \\ = 3.375 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$$

and using the data from experiment 2:

$$\text{Rate} = k.[A][C]^2$$

$$9.72 \times 10^{-3} = k[0.800][0.06]^2$$

$$k = \frac{9.72 \times 10^{-3}}{0.800 \times 0.06^2} \\ = 3.375 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$$

Note the units for the rate constant. These only hold for a reaction that is third order overall and other order reactions will have rate constants with different units.

The units can be calculated remembering that the units for rates are mol dm<sup>-3</sup> s<sup>-1</sup> and the units for concentrations are mol dm<sup>-3</sup>. Hence the units of the rate constant are:

Zero order overall	mol dm <sup>-3</sup> s <sup>-1</sup>
First order overall	s <sup>-1</sup>
Second order overall	mol <sup>-1</sup> dm <sup>3</sup> s <sup>-1</sup>
Third order overall	mol <sup>-2</sup> dm <sup>6</sup> s <sup>-1</sup>

In general (mol dm<sup>-3</sup>)<sup>q-1</sup> s<sup>-1</sup> where  $q$  is the overall order

The order of reaction can also be found from a graph showing the way in which the initial rate varies with the initial concentration of the reactant, all other factors being equal. This is illustrated in Figure 612.

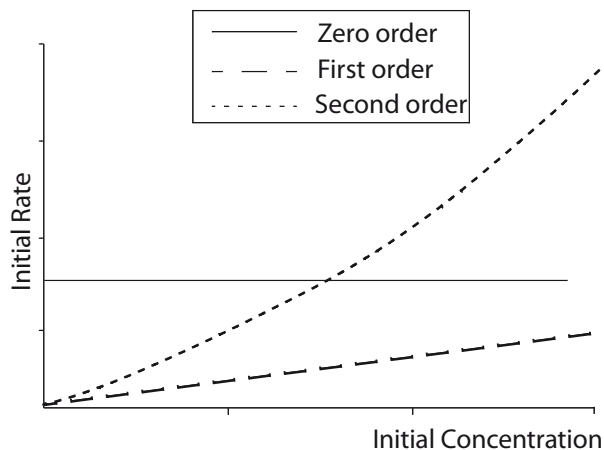


Figure 612 The effect of concentration on rate

The order of a reaction can also be found from a graph of concentration against time, which shows the effect of the reactants being used up on the rate of reaction. The gradient of the graph at any point gives the rate of reaction. If this is constant (i.e. the graph is a straight line) then the reaction must be **zero order** in the reactants whose concentrations are undergoing significant change, because the decrease in concentration is not affecting the rate of reaction (which we know from the constant gradient). If the reaction rate (the gradient of the line) is halved when the concentration

is halved, then the reaction is **first order**. If halving the concentration causes the rate (gradient) to decrease by a factor of 4, the reaction is **second order**  $(\frac{1}{2})^2 = \frac{1}{4}$  etc. To be really useful, such experiments should have all but one reagent in large excess, so that the order in the limiting reagent is what causes the reaction rate to change.

This is in fact the basis for a very powerful technique to simplify the rate equation. Consider a reaction that is second order overall in which the initial concentration of A is  $0.02 \text{ mol dm}^{-3}$  and the initial concentration of B is  $2 \text{ mol dm}^{-3}$ . When the reaction is complete (assuming the stoichiometry is 1 mole of A reacts with 1 mole of B), the final concentration of A is zero and that of B is  $1.98 \text{ mol dm}^{-3}$ , i.e. the concentration of B remains virtually unchanged, hence:

$$\text{Rate} = k.[A].[B] \approx k'.[A] \quad (\text{where } k' = k.[B])$$

A reaction of this type is called a “**pseudo first-order reaction**” because it obeys a first order rate law, but the observed rate constant ( $k'$ ) will depend on the concentration of another species (if  $[B]$  is doubled then the reaction rate will double and the half-life will decrease to half of its initial value). The same technique (making the concentration of one reagent much less than that of the

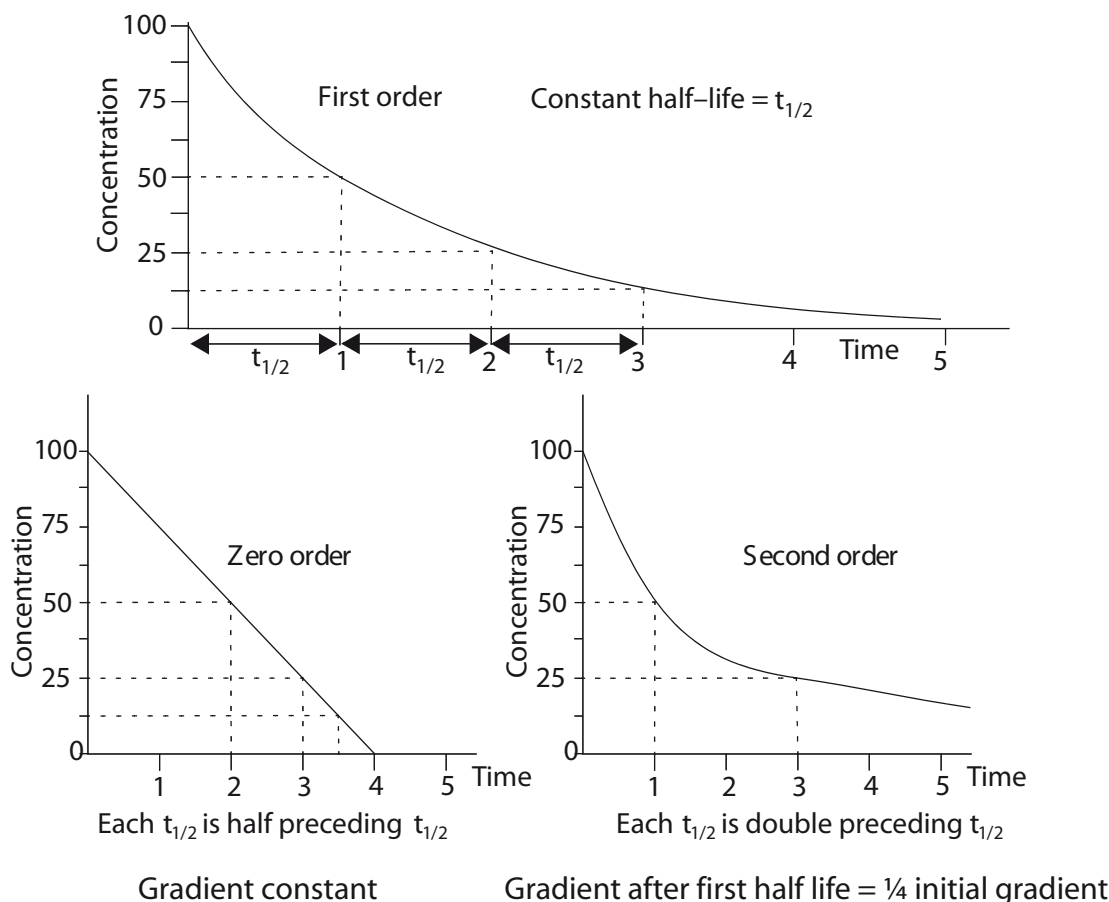


Figure 613 a, b and c. Graphs showing the variation of concentration with time for reactions of different orders



others) can be used to vary the observed order of reactions with other rate expressions.

It is easy to recognise a first order reaction from graphs of concentration (or something proportional to concentration) against time. This is because the concentration shows an exponential decrease, that is the time for the concentration to fall from its initial value to half its initial value, is equal to the time required for it to fall from half to one quarter of its initial value and from one quarter to one eighth etc. This time is known as the **half-life**  $t_{1/2}$  of the reaction and it is illustrated in Figure 613 which shows that the successive half lives of reactions of other orders vary in characteristic ways.

The first order exponential decay is the same as that found in **radioactive decay**. Because it remains constant, the half-life is an important quantity for these systems and it can be found from an appropriate graph (such as that above) or it may be found from the rate constant ( $k$ ) by substituting in the equation:

$$t_{1/2} = \frac{\ln 2}{k}$$

For example, if the rate constant of a first order reaction is  $0.005 \text{ s}^{-1}$ , then the half-life will be  $\frac{\ln 2}{0.005} = 139 \text{ s}$ .

This results from the integration of the first order rate expression. If the half-life is known, say from a concentration-time graph, then this equation may be rearranged to find the rate constant. For example if the half-life for a first order reaction is 4 minutes:

$$k = \frac{\ln 2}{(4 \times 60)} = 0.0289 \text{ s}^{-1}$$

## Exercise 16.1

Questions 1 to 4 refer to the rate expression for a chemical reaction given below:



1. Which one of the following statements is not true about this reaction?

- A It is first order in A.
- B It is second order in B.
- C It is first order in  $\text{H}^+$ .
- D It is third order overall.

2. The units of the rate constant ( $k$ ) will be:

- A  $\text{mol dm}^{-3} \text{ s}^{-1}$
- B  $\text{mol s}^{-1}$
- C  $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
- D  $\text{dm}^9 \text{ mol}^{-3} \text{ s}^{-1}$

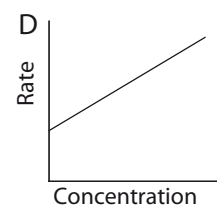
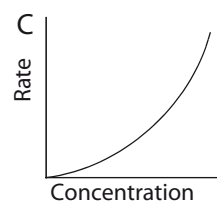
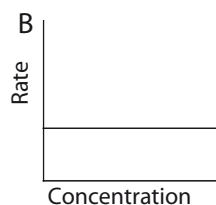
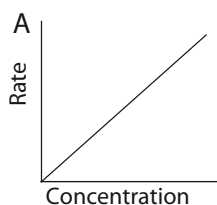
3. If the concentrations of A and B are both doubled, but the concentration of  $\text{H}^+$  remains constant, the rate would increase by a factor of:

- A 2
- B 4
- C 8
- D 16

4. Which one of the following would lead to the greatest increase in reaction rate?

- A Doubling the concentration of A only.
- B Doubling the concentration of B only.
- C Doubling the concentration of A and  $\text{H}^+$  only.
- D Doubling the concentration of B and  $\text{H}^+$  only.

5. Which one of the graphs shown would indicate that a reaction was zero order in the reactant whose concentration was being varied?



6. The following data refers to the acid catalysed iodination of propanone



Solution	$[\text{CH}_3\text{—CO—CH}_3]$ $\text{mol dm}^{-3}$	$[\text{I}_2]$ $\text{mol dm}^{-3}$	$[\text{H}^+]$ $\text{mol dm}^{-3}$	Initial Rate $\text{mol dm}^{-3} \text{ s}^{-1}$
1	0.2	0.008	1	$4 \times 10^{-6}$
2	0.4	0.008	1	$8 \times 10^{-6}$
3	0.6	0.008	1	$1.2 \times 10^{-5}$
4	0.4	0.004	1	$8 \times 10^{-6}$
5	0.4	0.002	1	$8 \times 10^{-6}$
6	0.2	0.008	2	$8 \times 10^{-6}$
7	0.2	0.008	4	$1.6 \times 10^{-5}$

- From the data in the table derive the rate expression for the reaction, explaining the evidence for the dependency on each of the species.
- Give the order with respect to  $\text{CH}_3\text{—CO—CH}_3$ ,  $\text{I}_2$  and  $\text{H}^+$ , and the overall order.
- Use the data from Solution 1 to calculate the value of the rate constant.

7. The data given below refer to the hydrolysis of a  $0.002 \text{ mol dm}^{-3}$  solution of an ester by  $0.2 \text{ mol dm}^{-3}$  aqueous sodium hydroxide.

Time (s)	60	120	180	240	300	360	420	480
[ester] ( $\text{mmol dm}^{-3}$ )	1.48	1.10	0.81	0.60	0.45	0.33	0.24	0.18

- Plot a suitable graph to determine the order of the reaction with respect to the ester, explaining your method.
- Use your graph to determine the half-life of the reaction and hence determine a value for the apparent rate constant, giving appropriate units.
- Why does this graph give no indication of the order with respect to the hydroxide ion?
- How would you modify the experiment to determine the dependence on hydroxide ion?
- Assuming that it is also first order in hydroxide ion, write a new rate expression.  
Use this to calculate a value for the rate constant, giving appropriate units.  
Why does this differ from the value found in b) and how are the two related?

## 16.2 REACTION MECHANISM (AHL)

16.2.1 Explain that reactions can occur by more than one step and that the slowest step determines the rate of reaction (rate-determining step).

16.2.2 Describe the relationship between reaction mechanism, order of reaction and rate-determining step.

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The chance of more than two particles colliding simultaneously with the correct geometry and minimum energy is very small. This means that if there are more than two reactants, the reaction must occur by a number of simpler reaction steps. In addition, many reactions that have apparently simple equations do not occur in this manner, but are the result of a number of steps. These steps involve species that are the product of an earlier step and are then completely consumed in a later step (so they do not appear in the stoichiometric equation). These species are known as “**intermediates**”. The simple stages by which a chemical reaction occurs are known as the mechanism of the reaction. The sum of the various steps of the mechanism must equal the balanced equation for the reaction.

The various steps in the reaction mechanism will have the potential to occur at different rates. The products cannot however be formed faster than the slowest of these steps and so this is known as the rate determining step (rds). An analogy would be that if people can come off a train at the rate of 20 per second, can travel up the escalator at a rate

of 10 per second, and can pass through the ticket barrier into the street at a rate of 50 per second, then they will still only reach the street at a rate of 10 people per second. Making larger doors on the train or putting in an extra ticket barrier will not make this any faster, only a change affecting the escalator, the slowest step, will increase the rate.

In summary, a mechanism is a model of how a reaction occurs. The rate of overall reaction is the rate of the slowest step. This slowest step is called the **rate determining step**. Species produced in earlier steps of the mechanism that are consumed in later steps are called intermediates. A mechanism must account for the overall stoichiometry of the reaction, the observed rate expression and any other available evidence (such as the effect of light or a catalyst).

There are only two kinds of fundamental process that can occur to bring about a chemical reaction. Firstly, a species can break up or undergo internal rearrangement to form products, which is known as a **unimolecular** process. As this only involves one species, a unimolecular step is first order in that species. Radioactive decay, for example, is unimolecular. Secondly, two species can collide and interact to form the product(s) and this is known as a **bimolecular** process. As this involves the collision of the two species then doubling the concentration of either will double the collision rate. Hence, it is first order in each and second order overall. Both unimolecular and bimolecular processes can be either reversible (lead to equilibrium) or irreversible (lead to complete reaction) depending on the relative stability of the reactants and products. Whether a particular reaction step is unimolecular or bimolecular, is known as the **molecularity** of that reaction step. In a bimolecular process, the species collide to initially give a transition state (or activated complex), which then breaks down to either form the products or reform the reactants.

AHL

A Unimolecular step	A Bimolecular step
<p>A unimolecular step involves a single species as a reactant.</p> $A \longrightarrow / \rightleftharpoons \text{Products}$ <p>Its rate law is therefore 1<sup>st</sup> order with respect that reactant.</p> $\text{rate} \propto [A]$	<p>A bimolecular steps involves collision of two species (that form a transition state or an activated complex that can not be isolated).</p> $A + B \longrightarrow / \rightleftharpoons \text{Products}$ <p>Its rate law is 1<sup>st</sup> order with respect to each of the colliding species and is therefore 2<sup>nd</sup> order overall.</p> $\text{rate} \propto [A][B]$

Figure 617 Comparing uni- and bi-molecular steps

A **transition state** is an unstable arrangement in which the bonds are in the process of being broken and formed. It therefore occurs at the maximum point on a potential energy diagram and cannot be isolated.

As outlined above, many chemical reactions occur by a series of simple steps known as the mechanism of the reaction. It is possible to write a number of mechanisms (that is a series of fundamental processes by which the reaction could occur) for any reaction and it is only possible to suggest which is the correct one by studying the kinetics of the reaction. Only species that are involved in the rate determining step, or in an equilibrium preceding it, can affect the overall rate of reaction. Hence, determining the rate expression for a reaction will help to identify the rate determining step and this will eliminate many possible mechanisms for the reaction.

Consider for example a reaction



as an illustration of how the rate expression will depend upon the mechanism and upon which step in the mechanism is the rate determining step.

There are three particles involved in the reaction, so it is most unlikely that this occurs as a single step. Many mechanisms for the reaction could be written and these would produce a variety of rate expressions. Some examples are given in Figure 618. Note that adding together the different steps always leads to the same overall equation as shown for the first two possible mechanisms in Figure 618.

Some of these mechanisms involve equilibria, a topic that is dealt with in greater detail in Chapter 7. For the present purposes it is enough to know that for the equilibrium,  $A + B \rightleftharpoons X$ , the  $[X]$  will depend on both the  $[A]$  and  $[B]$ . Similarly in the equilibrium,  $A + A \rightleftharpoons A_2$ , the  $[A_2]$  will be proportional to  $[A]^2$ . Note also that the concentration of the intermediate (X) never appears in the rate expression.

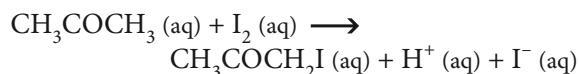
In I, the first bimolecular step is rate determining so that the rate will depend on the rate of collisions between A and B, hence the rate will be proportional to  $[A][B]$ . In II the second bimolecular step is rate determining so that the rate will depend on the rate of collisions between A and X, hence the rate will be proportional to  $[A][X]$ , but  $[X]$  will depend on both  $[A]$  and  $[B]$ , so that taking this into account the rate depends on  $[A]^2[B]$ . In V the rate depends on the unimolecular conversion of B to an intermediate X, so the rate only depends upon  $[B]$ .

	Mechanism	Rate expression
I	$A + B \longrightarrow X + C$ ; Slow rds $A + X \longrightarrow D$ ; Fast $(A + B + A + X \longrightarrow X + C + D$ $= 2A + B \longrightarrow C + D \text{ overall})$	$\text{Rate} \propto [A][B]$
II	$A + B \rightleftharpoons X$ ; Fast $A + X \longrightarrow C + D$ ; Slow rds $(A + B + A + X \longrightarrow X + C + D$ $= 2A + B \longrightarrow C + D \text{ overall})$	$\text{Rate} \propto [A]^2[B]$
III	$A + A \rightleftharpoons A_2$ ; Fast $A_2 + B \longrightarrow C + D$ ; Slow rds	$\text{Rate} \propto [A]^2[B]$
IV	$A + A \rightleftharpoons A_2$ ; Slow rds $A_2 + B \longrightarrow C + D$ ; Fast	$\text{Rate} \propto [A]^2$
V	$B \longrightarrow X$ ; Slow rds $X + A \longrightarrow Y + C$ ; Fast $Y + A \longrightarrow D$ ; Fast	$\text{Rate} \propto [B]$

Figure 618 Some possible mechanisms for the reaction;  
 $2A + B \longrightarrow C + D$

Note that III and IV only differ in which of the two steps is the rate determining step. This is not necessarily fixed, for example at very low  $[B]$  the second step could be the rate determining step (mechanism III), but at very high  $[B]$  the second step will become much faster so that now the first step might be rate determining (mechanism IV). Because  $A_2$  will react with B as soon as it is formed, the first step is now no longer an equilibrium. Note also that both mechanism II and mechanism III lead to the same rate expression and so some other means (such as trying to get some information about the intermediate X) would have to be used to decide which (if either) was operating.

Consider as another example the reaction between propanone and iodine:



This would appear to be a simple bimolecular process, but if this were the case, then the rate of reaction would be expected to depend on the concentrations of both the



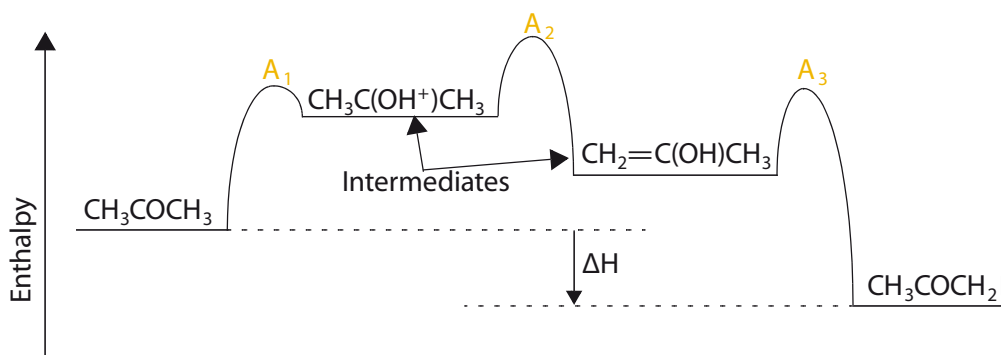


Figure 619 P.E. diagram for the iodination of propanone

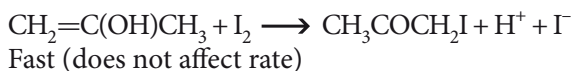
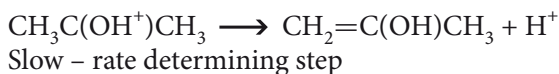
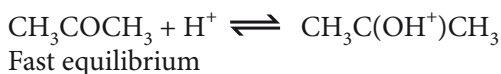
propanone and the iodine hence the rate expression would be:

$$\text{Rate} = k [\text{CH}_3\text{COCH}_3] [\text{I}_2]$$

In practice it is found that the reaction is catalysed by acids and that the rate is independent of the concentration of iodine hence the reaction is first order in both propanone and hydrogen ions, but zero order in iodine. Hence the rate expression is:

$$\text{Rate} = k [\text{CH}_3\text{COCH}_3] [\text{H}^+]$$

This means that one molecule of propanone and one hydrogen ion must be involved in the rate determining step, or in equilibria occurring before this. The commonly accepted mechanism for this reaction is:



This mechanism agrees with the experimentally determined rate expression. The rate expression can never prove that a particular mechanism is correct, but it can provide evidence that other possible mechanisms are wrong.

(Good TOK point – an example of a difficulty that besets all processes of inductive logic.)

The species  $\text{CH}_3\text{C}(\text{OH}^+)\text{CH}_3$  and  $\text{CH}_2=\text{C}(\text{OH})\text{CH}_3$  are intermediates; they have a finite life and occur at a potential energy minimum on the reaction diagram. In this reaction mechanism there would be a number of transition states, firstly ( $A_1$ ) between  $\text{CH}_3\text{COCH}_3$  and  $\text{H}^+$  before forming  $\text{CH}_3\text{C}(\text{OH}^+)\text{CH}_3$  secondly ( $A_2$ ) when  $\text{CH}_3\text{C}(\text{OH}^+)\text{CH}_3$  starts to break up to form  $\text{CH}_2=\text{C}(\text{OH})\text{CH}_3$  and  $\text{H}^+$  and finally ( $A_3$ ) in the reaction of this with iodine. These do not have a finite life and occur at potential energy maxima on the reaction diagram. This is illustrated in Figure 619 and the differences between intermediates and transition states (activated complexes) are summarised in Figure 620.

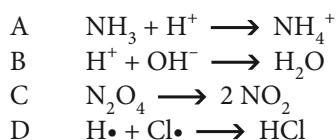
Intermediates	Transition States
Exist for a finite time	Have only a transient existence
Occur at a P.E. minimum	Occur at a P.E. maximum
Formed in one step of a reaction and consumed in a subsequent step	Exist part way through every step of a reaction

Figure 620 Differences between intermediates and transition states

The differences between intermediates and transition states can also be illustrated by the  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$  mechanisms for the nucleophilic substitution reactions of halogenoalkanes.

## Exercise 16.2

1. Which one of these steps is unimolecular?



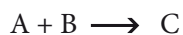
2. Which one of the following is **not** a difference between an activated complex and an intermediate?

- A An activated complex occurs at a potential energy maximum and an intermediate at a minimum.  
 B An activated complex cannot take part in bimolecular reactions, but an intermediate can.  
 C An activated complex does not exist for a finite time but an intermediate does.  
 D An activated complex can reform the reactants, but an intermediate cannot.

3. The rate determining step of a mechanism is the one which

- A occurs most rapidly.  
 B occurs most slowly.  
 C gives out the most energy.  
 D gives out the least energy.

4. Which one of the following mechanisms would give a first order dependence on A and zero order on B for the reaction below?



- A  $\text{A} + \text{X} \longrightarrow \text{Y}$  (fast) then  
 $\text{Y} + \text{B} \longrightarrow \text{C} + \text{X}$  (slow)  
 B  $\text{B} \longrightarrow \text{X}$  (slow) then  
 $\text{X} + \text{A} \longrightarrow \text{C}$  (fast)  
 C  $2\text{A} \longrightarrow \text{A}_2$  (slow) then  
 $\text{A}_2 + \text{B} \longrightarrow \text{C}$  (fast)  
 D  $\text{A} \longrightarrow \text{X}$  (slow) then  
 $\text{X} + \text{B} \longrightarrow \text{C}$  (fast)

5. A reaction involves two reactants, A and B. The initial reaction rate was measured with different starting concentrations of A and B and the following results were obtained at 25 °C:

[A] mol dm <sup>3</sup>	[B] mol dm <sup>3</sup>	Initial rate mol dm <sup>3</sup> s <sup>-1</sup>
0.2	0.2	$3.2 \times 10^4$
0.4	0.4	$1.3 \times 10^3$
0.4	0.8	$1.3 \times 10^3$

- a) Deduce the order of the reaction in A, in B and the overall order. Hence write a rate expression for the reaction.  
 b) Calculate a value for the rate constant, giving suitable units.  
 c) What initial rate would you expect if the initial concentrations of both reactants were 0.1 mol dm<sup>-3</sup>?  
 d) If the overall equation for the reaction is  $\text{A} + \text{B} \longrightarrow \text{C} + \text{D}$ , write a mechanism, indicating which step is the rate determining step, that is:  
 i consistent with the rate expression found.  
 ii inconsistent with the rate expression found.

## 16.3 ACTIVATION ENERGY (AHL)

16.3.1 Describe qualitatively the relationship between the rate constant ( $k$ ) and temperature ( $T$ ).

16.3.2 Determine activation energy ( $E_a$ ) values from the Arrhenius equation by a graphical method.

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In a fluid, there is a distribution of energy amongst the particles known as the Maxwell-Boltzmann distribution (see Section 6.3). As the temperature increases, the number of particles with a high energy increases, though there are still some particles with very little energy. The result is a flattening of the distribution curve, because the total area under it must remain constant (refer to figure 609, reproduced again as Figure 622 for convenience).

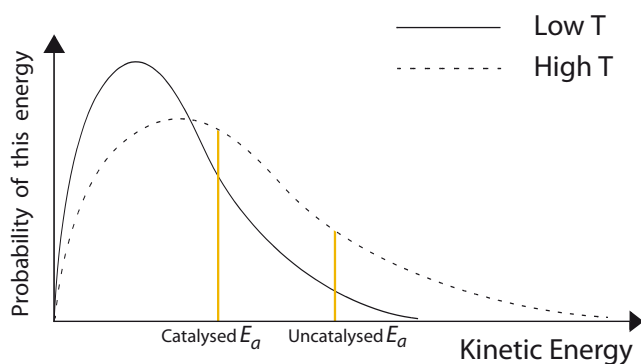


Figure 622 The distribution of kinetic energy at two different temperatures

All chemical reactions require a certain minimum energy, the activation energy ( $E_a$ ), for the reaction to occur. As can be seen from Figure 622, at the higher temperature a greater proportion of the molecules have an energy greater than the activation energy, i.e. there is a greater proportion of the total area under the curve to the right of the  $E_a$  line (either the catalysed or uncatalysed) on the higher temperature curve than on the lower temperature curve. This is usually the major reason why reactions occur more rapidly at higher temperatures.

For many reactions it is found that the effect of temperature on the rate constant for a reaction ( $k$ ) is given by the expression:

$$k = A e^{\left(-\frac{E_a}{RT}\right)}$$

where  $E_a$  is the activation energy,  $T$  the absolute temperature (in Kelvin),  $R$  the gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ) and  $A$  is called the Arrhenius constant (or the pre-exponential factor). It is dependent on collision rate and steric factors, that is any requirements regarding the geometry of the colliding particles. This equation is known as the **Arrhenius equation** after the Swedish chemist, *Svante August Arrhenius*, who first proposed it.

The expression indicates that the rate constant  $k$  depends exponentially on temperature, which is why temperature has such a large effect on reaction rate. Rather satisfyingly the expression for the area under the Maxwell-Boltzmann distribution curve in excess of  $E_a$  also gives an exponential dependence if  $E_a \gg RT$ . If we take logarithms to the base  $e$  (natural logarithms ( $\ln$ ) - a mathematical procedure you may possibly not have met) and then rearrange, the Arrhenius equation is converted to:

$$\ln k = \ln A - \left(\frac{E_a}{R}\right) \frac{1}{T}$$

This is the equation of a straight line so, as shown in Figure 623 below, a graph of  $\ln k$  against  $\frac{1}{T}$  will be linear with gradient  $-\frac{E_a}{R}$  and an intercept on the y-axis of  $\ln A$ .

The activation energy for a reaction can therefore be found by measuring the rate of reaction at different temperatures, with all the other conditions unchanged (so that  $\text{rate} \propto k$ ), and then plotting  $\ln(\text{rate})$  against  $\frac{1}{T}$  (Note again,  $T$  must be in Kelvin, not  $^{\circ}\text{Celsius}$ ).

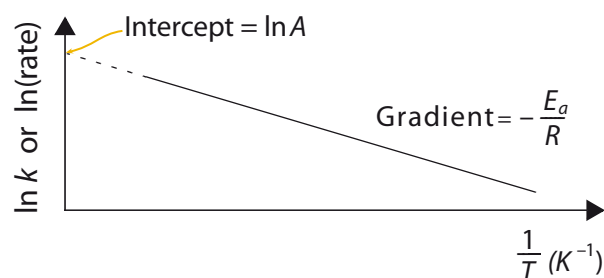


Figure 623 Determining the activation energy graphically

## Exercise 16.3

1. Which one of the following is not true about the activation energy of a reaction?

- A It is related to the enthalpy change ( $\Delta H$ ) of the reaction.
- B It is decreased by the addition of a catalyst.
- C It is the minimum amount of energy that the reactants must have in order to form the products.
- D The greater the activation energy the lower the rate of reaction.

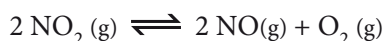
2. The activation energy of a chemical reaction can be determined by measuring the effect on reaction rate of varying

- A the temperature.
- B the concentration of the reagents.
- C the concentration of the catalyst.
- D the surface area in contact.

3. The temperature at which a reaction is carried out is increased from 20 °C to 40 °C. If the half-life of the reaction was initially  $t$ , the half-life at the higher temperature will be:

- A  $2t$
- B  $\frac{1}{2}t$
- C  $t^2$
- D It would depend on the size of the activation energy.

4. The activation energy for the reaction below is  $112 \text{ kJ mol}^{-1}$  and  $\Delta H$  is  $+57 \text{ kJ mol}^{-1}$ .



- a) Draw an energy level diagram illustrating the energy changes for this reaction. Clearly mark and label the activation energy  $E_a$  and the enthalpy change ( $\Delta H$ ).
- b) On the same diagram, using dotted lines, show the effect of a platinum catalyst, clearly labelling the change 'With catalyst'. Would the platinum be acting as a homogeneous or heterogeneous catalyst?
- c) Is the reaction exothermic or endothermic? When it occurs will the container become hotter, or cooler?

- d) If the temperature was increased, how would this affect the rate of reaction? Explain this in terms of the collision theory of reactions (a diagram might help).
- e) What other factor (i.e. **not** temperature or catalyst) could be changed to increase the rate of reaction – be precise, remembering that these are all gases.
- f) Nitrogen dioxide is a brown gas, whereas nitrogen monoxide is colourless. Suggest how you might be able to measure the rate of reaction.

5. When aqueous solutions of benzenediazonium chloride decompose, they evolve nitrogen gas. The table below gives the volume of gas obtained at different times for such a decomposition at 70 °C.

Time min	Volume $\text{cm}^3$
1	5
2	9
3	13
4	17
5	21
7	28
9	33
12	40
16	48
20	54

- a) If, when decomposition was complete, the total volume of gas released was  $70 \text{ cm}^3$ , graphically determine the order of the reaction. What further data, if any, would you need to calculate a value for the rate constant?
- b) Draw the apparatus you could use to obtain such data and state what precautions you would take.
- c) If you wanted to determine the activation energy for this reaction, what further experiments would you carry out? How would you use the data from these to determine the activation energy?