26 Reaction kinetics

For A Level you need to be able to manipulate data about rates of reactions in a more mathematical way. Some of this will come from practical work or from data based on practical work.

Order of reaction

To describe rate relationships in a reaction mathematically, a rate equation is used. These have the form:

$$\text{rate} = k[\text{A}]^m[\text{B}]^n$$

- Here, k is the **rate constant** for the reaction between substances A and B, and m and n are the powers to which the concentrations of these substances are raised in the experimentally determined rate equation.
- Each is called the **order** with respect to each substance. For the reactions in A Level work, m and n can be 0, 1 or 2.
- It is important to remember that not all reactions take place in a single step.
- For multi-step reactions, one step will *always* be slower than all the others. This is called the **rate-determining step**, because it is on this that the overall reaction rate depends.

KEY TERM

The **rate-determining step** is the slowest step in a multi-step reaction and the overall reaction rate depends on this.

It is easier to understand what this means by looking at some examples. Consider the reaction:

$$\text{A} + \text{B} \rightarrow \text{products}$$

If you measure the way in which the rate of this reaction changes depending on the concentrations of A and B, you might find that doubling the concentration of A doubles the rate. You might also find that doubling the concentration of B doubles the rate.

This tells us that the order with respect to A is 1, and that the order with respect to B is also 1 – so the overall order of the reaction is 2. The rate equation could be written:

$$\text{rate} = k[\text{A}]^1[\text{B}]^1$$

However, you do not need to show *m* and *n* when they are 1:

$$\text{rate} = k[\text{A}][\text{B}]$$

In another reaction:

$$\text{X} + \text{Y} \rightarrow \text{products}$$

the rate might not depend on Y reacting with X, but on X breaking down and then Y reacting with those products. When this is the case, the rate equation has the form:

$$\text{rate} = k[\text{X}]^1[\text{Y}]^0$$

Remembering that anything to the power 0 equals 1, this rate equation can be written:

$$\text{rate} = k[\text{X}]$$

NOW TEST YOURSELF

1 Why does the slowest step in a reaction decide the overall rate?

Deducing order by the initial rates method

Most reaction kinetic studies are based on experimental work. Consider a reaction for which the rate can be measured at the start. Data from such an experiment are given in Table 26.1.

Table 26.1

Run	Initial [A]/mol dm^{-3}	Initial [B]/mol dm^{-3}	Initial rate/mol dm^{-3} s^{-1}
1	1.00	1.00	1.25×10^{-2}
2	1.00	2.00	2.5×10^{-2}

Run	Initial [A]/mol dm^{-3}	Initial [B]/mol dm^{-3}	Initial rate/mol dm^{-3} s^{-1}
3	2.00	2.00	2.5×10^{-2}

Look at runs 1 and 2 – if you double the concentration of B and keep the concentration of A constant, then the rate doubles. Look at runs 2 and 3 – doubling the concentration of A and keeping the concentration of B constant has no effect on the rate. This tells us that the reaction is first order with respect to B and zero order with respect to A. In other words, A does not feature in the rate equation. You can now calculate the rate constant:

$$\text{rate} = k[\text{B}]$$

$$2.5 \times 10^{-2}\ \text{mol dm}^{-3}\ \text{s}^{-1} = k \times 2.0\ \text{mol dm}^{-3}$$

$$k = 1.25 \times 10^{-2}\ \text{s}^{-1}$$

Deducing order from graphs

Another way of deducing the order of a reaction with respect to a given reagent is to look at a graph of concentration against time. Zero-order (Figure 26.1(a)) and first-order reactions (Figure 26.1(b)) have characteristic shapes.

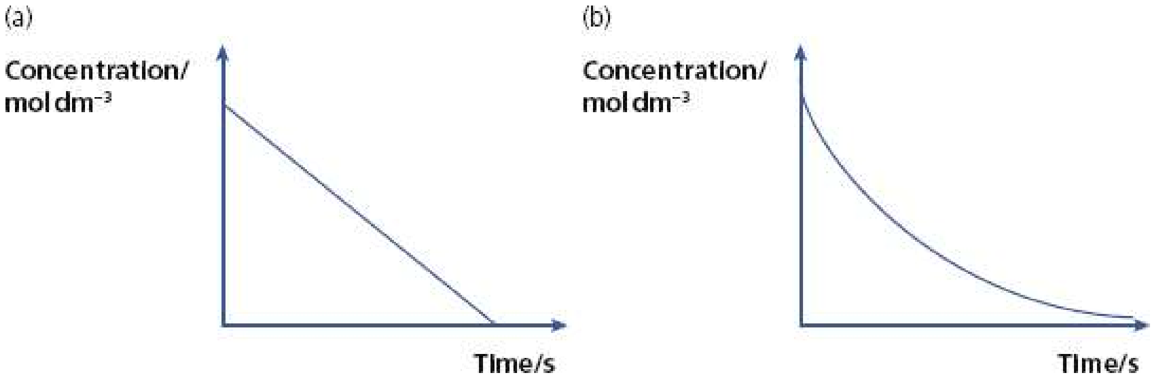

Figure 26.1 Concentration–time graphs for (a) a zero-order reaction and (b) a first-order reaction

It is also possible to compare graphs of rate against concentration (Figure 26.2).

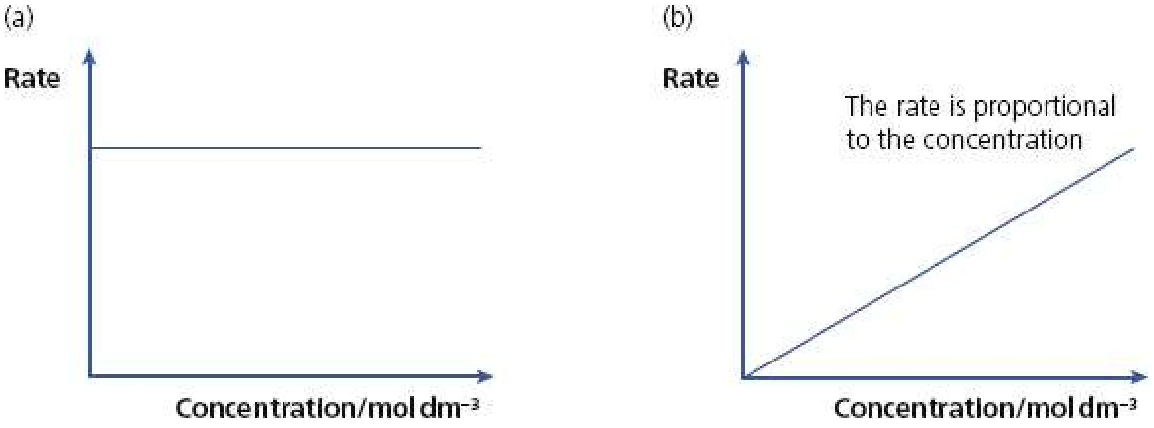

Figure 26.2 Rate–concentration graphs of (a) a zero-order reaction and (b) a first-order reaction

These graphs show that in a zero-order reaction, the rate is independent of concentration and gives a horizontal line (Figure 26.2(a)). For a first-order reaction, the reaction shows a constant time for the concentration of a reactant to halve (Figure 26.1(b)). This is known as the **half-life** of the reaction and is similar to the half-life concept in radioactive decay.

A half-life can be used to calculate the rate constant of a reaction. Look at this reaction:

$$CH_3N_2CH_3(g) \rightarrow C_2H_6(g) + N_2(g)$$

When the compound is heated it decomposes into the two gases shown. No other reactants are needed so:

$$\text{rate} = k[CH_3N_2CH_3(g)]$$

The half-life of this reaction at 500 K is about 1750 s. This means that if the starting concentration is 0.10 mol dm^{-3}, after 1750 s the concentration will have halved to 0.05 mol dm^{-3}. After another 1750 s, the concentration will have halved to 0.025 mol dm^{-3}, and so on.

A half-life can be used to calculate the rate constant, k. For a first-order reaction:

$$\begin{aligned} k &= \frac{0.693}{t_{1/2}} \\ &= \frac{0.693}{1750} \\ &= 3.96 \times 10^{-4}\,s^{-1} \end{aligned}$$

Multi-step reactions and predicting order

Reactions can happen in a single step or more than one step (multi-steps). For the examination, you need to be able to predict the order of a reaction from a given mechanism (and vice versa).

Consider this reaction of a primary halogenoalkane:

$$C_4H_9Br + OH^- \rightarrow C_4H_9OH + Br^-$$

This could occur in one step as shown above or in two steps:

slow step: $C_4H_9Br \rightarrow C_4H_9^+ + Br^-$

fast step: $C_4H_9^+ + OH^- \rightarrow C_4H_9OH$

- If the first mechanism is correct, you would predict that the reaction is first order with respect to both C_4H_9Br and OH^-.
- If the second mechanism is correct you would predict that the reaction is first order with respect to only C_4H_9Br, because this is the rate-determining step.
- The slowest step is *always* the one (bottleneck) that determines the rate (the rate-determining step).
- In this example, practical evidence suggests that the first mechanism is correct.

NOW TEST YOURSELF

2 The reaction between $(CH_3)_3Br$ and OH^- ions can happen by two possible mechanisms:

$$(CH_3)_3Br + OH^- \rightarrow (CH_3)_3OH + Br^-$$

or

$(CH_3)_3Br \rightarrow (CH_3)_3^+ + Br^-$ slow

$(CH_3)_3^+ + OH^- \rightarrow (CH_3)_3OH$ fast

If the rate equation for the reaction is:

$$\text{rate} = k[(CH_3)_3Br]$$

which mechanism is correct and why?

Experimental techniques for studying rates

It is important to consider the methods that are available to follow the progress of a reaction and to determine the rate.

Sampling followed by titration

Small amounts of the reaction mixture are withdrawn by pipette at regular intervals. Further reaction in this sample is prevented, often by adding a large volume of a common inert solvent. The concentration of one of the reactants or products is then determined by titration of the samples. Common examples are the formation of an acid and an iodination reaction.

Using a colorimeter

This method only works if one of the reactants or products is coloured. It has advantages over titration in that no sampling is needed and it gives an almost instantaneous result. An example is the formation of a transition metal complex.

Measurement of gas evolved

One of the products has to be a gas for this method to work. The volume of the gas is measured in a syringe or by the displacement of water from an upturned burette. An example is the reaction between an acid and a carbonate.

Catalysis

You will already have come across the use of catalysts in your GCSE work. You need to know how catalysts are able to speed up reactions. Catalysts can be:

- homogeneous (in the same physical state as the reactants)
- heterogeneous (in a different physical state from the reactants)

The Haber process

You saw in Chapter 7 how this equilibrium process was made economic by the use of an iron catalyst. The catalyst is heterogeneous – in a different phase from the gases. Transition metals are particularly good at acting as catalysts because their atoms have unfilled d-orbitals. The gases are adsorbed onto the surface of the metal, forming weak bonds (Figure 26.3). This can have one of two consequences:

- The formation of bonds with the metal surface may weaken the bonds within the gas molecules.
- The orientation of the adsorbed molecules may be favourable for the reaction.

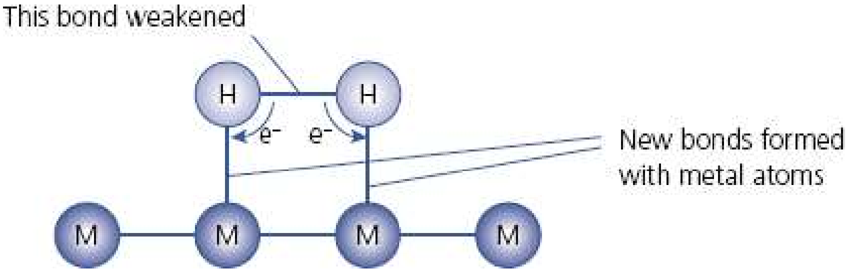

Figure 26.3 Adsorption of a gas onto the surface of a metal catalyst

Catalytic converters in vehicle exhausts

- Catalytic converters have become important in recent years – they are designed to remove pollutant gases from vehicle exhausts.
- The problem is complex because some pollutants, such as carbon monoxide, have to be oxidised while others, such as nitrogen oxides, have to be reduced.
- The converter consists of a ceramic honeycomb with a very thin coat of platinum, rhodium and palladium (all expensive metals). The platinum and rhodium help to reduce the NO_x to nitrogen, while platinum and palladium help to oxidise the CO and unburnt hydrocarbons to carbon dioxide and water.
- The car has to run on unleaded petrol because lead would ‘poison’ the catalyst, making it ineffective.
- This is a heterogeneous system.

Nitrogen oxides in the atmosphere

- Nitrogen(IV) oxide is unchanged by the reaction and is thought to form a weak intermediate with sulfur dioxide.
- This is an example of homogeneous catalysis – the reactants and the catalyst are in the same phase, in this case gases.
- Studies on acid rain have shown that in the atmosphere the presence of oxides of nitrogen, particularly nitrogen(IV) oxide (NO_2), increases the rate of oxidation of sulfur dioxide to sulfur trioxide.

The role of Fe^{2+} in the $I^-/S_2O_8^{2-}$ reaction

The oxidation of iodide ions by peroxodisulfate ions is another example of homogeneous catalysis. In this case, all the species are in the aqueous phase. It is believed that this oxidation occurs in two steps in the presence of Fe^{3+} ions:

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

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

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

Although there are two steps in the reaction, the overall activation energy is lower than in the single-step reaction, as can be seen in Figure 26.4.

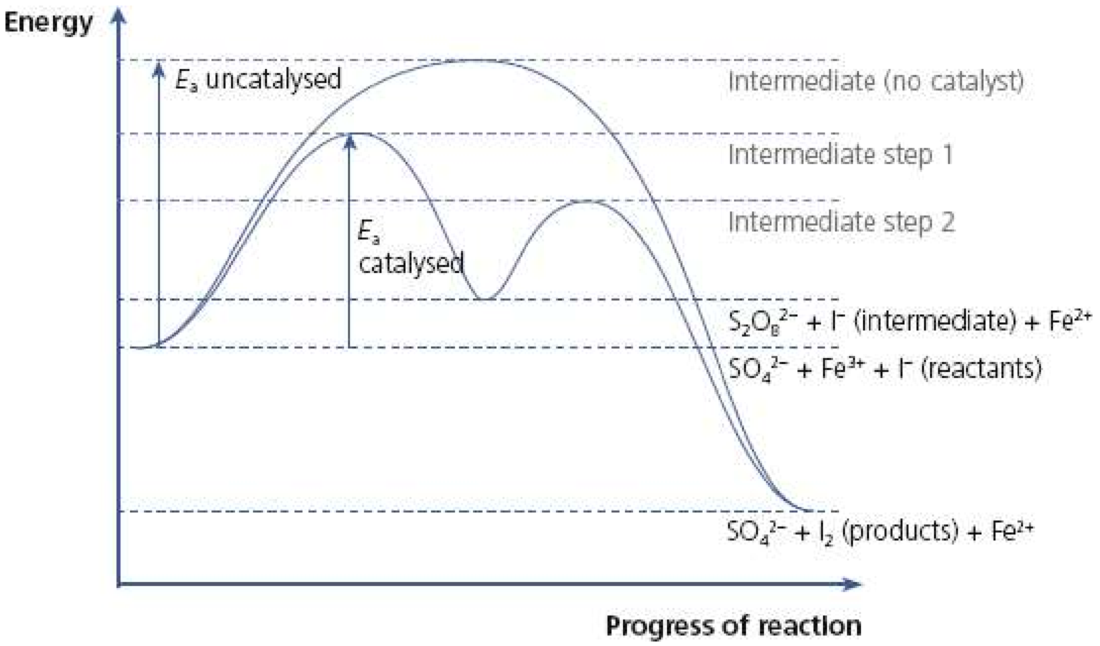

Figure 26.4 The effect of a catalyst on a reaction profile

NOW TEST YOURSELF

3 a What is the difference between a heterogeneous catalyst and a homogeneous catalyst?

b Suggest what this means in practical terms.

REVISION ACTIVITY

a The table shows some rate data from an experiment.

Run	Initial [A]/mol dm^{-3}	Initial [B]/mol dm^{-3}	Initial rate/mol dm^{-3} s^{-1}
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3	2.00	2.00	2.5×10^{-2}

Use the data to deduce the rate equation for the reaction, explaining your answer.

b Car engines produce a number of pollutant gases. Most of these are converted to less harmful gases using catalytic converters.

  i What metals are commonly used in catalytic converters?

  ii What are the following pollutants converted into: NO_x, CO, unburnt hydrocarbons?

c **i** Give an example of a homogeneous catalyst.

  ii Write equations to show this substance behaving as a homogeneous catalyst.

END OF CHAPTER CHECK

By now you should be able to:

- explain and use the terms rate equation, order of reaction, overall order of reaction, rate constant, half-life, rate-determining step and intermediate
- understand and use rate equations of the form rate = $k[A]^m[B]^n$ for which m and n are 0, 1 or 2; deduce the order of a reaction from concentration–time graphs or from experimental data from an initial rates or half-life method; calculate an initial rate from concentration data; construct a rate equation
- show understanding that the half-life of a first-order reaction is independent of concentration and use the half-life of a first-order reaction in calculations
- calculate the numerical value of a rate constant using the initial rates and the rate equation; using half-life and the equation

  $$k = \frac{0.693}{t_{1/2}}$$

- for a multi-step reaction suggest a reaction mechanism consistent with the rate equation; predict the order that would result from a given mechanism and rate-determining step; deduce a rate equation using a given mechanism and rate-determining step; identify an intermediate or catalyst and the rate-determining step from a given mechanism

- describe qualitatively the effect of temperature change on the rate constant and hence the rate of reaction
- explain that catalysts can be homogeneous or heterogeneous
- describe the mode of action of a heterogeneous catalyst, e.g. iron in the Haber process; palladium, platinum and rhodium in catalytic converters in exhaust systems
- describe the mode of action of a homogeneous catalyst, e.g. atmospheric oxides of nitrogen in oxidising atmospheric sulfur dioxide; Fe^{2+} and Fe^{3+} in the $I^-/S_2O_8^{2-}$ reaction