Rate of reaction

A study of reaction rates (chemical kinetics) allows us to understand exactly how reactions work. You cannot deduce a reaction mechanism simply by examining the ordinary balanced chemical equation. Experimental work to determine the reaction rate leads to the rate equation, which, in turn, leads to the reaction mechanism (see page 12).

\[
\text{rate of reaction} = \frac{\text{change in concentration}}{\text{time}}, \text{ or } \frac{\Delta c}{\Delta t}
\]

Rate equations

Rate equations show the relationship between the rate and the powers to which the reactant concentrations are raised. If two reactants, A and B, react together then measurements of reaction rates with different concentrations of A and B (see below) could give the rate equation

\[
\text{rate} = k[A]^x[B]^y
\]

In this case:
- k is the rate constant, which is constant at a particular temperature
- [A] and [B] are the concentrations of substances A and B
- x is the order with respect to A, and y is the order for B
- The overall order of reaction is the sum of the individual orders, \(x + y\).

**Worked Example**

Studies of some reactions gave the following rate equations:

a. rate = \(k[A][B]^2\)

b. rate = \(k[A]^2[B]^3\)

c. rate = \(k[A]^2[B]^2\)

d. rate = \(k[A][B]\)

Which reactions have the same overall order, and which rate is independent of the concentration of one reactant?

Reactions a, b are both third order overall. Reaction b is zero order with respect to reactant A, and so its rate is not affected by varying the amount of reactant A. We can write rate = \(k[B]^3\).

Measuring reaction rates

Rates of reaction are measured by monitoring the rate of change of an observable property.

- **Colorimetry** measures the intensity of a colour in a reaction mixture with time, such as in the oxidation of iodide ions to give brown iodine. In **clock reactions** the reaction is timed until a sudden colour change happens when a certain amount of product is formed.
- **Mass change** is used when a gas is produced. For example, when calcium carbonate reacts with acids to release carbon dioxide the mass of the flask decreases.
- **Volume change** is an alternative to mass changes for gases. For example, magnesium reacts with acids to release hydrogen, which can be collected in a syringe.
- **Titrimetric analysis** uses titrations to measure changing concentrations of a reactant or product – for example, the fall in acid concentration during esterification.
Graphs and tangents

The simplest type of relationship between variables is the linear one of general form $y = mx + c$, where $m$ is the slope or gradient and $c$ the intercept on the y-axis.

- The gradient of a curve is found by drawing a tangent. The gradient of the tangent to the concentration–time graph at a particular time gives the rate at that moment.
- The initial rate of reaction is found from the gradient of the tangent to the concentration–time graph at $t = 0$.
- It is often difficult to monitor reaction rates or concentration continuously. In practice you carry out a series of reactions where you vary the initial concentration of each reactant in turn. You then plot a graph of initial rate against initial concentration for each reactant.
- You can find the orders from the shape of each graph, and the value of $k$ and units by substituting your measurements into the rate equation (e.g. $k = \frac{\text{rate}}{[A][B]^2]$).

If the gradient is constant, showing that the rate is unaffected by the concentration of a reactant, it is a zero order reaction for that reactant.

The half-life decreases as the concentration falls. The gradient is the rate constant $k$, so the rate equation is $\text{rate} = k[A]^0$.

If the gradient changes exponentially, it is a first order reaction.

The half-life is constant and the rate is $k[A]^1$.

If the gradient changes from very high at $t = 0$ and then slows down, it is a second order reaction.

The half-life increases as the concentration falls and the rate is $k[A]^2$.

How the reaction rate varies with time for zero, first and second order reactions

Half-life

The half-life is the time needed for any reactant concentration to fall to half of its initial value.

**Worked Example**

Calculate the half-life for the decomposition of $\text{SO}_2\text{Cl}_2$ starting with concentrations of (a) 0.50 mol dm$^{-3}$, (b) 0.30 mol dm$^{-3}$ and (c) 0.20 mol dm$^{-3}$.

**Quick Questions**

1. What is the order of a reactant whose doubled concentration doubles the rate?
2. Why does the addition of starch make it easier to follow the rate of a reaction producing iodine?
3. What is special about the half-life of a first order chemical reaction? Does this include radioactive decay?
4. Describe the shape of a rate–concentration graph for a zero order process.
When reactant molecules collide, it may result in a chemical reaction. There is an energy requirement before this can happen. The activation energy is the minimum energy needed by reactant particles (molecules or ions) before products can form.

The diagram shows that the reaction is:
- exothermic – the products are at a lower energy level than the reactants
- subject to an energy barrier, the activation energy, in route 1
- able to follow an alternative pathway in route 2, with a lower barrier.

A catalyst increases the reaction rate by providing an alternative reaction pathway with a lower activation energy. Such catalysed reactions are faster.

Catalysts and reactants can be in the same physical state, called homogeneous – for example, all liquids. Or they can be in different states, when they are called heterogeneous.

Many catalysts are transition metals (or their compounds) because they have variable oxidation states and can alter the numbers of bonds available to reactants.
Effect of temperature on rates

When the temperature increases, the rate of a reaction increases too because the rate constant increases.

The rate constant $k$ is only a constant for a particular temperature. Changing the temperature changes the value of $k$ because the proportion of molecules that have the required energy (greater than the activation energy) is increased and the colliding particles have a greater average energy.

The Arrhenius equation shows the relationship between the rate constant $k$ and the temperature $T$ (in kelvin). The logarithmic (ln) form of this equation is:

$$\ln k = \frac{-E_A}{RT} + \text{a constant}$$

- $E_A$ is the activation energy for the reaction
- $R$ is the gas constant and has the value $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$
- $T$ is the kelvin temperature (absolute temperature)
- Gradient $= \frac{-E_A}{R}$

Working out the value of an activation energy:
This shows that a plot of ln $k$ against $\frac{1}{T}$ gave a straight line whose gradient is $\frac{-E_A}{R}$.

Investigating the activation energy of a reaction

If we know the rate equation for a reaction, it is easy to calculate the rate constant $k$ using the rate of reaction for a known concentration of reactants. Calculating the activation energy requires the results from experiments at a range of different temperatures, to give values of the rate constant $k$ at each temperature.

A suitable reaction to study is the oxidation of iodide ions by iodate(V) ions in acidic solution. The equation is:

$$\text{IO}_3^-\text{(aq)} + 5\text{I}^-\text{(aq)} + 6\text{H}^+\text{(aq)} \rightarrow 3\text{I}_2\text{(aq)} + 3\text{H}_2\text{O(l)}$$

A small known amount of sodium thiosulfate is added at the start of the reaction together with starch as the indicator. The iodine released by the oxidation of the iodide ions first reacts with the thiosulfate, so the mixture remains colourless initially but then suddenly turns starch blue-black when all the thiosulfate has reacted. This is an example of a clock reaction with a built-in time delay that depends only on the concentration of the iodide and iodate ions. The relative initial rate of production of iodine can be found from $\frac{1}{t}$, where $t$ is the time delay.

The value for the activation energy can be found graphically as described above.

### Worked Example

Use the data to find the value of the activation energy.

<table>
<thead>
<tr>
<th>Temperature/K</th>
<th>Rate constant $k$/dm$^3$ mol$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>670</td>
<td>$1 \times 10^{-4}$</td>
</tr>
<tr>
<td>700</td>
<td>$5 \times 10^{-4}$</td>
</tr>
<tr>
<td>780</td>
<td>$1.5 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

Plotting a line graph of ln $k$ (y-axis) against $1/T$ gives a straight line of negative slope. Putting the negative gradient equal to $\frac{-E_A}{R}$ gives the activation energy $E_A$ as about $+190 \text{ kJ mol}^{-1}$, depending on how you draw the line.

### Quick Questions

1. Identify the type of catalysis in hydrogenating oils to give margarine using a nickel catalyst.
2. How does temperature affect the rate constant $k$?
3. What is the purpose of adding sodium thiosulfate in the iodine clock reaction?
Mechanisms and rate-determining steps

Reactions do not just happen whenever all the relevant molecules collide at once – they happen in steps. The slowest step controls how fast the overall reaction occurs – it is called the rate-determining step.

Kinetic measurements establish the order of the reaction for each species. For a reaction between A, B and C the rate equation could be:

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

Since substance B does not occur in the rate equation, any step involving molecule B must be fast. This rate equation demonstrates that:

- the reaction is first order with respect to A – so A is involved in the rate-determining step
- the reaction is second order with respect to substance C – so two moles of C are involved in the rate-determining step.

Nucleophilic substitution mechanisms of halogenoalkanes

Two substitution mechanisms are possible when an iodoalkane reacts with aqueous alkali:

$$\text{R} - \text{I} + \text{OH}^- \rightarrow \text{R} - \text{OH} + \text{I}^-$$

Only the experimental rate data can show which mechanism actually takes place.

Nucleophilic substitution of a primary halogenoalkane

- The single step illustrated for the substitution of 1-iodopropane, a primary halogenoalkane, involves two different species – both the hydroxide ion and the primary halogenoalkane.
- The reaction will be second order – it depends on the concentration of both the hydroxide ion and the primary halogenoalkane.

So, rate = $k[R][OH^-]$

We call this an $S_{N2}$ mechanism, meaning substitution/nucleophilic/second order.

Tertiary halogenoalkanes hydrolyse by the alternative $S_{N1}$ mechanism, meaning substitution/nucleophilic/first order.

Nucleophilic substitution of a tertiary halogenoalkane

- The C — halogen bond breaks first (slow step) followed by attack by the hydroxide ion (fast step).
- The slow step involves only one species and does not depend on the concentration of hydroxide ions. Hence the reaction is first order overall:

$$\text{rate} = k[R]$$
The mechanism must be consistent with the evidence:
- if the reaction is second order overall it must involve two different species
- if the reaction is first order overall (only one species in the rate equation) then this is the rate-determining step and it must be a two-step reaction.

**Kinetics of the reaction between propanone and iodine in acid solution**

\[ \text{I}_2 + \text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_2\text{ICOCH}_3 + \text{HI} \]

- Hydrogen ions catalyse this reaction.
- The rate equation has the form of rate = \( k[\text{CH}_3\text{COCH}_3][\text{I}_2][\text{H}^+] \)
- Varying the concentration of each species in turn gives the order of each species – \( x, y \) and \( z \).
- The reaction can be followed by titrating the remaining unreacted iodine with standard sodium thiosulfate using starch indicator. Alternatively, a colorimeter can be used to monitor the brown colour of the iodine.
- Experimental data shows the reaction to be first order with respect to both propanone and hydrogen ions, but zero order for iodine.
- The reactant iodine is not in the rate equation at all but hydrogen ions are present, despite not being reactants.

### Worked Example

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Iodine/mol dm(^{-3})</th>
<th>Propanone/mol dm(^{-3})</th>
<th>Hydrogen ions/mol dm(^{-3})</th>
<th>Relative rate of reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.006</td>
<td>0.6</td>
<td>0.6</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0.006</td>
<td>0.12</td>
<td>0.6</td>
<td>1.9</td>
</tr>
<tr>
<td>3</td>
<td>0.006</td>
<td>1.8</td>
<td>0.6</td>
<td>3.1</td>
</tr>
<tr>
<td>4</td>
<td>0.006</td>
<td>0.6</td>
<td>1.2</td>
<td>2.1</td>
</tr>
<tr>
<td>5</td>
<td>0.012</td>
<td>0.6</td>
<td>0.6</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Data from the reaction of iodine with propanone in acid solution

Use this data to establish which species are involved in the rate-determining step.

Within the limits of experimental error, we can see that:
- (Expt 1 \(\rightarrow\) 2) doubling the concentration of propanone doubles the rate (first order)
- (Expt 1 \(\rightarrow\) 4) doubling the concentration of hydrogen ions doubles the rate (first order)
- (Expt 1 \(\rightarrow\) 5) doubling the concentration of iodine has no effect on the rate (zero order)

The rate-determining step involves both propanone and hydrogen ions, but not iodine.

### Using a colorimeter to study rates

The chosen filter should let through only the wavelength to be absorbed by the coloured iodine solution. Since iodine solution is brown-red, a blue-green filter is used.

### Quick Questions

1. Why are some species in the stoichiometric equation absent from the rate equation?
2. What is the meaning of the term ‘\(S_n\)1 mechanism’?
3. Suggest two practical techniques to monitor a reaction involving iodine solution.
### Topic 1: How fast? Rates checklist

By the end of this topic you should be able to:

<table>
<thead>
<tr>
<th>Revision spread</th>
<th>Checkpoints</th>
<th>Specification section</th>
<th>Revised</th>
<th>Practice exam questions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rate of reaction</strong></td>
<td>Understand these terms: rate of reaction, rate equation, order of reaction, rate constant, half-life</td>
<td>4.3a</td>
<td>☐</td>
<td>☐</td>
</tr>
<tr>
<td></td>
<td>Describe one experimental method to obtain rate data, choosing from colorimetry, mass change or gas volume change</td>
<td>4.3b</td>
<td>☐</td>
<td>☐</td>
</tr>
<tr>
<td></td>
<td>Describe a reaction that is used to find the rate of reaction and its half-life, e.g. a clock reaction</td>
<td>4.3c</td>
<td>☐</td>
<td>☐</td>
</tr>
<tr>
<td></td>
<td>Draw and interpret graphs of concentration or volume against time</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Draw and interpret concentration–time and rate–concentration graphs</td>
<td>4.3d</td>
<td>☐</td>
<td>☐</td>
</tr>
<tr>
<td></td>
<td>Use experimental data from zero, first and second order reactions to work out the: i) half-life, ii) order, iii) rate equation</td>
<td>4.3f</td>
<td>☐</td>
<td>☐</td>
</tr>
<tr>
<td><strong>Activation energy and catalysis</strong></td>
<td>Understand these terms: activation energy, heterogeneous and homogeneous catalysis</td>
<td>4.3a</td>
<td>☐</td>
<td>☐</td>
</tr>
<tr>
<td></td>
<td>Use experimental data from zero, first and second order reactions to work out the activation energy given the Arrhenius equation</td>
<td>4.3f</td>
<td>☐</td>
<td>☐</td>
</tr>
<tr>
<td></td>
<td>Know how to carry out a practical investigation to find an activation energy, for example in the oxidation of iodide ions by iodate(V) ions</td>
<td>4.3g</td>
<td>☐</td>
<td>☐</td>
</tr>
<tr>
<td><strong>Mechanisms and rate-determining steps</strong></td>
<td>Understand the term rate-determining step</td>
<td>4.3a</td>
<td>☐</td>
<td>☐</td>
</tr>
<tr>
<td></td>
<td>i) Describe the reaction between iodine and propanone in acidic solution</td>
<td>4.3e</td>
<td>☐</td>
<td>☐</td>
</tr>
<tr>
<td></td>
<td>ii) Use experimental data to find the orders, and hence discuss a possible mechanism for this reaction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Use experimental data from zero, first and second order reactions to work out the rate-determining step in a reaction mechanism</td>
<td>4.3f</td>
<td>☐</td>
<td>☐</td>
</tr>
<tr>
<td></td>
<td>Study the hydrolysis reactions of halogenoalkanes to understand the different mechanisms, and deduce proposed mechanisms that are consistent with experimental data for the orders of reactions</td>
<td>4.3h and i</td>
<td>☐</td>
<td>☐</td>
</tr>
<tr>
<td></td>
<td>Explain what we mean by $S_\text{N1}$ mechanisms and $S_\text{N2}$ mechanisms in the nucleophilic substitution reactions of halogenoalkanes</td>
<td>4.3j</td>
<td>☐</td>
<td>☐</td>
</tr>
</tbody>
</table>
Two gases A and B react according to the equation: A(g) + 2B(g) → AB₂(g)

A series of kinetics experiments performed at constant temperature gave the following results:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial concentration of A/mol dm⁻³</th>
<th>Initial concentration of B/mol dm⁻³</th>
<th>Initial rate/mol dm⁻³s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0500</td>
<td>0.100</td>
<td>1.00 × 10⁻⁴</td>
</tr>
<tr>
<td>2</td>
<td>0.0500</td>
<td>0.200</td>
<td>3.92 × 10⁻⁴</td>
</tr>
<tr>
<td>3</td>
<td>0.1000</td>
<td>0.100</td>
<td>1.95 × 10⁻⁴</td>
</tr>
</tbody>
</table>

a i Calculate, showing your working, the orders of reaction with respect to A and to B. (3)
ii Write the rate equation for the reaction. (1)
iii Calculate the rate constant k for the reaction using the results from experiment 3. State its units. (2)

b Explain, in terms of collision theory, why the rate of reaction increases with an increase in temperature. (3)

Examiner tip

a i Looking at experiments 1 and 2, as concentration of B doubles, the rate increases four times so the reaction is second order with respect to B. (1)
Looking at experiments 1 and 3, as concentration of A doubles, the rate doubles so it is first order with respect to A. (1)
You must indicate that the concentration of one of the reactants stays the same for the pair of values chosen for comparison to gain the third mark. (1)

ii The rate equation is rate = k[A][B]² (1)
Note that this now presents the same information as (a)(i) in a different form. If your values for (a)(i) are wrong, say both second order, but the rate equation in (a)(ii) matches theses values, you may still get the consequential marks.

iii \[ k = \frac{1.95 \times 10^{-4} \text{ mol dm}^{-3} \text{s}^{-1}}{0.100 \text{ mol dm}^{-3} \times (0.100 \text{ mol dm}^{-3})^2} = 0.195 \text{ dm}^2 \text{ mol}^{-2} \text{s}^{-1} \] (1)

Answers to three significant figures would be appropriate with this data but examiners may not insist on this in awarding marks.
A common error is to ignore the instruction in the question to calculate the value of k for experiment 3.

b Explain, in terms of collision theory, why the rate of reaction increases with an increase in temperature. (3)
2. In aqueous solution, propanone and bromine react as follows:
\[ \text{CH}_3\text{COCH}_3(aq) + \text{Br}_2(aq) \rightarrow \text{CH}_3\text{COCH}_2\text{Br}(aq) + \text{HBr}(aq) \]
This reaction is zero order with respect to bromine. What can we deduce from this? Choose the correct response:
A. The slowest step involves bromine
B. The rate of reaction has a constant value
C. Bromine is a catalyst
D. Bromine is not involved in the rate-determining step

Examiner tip
The slow rate-determining step cannot involve the bromine because it is zero order. The answer is D. (1)

3. When aqueous sodium hydroxide reacts with 2-bromo-2-methylpropane, the rate equation is:
\[ \text{rate} = k[2\text{-bromo-2-methylpropane}] \]
What is the first step in the reaction mechanism? Choose the correct response:
A. Electrophilic attack by hydroxide ions on the C—Br bond
B. Breaking of the C—Br bond producing a carbocation
C. The C—Br bond breaks as the C—O bonds forms
D. Nucleophilic attack by hydroxide ions on the carbon in the C—Br bond

Examiner tip
This compound reacts by an SN1 mechanism to give a stable carbocation. The answer is B. (1)

Check that you can explain the differences between SN1 mechanisms and SN2 mechanisms in terms of how easily carbocations can form and their stabilities. This is a common question.
Practice exam questions

1 In acid solution, ethanedioic acid (oxalic acid) is oxidized by the addition of an aqueous solution of potassium manganate(VII). During a titration, it was noticed that the rate at which the manganate(VII) decolorised accelerated significantly just after the start of the addition from the burette. This suggests that:

A the reaction is endothermic  
B the potassium ion is a catalyst  
C a product of the reaction is catalysing the oxidation  
D the reaction is slightly exothermic. (1)

2 a In a rate of reaction experiment between two substances A and B, the overall order of the reaction was found to be 2.
Write three possible rate equations for such a second order reaction between A and B. (3)

b At a certain temperature, the rate of reaction between nitrogen monoxide, NO, and hydrogen, H₂, was investigated. The following data were obtained.

<table>
<thead>
<tr>
<th>[NO]/mol dm⁻³</th>
<th>[H₂]/mol dm⁻³</th>
<th>Rate of reaction/mol dm⁻³ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>0.02</td>
</tr>
<tr>
<td>1.0</td>
<td>3.0</td>
<td>0.06</td>
</tr>
<tr>
<td>3.0</td>
<td>1.0</td>
<td>0.18</td>
</tr>
</tbody>
</table>

i Use the data above to deduce the rate equation for this reaction. (3)

ii Use your answer to (b) (i) to calculate the value of the rate constant, with its units. (2)

3 The rate of the decomposition of nitrous oxide:

\[ 2 \text{N}_2\text{O}(g) \rightarrow 2 \text{N}_2(g) + \text{O}_2(g) \]

has been studied at different temperatures. The rate constant \( k \) was determined at each temperature.

The relationship between the rate constant and the temperature \( T \) is given by the Arrhenius equation:

\[ \ln k = -\frac{E_A}{RT} + \ln A \]

where \( E_A \) is the activation energy for the reaction, \( R \) is the gas constant (8.314 J K⁻¹ mol⁻¹), and \( k \) is the rate constant at temperature \( T \).

a Given values of \( k \) at different temperatures \( T \), what graph would you plot and how would you use it to determine the activation energy? (2)

b A plot of the data gave a straight line with gradient \(-2.95 \times 10^4 \text{K}^{-1}\).
Find the activation energy for the reaction, in kJ mol⁻¹, to three significant figures. (2)

(From Edexcel Unit test 5 Q2, June 08)