

FACTFILE: GCE CHEMISTRY

4.3 RATES OF REACTION



Learning Outcomes

Students should be able to:

- 4.3.1** Use simple rate equations in the form:
rate = $k[A]^x[B]^y$ (where x and y are 0, 1 or 2);
- 4.3.2** understand the terms: • rate of reaction;
• order; and • rate constant;
- 4.3.3** deduce simple rate equations from experimental data; and
- 4.3.4** deduce, from a concentration-time or a rate concentration graph, the rate of reaction and/or the order with respect to a reactant.
- 4.3.5** recall that there is a relationship between the rate equation and mechanism, for example SN1 and SN2 mechanisms for the alkaline hydrolysis of primary and tertiary halogenoalkanes;
- 4.3.6** deduce simple rate equations from experimental data; and
- 4.3.7** suggest experimental methods suitable for the study of the rate of a reaction, for example iodine titrations and colorimetry;
- 4.3.8** explain, qualitatively, the effect of temperature and activation energy on rate constant

Rate of reaction

The rate of a reaction can be measured based on how fast the concentration of a reactant is decreasing or how fast the concentration of a product is increasing, i.e.

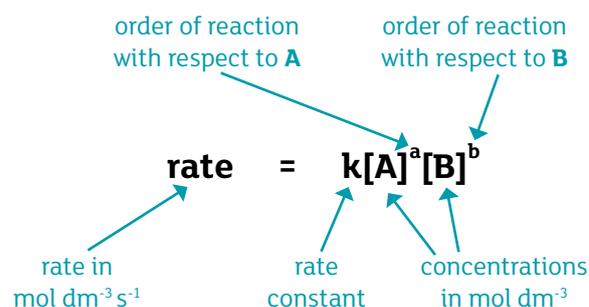
The rate of reaction is the change of the concentration (amount) of a reactant or product with respect to time.

The units of rate are concentration per unit time, for example $\text{mol dm}^{-3} \text{s}^{-1}$ (mol per dm^3 per second).

Rate equations

A rate equation shows how the rate of a reaction is linked to concentration. Square brackets around a substance, for example $[\text{HCl}]$ or $[\text{H}^+]$ all indicate concentration, in mol dm^{-3} of the substance which is inside the brackets.

A rate equation for a reaction $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$ is shown below



The order with respect to a given reactant is the power to which the concentration of this reactant is raised in the rate equation.

The overall order is the sum of the powers to which the concentration terms are raised in the rate equation.

The rate constant, k, is the proportionality constant which links the rate of reaction to the concentrations in the rate equation.

For example

For the rate equation $\text{rate} = k[\text{A}]^2[\text{B}]^2$

The order with respect to A is 2

The order with respect to B is 2

The overall order is $2+2 = 4$

A **zero order** reaction is one in which the rate is independent of concentration i.e changing concentration of reactant has no effect on the rate. A reaction may be zero order with respect to a particular reactant, and this reactant does not appear in the rate equation.

Units of k

Rate has the units $\text{mol dm}^{-3} \text{s}^{-1}$. The units of the rate constant depend on the overall order of the reaction and need to be calculated.

For example

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

Substitute the units for rate, and the units for concentration

$$\text{mol dm}^{-3} \text{s}^{-1} = k (\text{mol dm}^{-3})^2 (\text{mol dm}^{-3})$$

$$\cancel{\text{mol dm}^{-3}} \text{s}^{-1} = k (\cancel{\text{mol dm}^{-3}})^2 (\cancel{\text{mol dm}^{-3}})$$

$$\text{s}^{-1} = k (\text{mol dm}^{-3})^2$$

rearranging to find k

$$\frac{\text{s}^{-1}}{(\text{mol dm}^{-3})^2} = k$$

$$(\text{mol dm}^{-3})^{-2} \text{s}^{-1} = k$$

$$\text{mol}^{-2} \text{dm}^6 \text{s}^{-1} = k$$

The table below shows the units of the rate constant for common overall orders.

Overall order of Reaction	Units of rate constant, k
1	s^{-1}
2	$\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$
3	$\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$
4	$\text{mol}^{-3} \text{dm}^9 \text{s}^{-1}$
5	$\text{mol}^{-4} \text{dm}^{12} \text{s}^{-1}$

Effect of changes in concentration on rate

For the reaction: $\text{B} + \text{X} + \text{Y} \rightarrow \text{E} + \text{F}$, the rate equation is: $\text{rate} = k[\text{B}]^2[\text{Y}]$.

Order with respect to B = 2

Order with respect to Y = 1

Order with respect to X = 0, as it does not appear in the rate equation.

Overall order = $2+1 = 3$

Changing the concentration of a reactant may have an effect on rate. For this rate equation, $\text{rate} = k[\text{B}]^2[\text{Y}]$ so for example

If [X] is x 2, x 10 etc the rate is unaffected as it is zero order.

If [Y] is x 2 then the rate is x 2, or if [Y] is x 10 then rate is x 10, as it is first order.

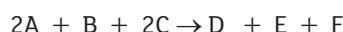
If [B] is x 2 then the rate is x4 (2^2) or if [B] is x 3 then rate is x 9 (3^2) or if [B] is x1/2 then rate is x 1/4 ($(1/2)^2$) as it is second order.

Deducing rate equations from experimental data

Rate equations bear no relation to the balanced symbol equation and they can only be determined experimentally. To determine a rate equation, examine the experimental data, and observe the effect, if any, on the rate, of changing the concentration of one reactant, when the other reactant concentration is constant.

Example

The following data was collected for the reaction:



[A]/ mol dm ⁻³	[B]/ mol dm ⁻³	[C]/ mol dm ⁻³	rate of reaction/ mol dm ⁻³ s ⁻¹
1.0	0.50	0.40	1.8×10^{-4}
1.0	0.40	0.40	1.8×10^{-4}
1.0	0.30	0.20	9.0×10^{-5}
0.10	0.20	0.40	1.8×10^{-5}

Find the rate equation, and the value of and units of k.

Compare experiment 1 and 2 (rows 1 and 2)

[A] is constant; [C] is constant; [B] has changed but the rate is constant, hence the order with respect to B is zero

Compare experiment 1 and 4

[A] is changed - it is $\times 1/10$ [B] has changed but you already know that the order is zero for B and this has no effect on the rate, [C] is constant. The rate is $\times 1/10$ hence the order with respect to A is 1

Compare experiment 1 and 3

[A] is constant; [B] has changed but you already know that the order is zero for B and this has no effect on the rate; [C] is changed - it is $\times 1/2$. The rate is $\times 1/2$ hence the order with respect to C is 1

The rate equation is rate = k [A][C]

To determine the value of the rate constant, substitute in any values from the table, for example using row 1

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

$$1.8 \times 10^{-4} = k (1.0 \times 0.4)$$

$$k = 0.00045$$

To determine the units of k

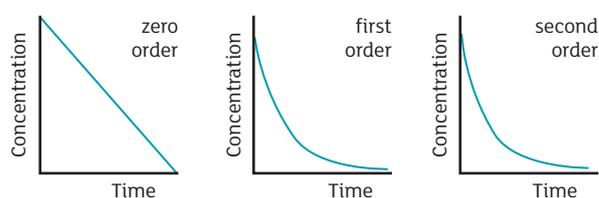
$$\text{mol dm}^{-3} \text{ s}^{-1} = k (\text{mol dm}^{-3}) (\text{mol dm}^{-3})$$

$$k = \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

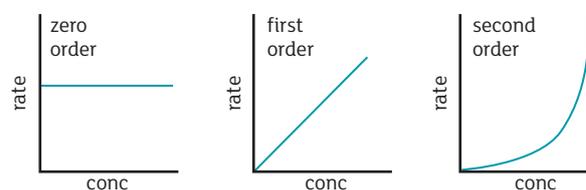
The equation is rate = k [A][C] and k = 0.00045 mol⁻¹ dm³ s⁻¹

Using graphs

For a concentration-time graph the rate is the gradient. When the line is curved to find the gradient, you need to take the gradient of the tangent to the line at different points.



A rate-concentration graph can be plotted to deduce the order of a reaction.

**Experimental methods for studying rates of reaction**

Measuring the rate of a chemical reaction depends on being able to measure a change in the amount or concentration of a reactant or product during the reaction. Different methods which may be used include:

1. Using a colorimeter – A colorimeter measures the amount of light absorbed when it passes through a solution and is recorded as absorbance. It is used for coloured reactants or products. The chosen filter should let through only the wavelength to be absorbed by the coloured solution. A calibration curve should be drawn first with known concentrations of the reactant or product so that a colorimeter reading can be directly related to the concentration.

The reaction mixture is placed in a colorimeter and at different times, the colorimeter reading is taken and converted to concentration using the calibration curve.

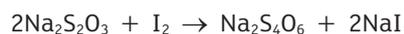
A graph of concentration against time is drawn. A gradient of a tangent at any concentration on the graph gives the rate at that concentration. The gradient of the tangent at different concentrations is found and a graph of rate against concentration is plotted to determine the order.



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A colorimeter can be used to measure the rate of a reaction.

2. Titrating .The reaction is started by mixing the solutions and a sample is removed by pipette at various times. The sample is often quenched to stop the reaction by rapid cooling or adding a large volume of water or a chemical to remove a reactant. The samples are then titrated to find the concentration of the reactant or product and a graph of concentration against time can be drawn. Finding the gradient of tangents at different concentrations on the graph gives the rate at that concentration. To find the order plot rate against concentration. This method can be used to determine the rate of an esterification reaction; the samples are titrated with alkali. To determine the rate of a reaction involving iodine, for example propanone reacting with iodine in the presence of an acid catalyst, this method can also be used. The remaining unreacted iodine is titrated with standard sodium thiosulfate solution, until straw/yellow, then starch indicator added and the titration continued until the starch changes from blue-black to colourless.



3. Measuring pH over time using a pH meter, and calculating the hydrogen ion concentration using $[\text{H}^+] = 10^{(-\text{pH})}$. A graph of $[\text{H}^+]$ against time can be drawn and again gradients of tangents at various $[\text{H}^+]$ can be taken and the gradient is equal to the rate at this H^+ concentration. A graph of concentration against time can be drawn and the shape gives the order.

4. Monitoring the volume of a gaseous product over time, using a **gas syringe** or by using a balance and measuring **loss in mass**.

Mechanism and rate – hydrolysis of primary and tertiary halogenoalkanes

If a reaction involves several steps, some of them may occur at a faster speed than others, yet the reaction cannot go any faster than the slowest step.

The rate determining step is the slowest step in the reaction mechanism. It determines the overall rate.

All species in the rate determining step feature in the rate equation.

There is a relationship between the rate equation and mechanism. For example the alkaline hydrolysis of a primary halogenoalkanes has an $\text{S}_{\text{N}}2$ mechanism. The rate equation is

$$\text{rate} = k [\text{OH}^-][1^\circ \text{halogenoalkane}]$$

This means that both the hydroxide ion and halogenoalkane are involved in the slowest, rate determining step.

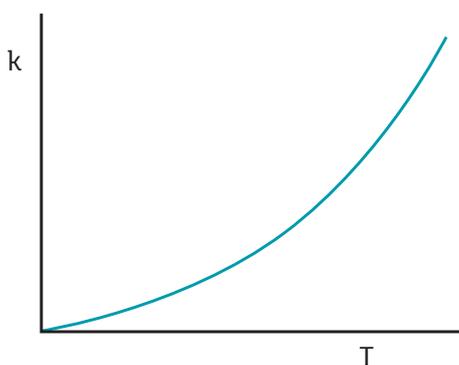
The alkaline hydrolysis of tertiary halogenoalkanes has an $\text{S}_{\text{N}}1$ mechanism. The rate equation is

$$\text{rate} = k [3^\circ \text{halogenoalkane}]$$

This means that only the halogenoalkane is involved in the slowest, rate determining step, as is shown in the mechanism where the slowest step only involves the halogenoalkane. (see AS2)

Effect of temperature on rate constant

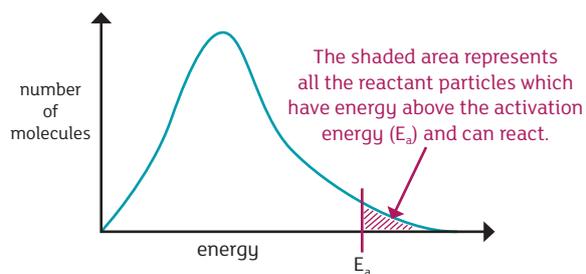
The rate constant is a temperature dependent constant. Its value for a specific reaction, at a particular temperature is constant, but the value increases exponentially as temperature increases. A graph of the rate constant (k) against temperature (measured in kelvin) would be as shown below:



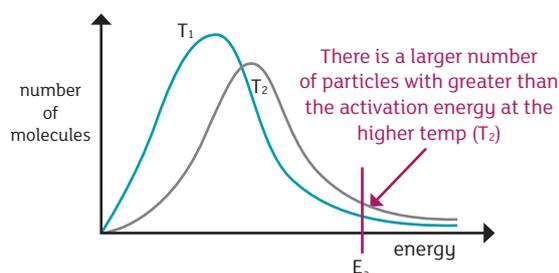
Effect of temperature on the activation energy.

A reaction only occurs if the colliding particles have the activation energy E_a (the minimum amount of energy needed for a reaction to occur). At higher temperature, the increased kinetic energy of the particles means that more particles exceed the activation energy and so there are many more successful collisions per unit time, leading to an increase in the rate of reaction.

This is a Maxwell Boltzmann curve.



The area under the curve gives the number of molecules, hence as the temperature is increased the curve moves to the right and widens, and so the number of molecules with the activation energy is greater and there is a faster rate of reaction.



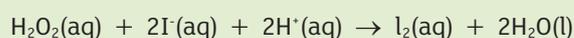


Revision Questions

- 1 The rate of reaction between X and Y is overall third order. Which one of the following rate equations is **not** correct?

- A Rate = $k[X]^1[Y]^3$
 B Rate = $k[X]^1[Y]^2$
 C Rate = $k[X]^2[Y]^1$
 D Rate = $k[X]^2[Y]^1[Z]^0$

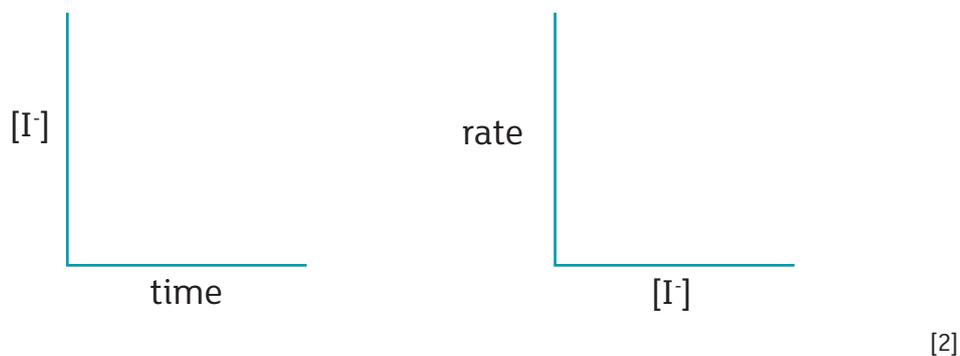
- 2 Acidified hydrogen peroxide oxidises iodide ions according to the equation below:



- a) Name the reagent and the expected result to show that iodine is produced in the reaction.

.....
 [2]

- b) (i) The reaction is first order with respect to iodide ions. Using the axes below draw the shapes of the graphs expected.



- (ii) The table below shows initial rates for the reaction for different concentrations of hydrogen peroxide and hydrogen ions at constant temperature.

experiment	$[\text{H}_2\text{O}_2(\text{aq})]$ (mol dm^{-3})	$[\text{H}^+(\text{aq})]$ (mol dm^{-3})	initial rate $\times 10^{-6}$ ($\text{mol dm}^{-3} \text{ s}^{-1}$)
1	0.00075	0.10	2.1
2	0.00150	0.10	4.2
3	0.00150	0.20	4.2

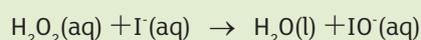
(iii) State the rate equation for the reaction between H_2O_2 and acidified I^- ions.

..... [1]

(iv) For experiment 1 the concentration of the iodide ions was 0.1 mol dm^{-3} . Calculate the value of the rate constant, stating its units if any.

.....
 [1]

c) The reaction takes place in two steps. The first step is rate determining and is:



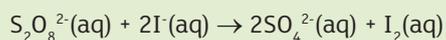
(i) What is meant by the **rate determining step**?

..... [1]

(ii) Suggest the equation for the second step in the reaction.

..... [2]

3 The following results were obtained in an experiment to determine the rate of reaction between persulfate ions ($\text{S}_2\text{O}_8^{2-}$) and iodide ions in aqueous solution.



concentration of $\text{S}_2\text{O}_8^{2-}/\text{mol dm}^{-3}$	concentration of $\text{I}^-/\text{mol dm}^{-3}$	initial rate/ $\text{mol dm}^{-3} \text{ s}^{-1}$
0.050	0.050	0.18
0.100	0.050	0.36
0.100	0.100	0.72

(i) Describe how you would study the rate of the reaction. The concentration of one of the reactants or products will need to be measured with respect to time and can then be used to determine the rate of the reaction.

.....

 [3]

Quality of written communication [2]

(ii) Deduce the order of reaction with respect to each of the reactants.

.....
..... [2]

(iii) Write the rate equation for the reaction.

..... [2]

(iv) Using the reaction explain what is meant by the overall order of a reaction.

..... [1]

(v) Calculate the rate constant and state its units.

.....
..... [2]

