

## 1. Measuring reaction rates

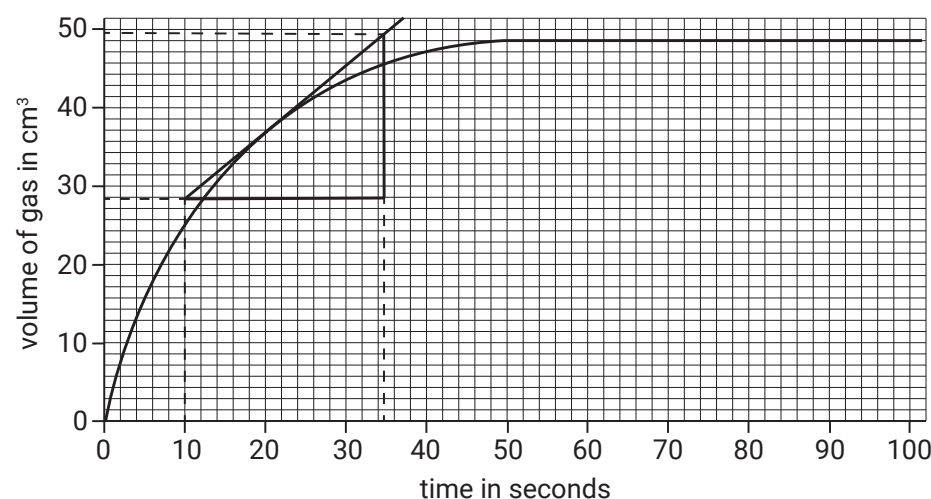
The reaction rate is the change in the number of reactants or products per unit time.

Common methods of measuring the rate

- Colorimetry:** This measures the change in the amount of a coloured substance being created or used up per unit time.
- Gas volume:** A gas syringe is used to measure the volume of gas produced per unit time.
- Mass:** An electric balance is used to measure the mass of gas released per unit time.
- Sampling and quenching:** Small samples of the reaction mixture are removed at regular time intervals. The samples are immediately quenched to stop the reaction, by putting them into an ice bath to lower the temperature or by adding cold water to reduce reactant concentrations. The sample is then analysed, e.g. by titration.

## 2. Calculating rates

$$\text{rate} = \frac{\text{change in concentration/amount/volume of gas}}{\text{time}}$$



A tangent is drawn to the curve and the gradient  $\frac{y}{x}$  gives the rate.

## 3. Rate equations and order of reactions

The rate of a chemical reaction depends on the concentrations of the reactants. However, depending on the **mechanism** of the reaction, some reactants have more of an effect on the rate than others.

Consider this reaction:  $A + 2B \rightarrow 2C + D$

Although the rate of this reaction may well depend on either or both of the reactant concentrations, [A] and [B], it cannot be assumed to be directly proportional to these concentrations.

By carrying out various experiments, it could be found, for example, that when [A] is **doubled** the rate of the reaction may:

- stay the same  $\rightarrow$  rate is not proportional to [A]
- double  $\rightarrow$  rate  $\propto$  [A]
- quadruple  $\rightarrow$  rate  $\propto$  [A]<sup>2</sup>.

These rate expressions can be written as rate equations with the introduction of a constant of proportionality. The rate equation including the **rate constant, k**, expresses the relationship between the rate of reaction and the concentrations of reactants.

The rate constant:

- remains constant for a given reaction at a given temperature
- is not affected by changing the concentrations of the reactants
- changes with a change in temperature.

Consider the rate equation

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

- m and n are commonly 0, 1 and 2 and are called the **orders of reaction** with respect to A and B.
- The orders are **not related** to the balancing numbers in the stoichiometric equation.

Order of reactions

- The order of reaction with respect to a particular reactant is the power/index to which the concentration terms must be raised to fit the rate equation.
- The overall order of a reaction is the sum of all the individual orders of reaction from the rate equation.

**Zero order reactions** e.g.  $\text{rate} = k [A]^0$

This means that the rate of reaction is constant and independent of the concentration of A. If the rate of reaction is constant, a graph of [A] against time is a straight, horizontal line.

$$\text{rate} = k \quad \text{so unit of } k \rightarrow \text{mol dm}^{-3} \text{ s}^{-1}$$

**First order reactions** e.g.  $\text{rate} = k [A]$

The reaction is first order with respect to A. If [A] doubles, the rate doubles. A graph of [A] against time is a shallow curve downwards.

$$\text{unit of } k \rightarrow \text{s}^{-1}$$

**Second order reactions** e.g.  $\text{rate} = k [A]^2$

This reaction is second order with respect to A. If [A] doubles, the rate quadruples (2<sup>2</sup>). A graph of [A] against time is a steep curve downwards.

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

This reaction is first order with respect to both A and B so overall order is 2.

$$\text{unit of } k \rightarrow \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

Deducing reaction order from experimental results

Expt	[NO] (mol dm <sup>-3</sup> )	[O <sub>2</sub> ] (mol dm <sup>-3</sup> )	[CO] (mol dm <sup>-3</sup> )	Rate (mol dm <sup>-3</sup> s <sup>-1</sup> )
1	2.00 × 10 <sup>-2</sup>	1.50 × 10 <sup>-2</sup>	1.50 × 10 <sup>-2</sup>	0.17
2	6.00 × 10 <sup>-2</sup>	1.50 × 10 <sup>-2</sup>	1.50 × 10 <sup>-2</sup>	1.53
3	2.00 × 10 <sup>-2</sup>	1.50 × 10 <sup>-2</sup>	3.00 × 10 <sup>-2</sup>	0.17
4	4.00 × 10 <sup>-2</sup>	3.00 × 10 <sup>-2</sup>	1.50 × 10 <sup>-2</sup>	0.68

Example: Calculate the rate equation for the reaction using the experimental data.

Looking at experiments 1 and 2, when [NO] triples and the concentrations of the other reactants remain constant, the rate is nine times higher  $\rightarrow 3^2 = 9$ .

$\rightarrow$  reaction is second order with respect to NO

Looking at experiments 1 and 3, when [CO] doubles and the concentrations of the other reactants remain constant, the rate does not change.

$\rightarrow$  reaction is zero order with respect to CO

Looking at experiments 1 and 4, when both [O<sub>2</sub>] and [NO] are doubled, the rate quadruples. Because the reaction is second order with respect to NO, then doubling [NO] would quadruple the rate. Doubling [O<sub>2</sub>] hasn't had any additional effect on the rate.

$\rightarrow$  reaction is zero order with respect to O<sub>2</sub>

Rate equation  $\text{rate} = k [\text{NO}]^2$

## 4. Rate determining step

The rate determining step is the **slowest step** in a multi-step reaction. The substances in the rate equation appear in the chemical equation for the rate determining step, and their orders correspond to the number of molecules that feature in that equation. This is different to the number of molecules in the overall equation.

$\text{rate} = k [\text{NO}_2] \rightarrow$  rate determining step contains NO<sub>2</sub>

$\text{rate} = k [\text{NO}]^2 \rightarrow$  rate determining step contains 2NO

$\text{rate} = k [\text{I}_2] [\text{H}_2] \rightarrow$  rate determining step contains I<sub>2</sub> and H<sub>2</sub>

## 5. The Arrhenius equation and catalysts

Temperature affects rate so it must affect the rate constant. This is quantified by the Arrhenius equation:

$$k = Ae^{\frac{-E_a}{RT}}$$

A  $\rightarrow$  frequency factor (treated as constant, same unit as k)

e  $\rightarrow$  mathematical constant (found on a scientific calculator)

E<sub>a</sub>  $\rightarrow$  activation energy (J mol<sup>-1</sup>) conversions from kJ mol<sup>-1</sup>

R  $\rightarrow$  gas constant (8.31 J K<sup>-1</sup> mol<sup>-1</sup>) (data booklet)

T  $\rightarrow$  temperature (K)

The Arrhenius equation can be rearranged giving

$$\ln k = \ln A - \frac{E_a}{RT}$$

Plotting  $\ln k$  against  $\frac{1}{T}$  gives a straight line with gradient  $\frac{-E_a}{RT}$   
[remember  $y = mx + c$ ]

Catalysts increase reaction rates by providing an alternative route with a lower activation energy. This affects the rate constant as shown by the Arrhenius equation.