Mastering Chemistry

- Book   6
- Topic 13   Industrial Chemistry

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43.1　The chemical industry (p.2)

◆ From hydropolymers for wound dressing to waste water treatment, chemicals help provide sanitary living conditions.

◆ Furthermore, from nanoparticle technology used in suncream to the ever expanding range of pharmaceutical products, the chemical industry improves the day to day quality of life for millions of humans and animals.

◆ Natural products, such as Vitamin C, are synthesised industrially to solve problems of inadequate or shrinking supply.

43.1 The chemical industry (p.2)

* The products of the chemical industry can be divided into three categories:

  * basic chemicals;

  * speciality chemicals;

  * consumer chemicals.

* Outputs of these chemicals range widely. Basic chemicals are produced in huge quantities (millions of tonnes).

* Some speciality chemicals are produced in smaller quantities (in kilograms) but with very high values.

43.1 The chemical industry (p.2)

◆ Basic chemicals include petrochemicals, synthetic polymers and basic inorganic chemicals (such as ammonia, nitric acid, chlorine and sodium hydroxide).

◆ The category of speciality chemicals covers a wide variety of chemicals for crop protection, paints, inks, dyes and pigments.

◆ It also includes chemicals used by various industries such as textiles and paper.

◆ An everyday example is household paints.

◆ With the production of new chemicals paint manufacturers are able to replace organic solvent-based paints with the more eco-friendly water-based paints.

43.1 The chemical industry (p.2)

◆ Another example is the latest type of ink developed for ink-jet printers (Fig. 43.1).

Ink for ink-jet printers

43.1 The chemical industry (p.3)

◆ Consumer chemicals are sold directly to the public. They include, for example, detergents, soaps and perfumes (Fig. 43.2).

Detergents, soaps and perfumes are consumer chemicals sold directly to the public

43.1 The chemical industry (p.3)

- The chemical industry is a very important contributor to the wealth of a country.

- World chemicals turnover was valued at 3.534 trillion euros in 2015.

- Global sales grew by 14% from 3.100 trillion euros in 2014 to 3.534 trillion euros in 2015.

- It was largely driven by China, where chemicals sales swelled impressively from 1.084 trillion euros in 2014 to 1.409 trillion euros in 2015 (Fig. 43.3).

- The chemical industry is growing. By 2035, the market is expected to reach around 5.6 trillion euros.

43.1 The chemical industry (p.3)

World chemical sales in billion euros (Source: Cefic Chemdata International 2016)
(* Rest of Europe covers Switzerland, Norway, Turkey, Russia and Ukraine
** Asia excluding China, India, Japan and South Korea)

43.2 The petrochemical industry (p.4)

◆ Chemicals derived from petroleum or natural gas — petrochemicals — are an essential part of the chemical industry today.

◆ The petrochemical industry only started to grow in the 1940s.

◆ Fig. 43.4 shows a petrochemical plant in China.

A petrochemical plant located in Nan hai in the Guangdong Province, China (Source: Photographic Services, Shell International Limited)

43.2 The petrochemical industry (p.4)

◆ Ethene is one of the most important major petrochemicals, by tonnage, that is manufactured.

◆ It is the building block for four major end products: polythene, epoxyethane◀, 1,2-dichoroethane (the precursor to vinyl chloride monomer) and ethylbenzene (the precursor to styrene).

▶ The structure of epoxyethane is

$$O$$

$$H_2C \longrightarrow CH_2 .$$
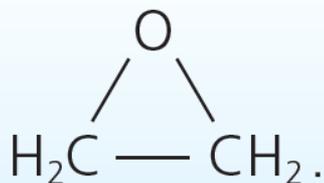
43.2 The petrochemical industry (p.4)

◆ The demand for the four major end products of ethene is shown in Fig. 43.5.
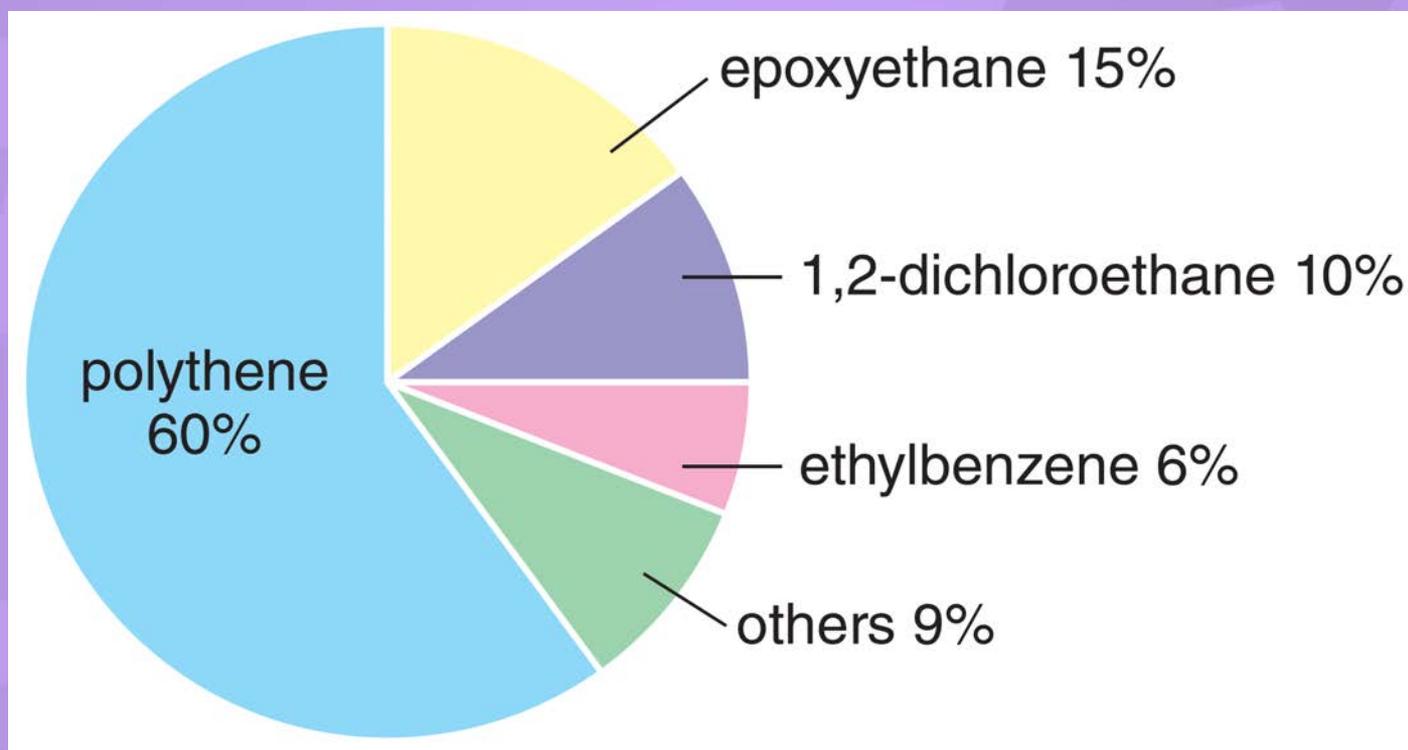
Demand for four major end products of ethene
**(Source: American Chemical Society)**

43.2 The petrochemical industry (p.5)

◆ Because of its huge and broad usage, ethene is often used as a benchmark for the performance of the petrochemical industry as a whole.

43.3 Steps in a chemical process in the chemical industry (p.5)

◆ Fig. 43.6 shows the steps in a chemical process in the chemical industry.
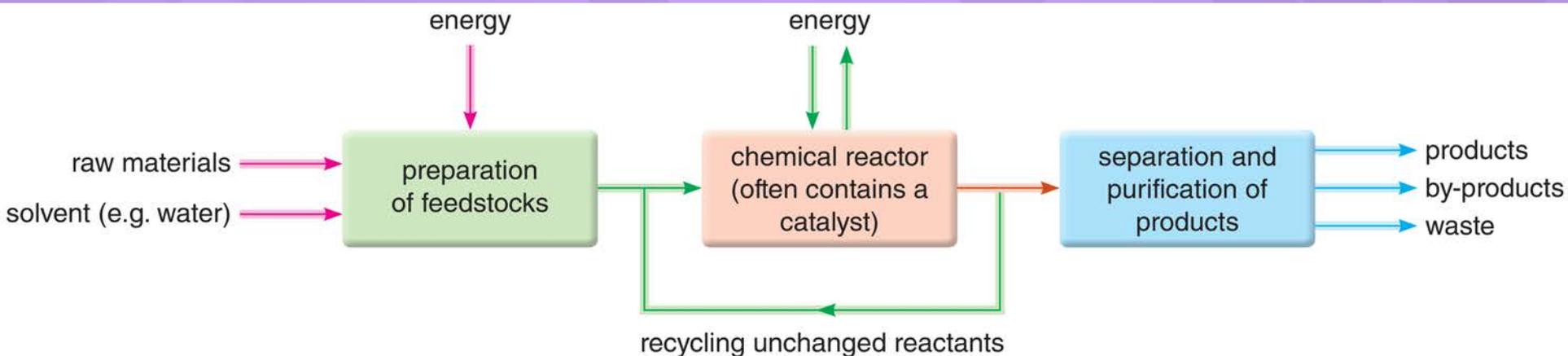
energy   energy

raw materials → **preparation of feedstocks** → **chemical reactor (often contains a catalyst)** → **separation and purification of products** → products / by-products / waste

solvent (e.g. water) →

recycling unchanged reactants

Steps in a chemical process in the chemical industry

43.3 Steps in a chemical process in the chemical industry (p.5)

- Raw materials are the starting point for any industrial chemical process.

- **Feedstocks**, the reactants that go into a chemical process, are made from the raw materials.

- For example, wintergreen plant is the raw material for the production of wintergreen ointment.

- Methyl salicylate, which is obtained from wintergreen leaves, is the feedstock for the production of the ointment.

43.3 Steps in a chemical process in the chemical industry (p.6)

◆ Often there is little choice of feedstocks and raw materials for a chemical process. You can see some examples in Table 43.1.

Table 43.1	Feedstocks and raw materials for some inorganic chemicals	
Product	**Feedstock**	**Raw materials**
Ammonia	methane, air, water	natural gas, air, water
Nitric acid	ammonia, air, water	natural gas / petroleum, air, water
Sulphuric acid	sulphur, air, water	natural gas / petroleum (desulphurisation yields the sulphur), air, water
Ethanoic acid	methanol, carbon monoxide, water	coal / natural gas, air, water

43.3 Steps in a chemical process in the chemical industry (p.6)

- The reactants are converted into products in the chemical reactor.

- The reactor often contains a catalyst.

- Generally, a mixture of chemicals leaves the reactor.

- The mixture includes the desired product, but it may include by-products (substances formed in addition to the desired product) and unchanged reactants as well.

- So the chemical plant has to include equipment to separate the main product and by-products and to recycle unchanged reactants.

43.3 Steps in a chemical process in the chemical industry (p.7)

Factors determining how a manufacturer makes a product

◆ Manufacturers in the chemical industry must be able to make a profit when producing products, otherwise they will go out of business.

◆ Many factors are considered when choosing the reaction or series of reactions for making a product. These include the:

  • yield of the product;

  • usefulness or otherwise of by-products;

  • rate of the reaction;

 • position of equilibrium, if it is a reversible reaction.

43.3 Steps in a chemical process in the chemical industry (p.7)

- **Chemical kinetics** is the study of rates of chemical reactions.

- This is an active research area in the chemical industry.

43.4 Rate of a reaction (p.7)

◆ As a chemical reaction, A + 2B → C, takes place, the concentrations of the reactants A and B decrease with time and the concentration of product C increases with time.

◆ You could measure the concentration of A, B or C with time and plot the results (Fig. 43.7).
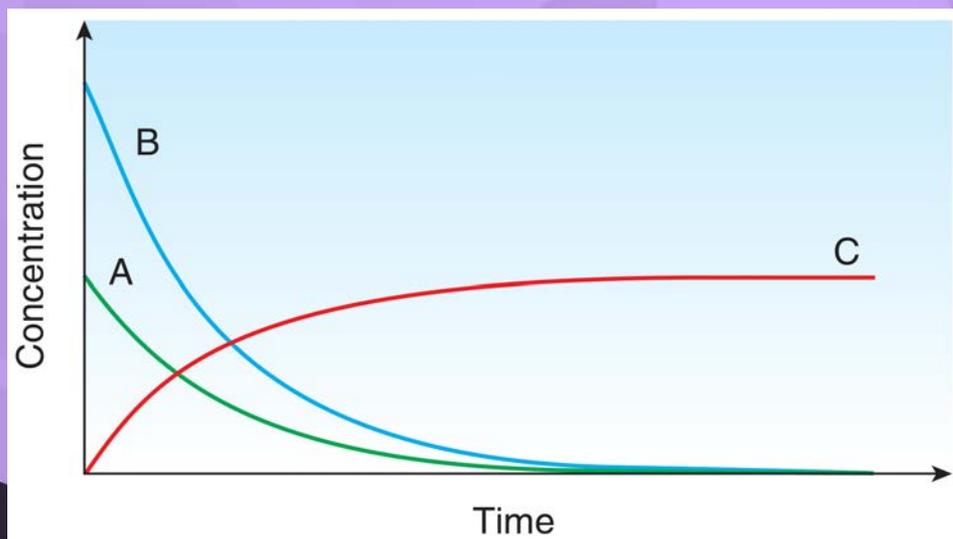
Change in concentration of reactants and product with time in the reaction
A + 2B → C

43.4 Rate of a reaction (p.8)

◆ The rate of a reaction can be expressed either in terms of how the concentration of a product increases with time, or how the concentration of a reactant decreases with time.

◆ So,

$$\text{reaction rate} = \frac{\text{change in concentration of product}}{\text{time}}$$

or

$$\text{reaction rate} = -\frac{\text{change in concentration of reactant}}{\text{time}}$$

43.4 Rate of a reaction (p.8)

◆ As the concentration of a reaction decreases with time, its change in concentration within a given time period would give a negative value.

◆ The addition of the negative sign in the second expression would give a positive value for the reaction rate.

◆ The equation tells that one particle of A reacts with two particles of B, so the concentration of B decreases twice as fast as that of A.

◆ Hence it is important to state whether you are following A, B or C when measuring the reaction rate.

43.4 Rate of a reaction (p.8)

The instantaneous rate of reaction at a particular time

- ◆ To find the instantaneous rate of change of concentration of C at a particular time, t, you draw a tangent to the concentration-time curve at that time and then find its slope, as shown in Fig. 43.8.

43.4 Rate of a reaction (p.8)

◆ At time t, instantaneous rate of reaction with respect to C = $\frac{b}{a}$.
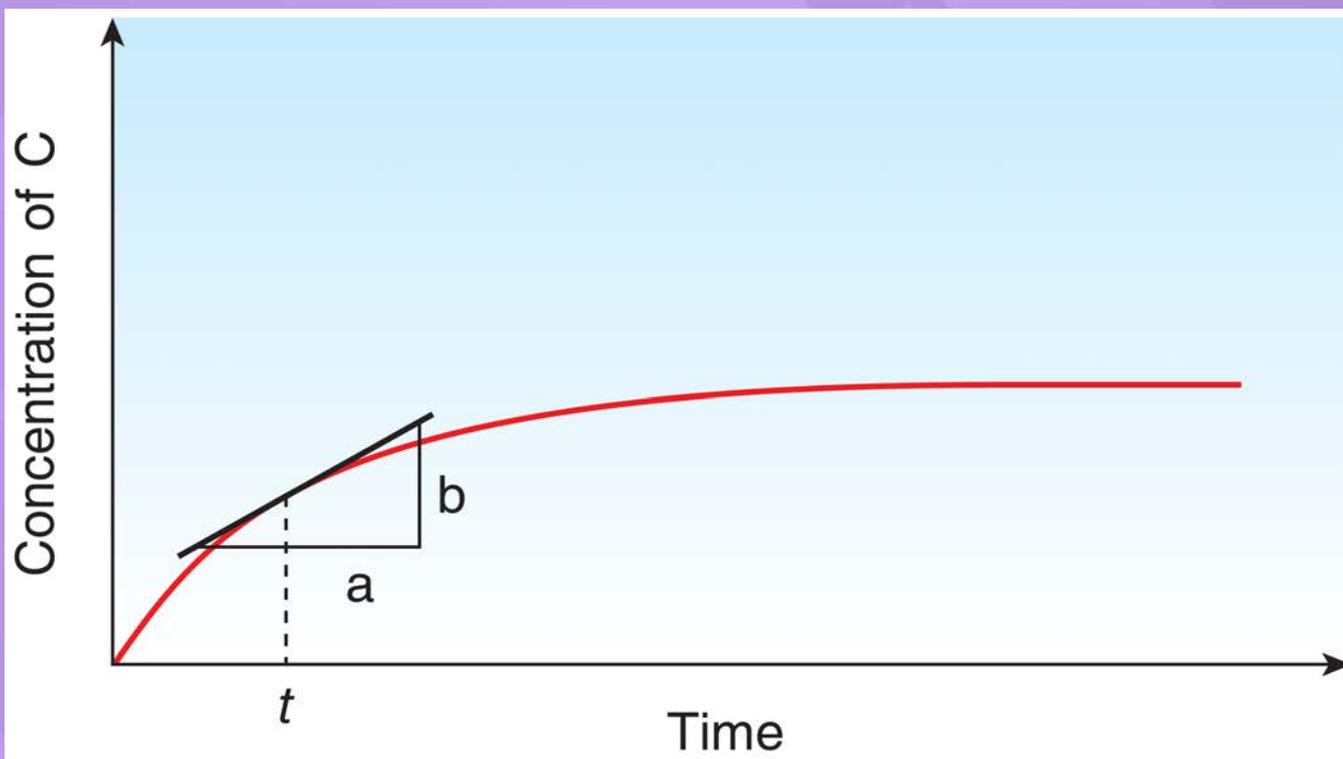
**Slope of the tangent to the concentration-time curve at time t
gives the instantaneous rate of reaction with respect to C**

43.4 Rate of a reaction (p.9)

◆ The initial rate of reaction is the instantaneous rate of reaction at time = 0.

◆ You can work this out by determining the slope of the tangent to the curve at time = 0 (Fig. 43.9).

◆ Initial rate of reaction with respect to C = $\dfrac{y}{x}$
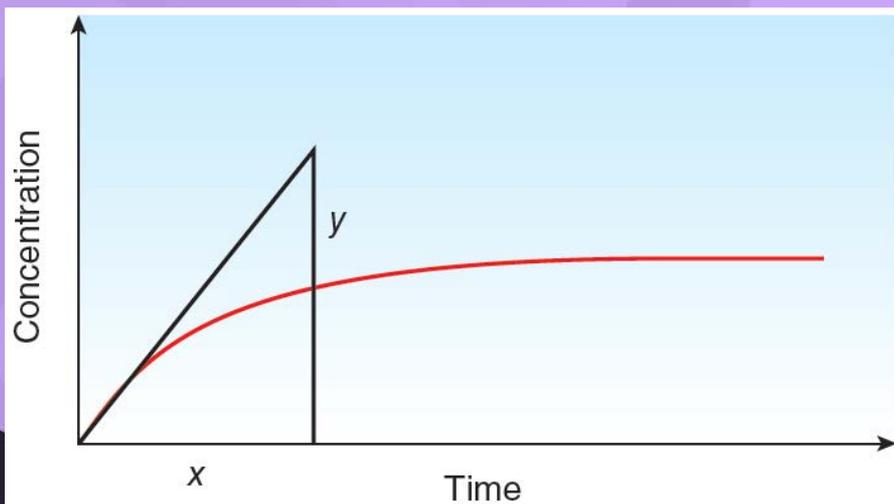
The slope of the tangent to the concentration-time curve at time zero is the initial rate of reaction with respect to C

43.5 Effect of change in concentration of a reaction species on rate of reaction (p.9)

- The rate of a chemical reaction depends on the concentrations of some or all of the reagents (reactants and catalysts) in the reaction vessel.

- Often, the rate of reaction is directly proportional to the concentration of the reaction species.

- That is, as the concentration of the reaction species is doubled, the rate of reaction doubles.

43.5 Effect of change in concentration of a reaction species on rate of reaction (p.9)

- However, this is not always the case. In some reactions, doubling the concentration of one reaction species has no effect on the rate, while doubling the concentration of another reaction species can double, or even quadruple, the rate of the reaction.

- You can attribute an order to each reaction species to show how its change in concentration affects the rate of the reaction.

43.5 Effect of change in concentration of a reaction species on rate of reaction (p.9)

◆ With all the other conditions remain unchanged, if doubling the concentration of reaction species A

a) causes the reaction rate to double, the **order of reaction** with respect to reaction species A is one;

b) does not affect the reaction rate, the order of reaction with respect to reaction species A is zero;

c) causes the reaction rate to increase four fold, the order of reaction with respect to reaction species A is two.

43.5 Effect of change in concentration of a reaction species on rate of reaction (p.10)

◆ Table 43.2 summaries the relationship between the change in the rate of reaction when doubling the concentration of reaction species

Table 43.2 Relationship between the change in the rate of reaction when doubling the concentration of reaction species A and the order of reaction with respect to the reaction species		
Change in concentration of reaction species A	Change in reaction rate due to change in concentration	Order of reaction with respect to reaction species A
Doubled	reaction rate remains the same	0
Doubled	reaction rate doubles	1
Doubled	reaction rate quadruples	2

43.6 Determining the order of reaction — method of initial rate (p.10)

◆ Most reactions involve more than one reaction species, and you have to do several trials to find the order of reaction with respect to each reaction species separately.

◆ In one method, the initial concentration of each reaction species is altered in turn to see what effect the change has on the reaction rate at the start of the reaction.

◆ The only point in the reaction at which the concentrations of the reaction species are definitely known is at the start of the reaction.

◆ Hence the rate at the start of the reaction is chosen.

◆ This is called the method of initial rate.

43.6 Determining the order of reaction — method of initial rate (p.10)

- The concentrations of other reaction species can be controlled by having a large excess of them so that their concentrations do not change significantly over the course of the reaction.

- Any change in the initial rate of the reaction is only caused by the change in the initial concentration of the reaction species under study.

43.6　Determining the order of reaction — method of initial rate (p.11)

Using the reciprocal of the time required to produce a small amount of a product as a measure of the initial rate

- One way of measuring the initial rate of a reaction is to measure how long the reaction takes to produce a small, fixed amount of one of the products.

- The time taken is called the reaction time.

- If the reaction rate is high (the reaction proceeds quickly), then the reaction time will be short.

- If the reaction rate is low (the reaction proceeds slowly), then the reaction time will be long.

43.6 Determining the order of reaction — method of initial rate (p.11)

◆ A good example of this method is the measurement of the rate of reaction between sodium thiosulphate solution and dilute hydrochloric acid:

$Na_2S_2O_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + SO_2(aq) + S(s) + H_2O(l)$

◆ As the reaction proceeds, sulphur forms and changes the turbidity of the reaction mixture.

43.6 Determining the order of reaction — method of initial rate (p.11)

◆ The reaction flask can be placed on a cross drawn on a piece of white paper and viewed from above (Fig. 43.10).
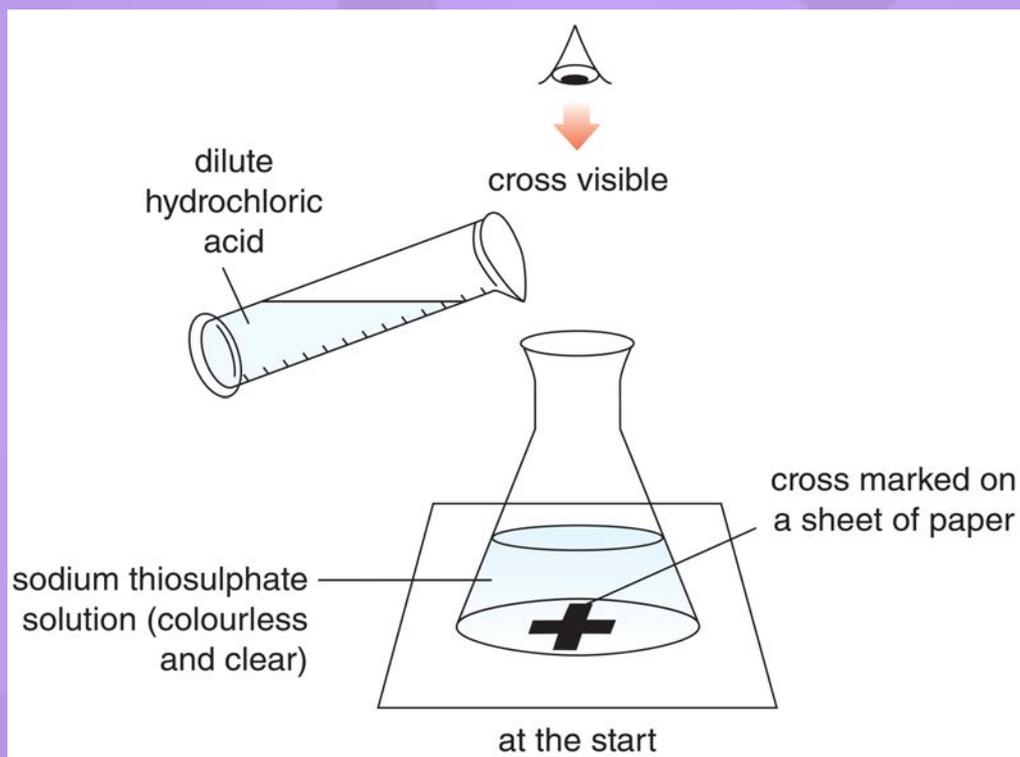
43.6 Determining the order of reaction — method of initial rate (p.11)

◆ When enough sulphur has formed, the reaction mixture would become so turbid that the cross is obscured (Fig. 43.11).

43.6 Determining the order of reaction — method of initial rate (p.12)

◆ Record the time for this to happen.

◆ Any change in the initial rate of the reaction is only caused by the change in the initial concentration of the reaction species under study.

◆ The time to reach this point can be measured using sodium thiosulphate solutions of different initial concentrations.

◆ In each trial, the total volume of each reaction mixture and the concentration of the hydrochloric acid must be kept constant at the start.

43.6 Determining the order of reaction — method of initial rate (p.12)

- For each reaction mixture, average rate of reaction from the start to this turbid stage =

$$\frac{\text{amount of sulphur needed to obscure the cross}}{\text{time to reach this turbid stage (t)}}$$

- The amount of sulphur needed to obscure the cross will be the same for each trial, so the average rate of reaction from the start to this turbid stage $\propto$

$$\frac{1}{\text{time to reach this turbid stage } (t)}$$

43.6 Determining the order of reaction — method of initial rate (p.12)

◆ When this turbid stage is reached, only a small amount of sulphur has formed and the reaction has only proceeded a small part of the way to completion.

◆ You can take the average rate from start to this turbid stage to be approximately equal to the initial rate.

Initial rate of reaction $\propto \dfrac{1}{\text{time to reach this turbid stage (t)}}$

43.6 Determining the order of reaction — method of initial rate (p.13)

◆ Table 43.3a shows the composition of reaction mixtures used and the reaction time t when the reaction mixture becomes so turbid that the cross is obscured.

Table 43.3a	Composition of reaction mixtures used and the reaction time t			
Trial	Composition of reaction mixture			Reaction time t (s)
	Volume of 0.15 mol dm^{-3} Na$_2$S$_2$O$_3$(aq) (cm^3)	Volume of water (cm^3)	Volume of 2 mol dm^{-3} HCl(aq) (cm^3)	
1	50.0	0.0	5.0	22.5
2	40.0	10.0	5.0	27.3
3	30.0	20.0	5.0	37.7
4	20.0	30.0	5.0	60.0
5	10.0	40.0	5.0	117.6

43.6 Determining the order of reaction — method of initial rate (p.13)

◆ Water is used in Trials 2–5 so as to keep the total volume of each reaction mixture constant.

◆ Thus, the initial concentration of sodium thiosulphate in each reaction mixture is directly proportional to the volume of sodium thiosulphate solution used.

◆ The same volume of acid is used in each reaction mixture so that the only variable is the change in the initial concentration of sodium thiosulphate in the reaction mixture.

43.6 Determining the order of reaction — method of initial rate (p.13)

◆ Table 43.3b shows the volume of sodium thiosulphate solution and the value of $\frac{1}{t}$ in each trial.

Table 43.3b	Volume of sodium thiosulphate solution and the value of $\frac{1}{t}$ in each trial	
Trial	Volume of 0.15 mol dm^{-3} Na$_2$S$_2$O$_3$(aq) (cm^3)	$\frac{1}{t}$ (s^{-1})
1	50.0	0.0444
2	40.0	0.0366
3	30.0	0.0265
4	20.0	0.0167
5	10.0	0.00850

43.6 Determining the order of reaction — method of initial rate (p.14)

- If $\frac{1}{t}$ is plotted against the volume of the thiosulphate solution used, a straight line plot through the origin is obtained (Fig. 43.12).

- This shows that the rate of the reaction is directly proportional to the concentration of sodium thiosulphate in the reaction mixture — the order of reaction with respect to sodium thiosulphate solution is one.

43.6 Determining the order of reaction — method of initial rate (p.14)
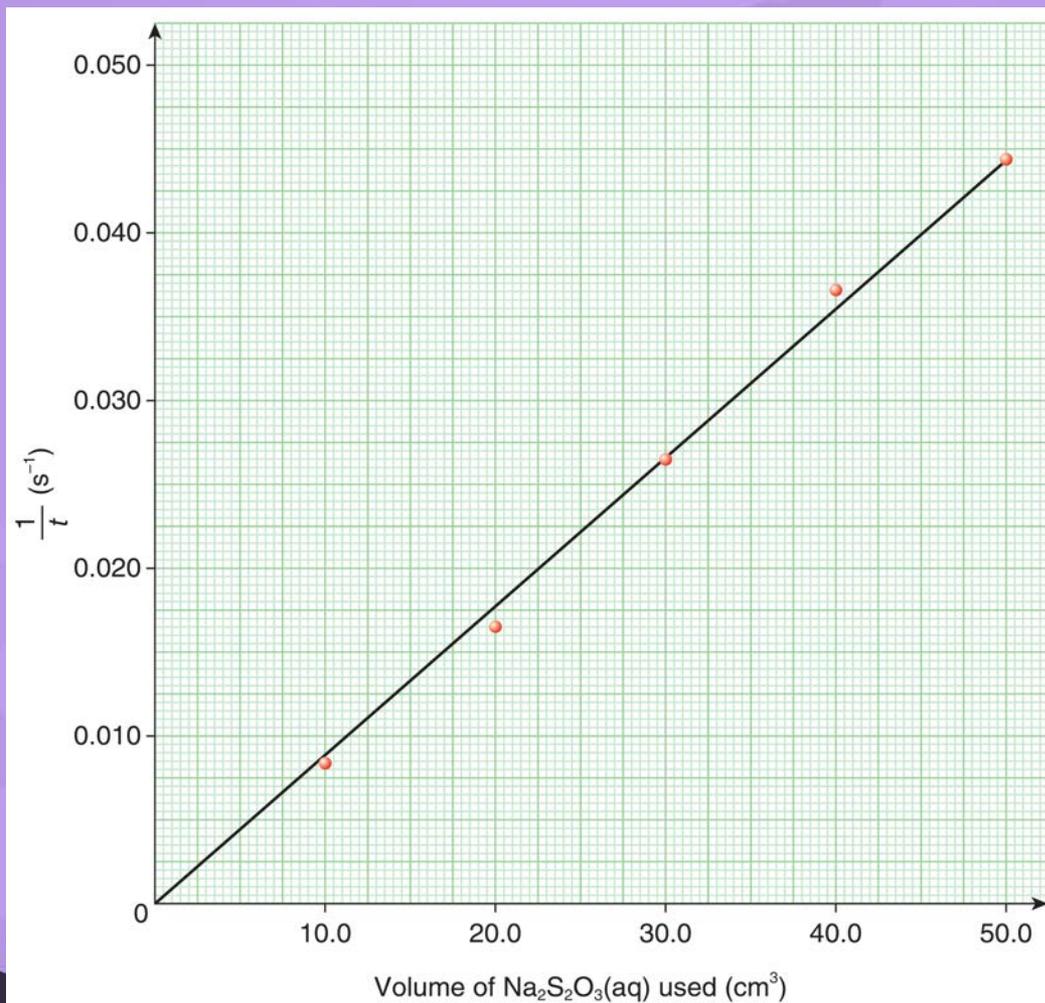
43.6 Determining the order of reaction — method of initial rate (p.16)

Q (Example 43.1)

Bromine oxidises methanoic acid in aqueous solution to carbon dioxide. The reaction is catalysed by $H^+(aq)$.

$$Br_2(aq) + HCOOH(aq) \xrightarrow{H^+(aq)} 2Br^-(aq) + 2H^+(aq) + CO_2(g)$$
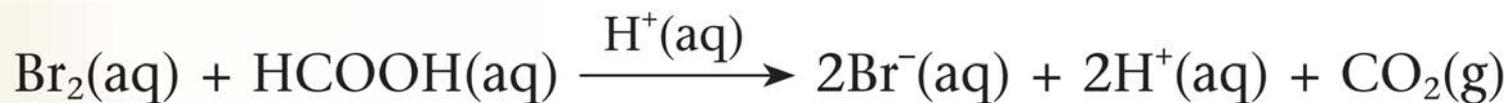
The table below listed the experimental data obtained at a certain temperature.

Trial	Volume of reagents used (cm^3)			Initial rate for the disappearance of $Br_2(aq)$ ($mol\ dm^{-3}\ s^{-1}$)
	$0.010\ mol\ dm^{-3}$ $Br_2(aq)$	$0.40\ mol\ dm^{-3}$ $HCOOH(aq)$	$H_2O(l)$	
1	2.0	10.0	8.0	2.40×10^{-5}
2	4.0	10.0	6.0	4.80×10^{-5}
3	8.0	10.0	2.0	9.60×10^{-5}

43.6 Determining the order of reaction — method of initial rate (p.17)

Q (Example 43.1)

a) Why was the concentration of HCOOH(aq) kept much higher than that of Br_2(aq)?

b) Deduce the order of the reaction with respect to Br_2(aq).

c) Suggest how the order of reaction with respect to HCOOH(aq) can be determined.

d) Based on Trial 1, deduce the initial rate of reaction with respect to Br^-(aq) under experimental conditions.

43.6 Determining the order of reaction — method of initial rate (p.17)

A

a) A large excess of methanoic acid was used so that its concentration would not change significantly over the course of the reaction. The only variable was the change in the concentration of bromine.

b) The initial rate doubled when the concentration of $Br_2(aq)$ in the reaction mixture was doubled, with other variables kept constant. Hence the order of the reaction with respect to $Br_2(aq)$ was one.

43.6 Determining the order of reaction — method of initial rate (p.17)

c) Repeat the experiment using the same reagents. All the trials use the same volume of Br_2(aq) but vary the volume of HCOOH(aq) used. Measure the initial rate in each trial.

Compare the initial rates to obtain the order of the reaction with respect to HCOOH(aq).

43.6 Determining the order of reaction — method of initial rate (p.17)

d) Initial rate of reaction with respect to $Br_2(aq)$

$= \dfrac{1}{2} \times$ initial rate of reaction with respect to $Br^-(aq)$

Base on Trial 1, the initial rate of reaction respect to $Br^-(aq)$

$= 2 \times 2.40 \times 10^{-5}$ mol dm^3 s^{-1}

$= 4.80 \times 10^{-5}$ mol dm^3 s^{-1}

43.6 Determining the order of reaction — method of initial rate (p.17)

Q (Example 43.2)

Phenolphthalein is a commonly used indicator for determining the end point in acid-alkali titrations.

Phenolphthalein is colourless in solutions at a pH of 8 or lower. The colourless form of phenolphthalein can be represented by the formula H_2Ph.

43.6 Determining the order of reaction — method of initial rate (p.17)

In the pH range of 8–10, the hydrogen atoms are rapidly removed from the colourless form of phenolphthalein by OH^- ions to give the pink Ph^{2-} ions according to the equation:

$H_2Ph(aq) + 2OH^-(aq) \rightarrow Ph^{2-}(aq) + 2H_2O(l)$
colourless   pink

43.6 Determining the order of reaction — method of initial rate (p.17)

At a pH above 10, the pink colour slowly fades as the Ph^{2-} ions react further with OH^- ions to give the colourless $PhOH^{3-}$ ions according to the equation:

$Ph^{2-}(aq) + OH^-(aq) \rightarrow PhOH^{3-}$
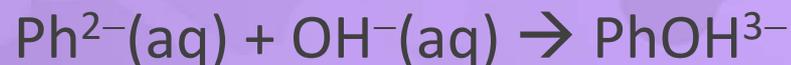
pink   colourless

A student was required to investigate how the rate of declourisation of phenolphthalein changes with the concentration of sodium hydroxide solution.

43.6 Determining the order of reaction — method of initial rate (p.17)

The student was provided with

• three samples of NaOH(aq) of different concentrations (1.00 mol dm^{-3}, $0.500 \text{ mol dm}^{-3}$, $0.250 \text{ mol dm}^{-3}$);

• A 0.01% phenolphthalein

The student mixed 5 cm^3 of 0.25 mol dm^{-3} NaOH(aq) with 1 cm^3 of 0.01% phenolphthalein in a cuvette and followed the absorbance of the mixture by using a colorimeter.

The procedure was repeated using 0.50 mol dm^{-3} and 1.0 mol dm^{-3} NaOH(aq).

43.6 Determining the order of reaction — method of initial rate (p.17)

The results obtained are shown below.
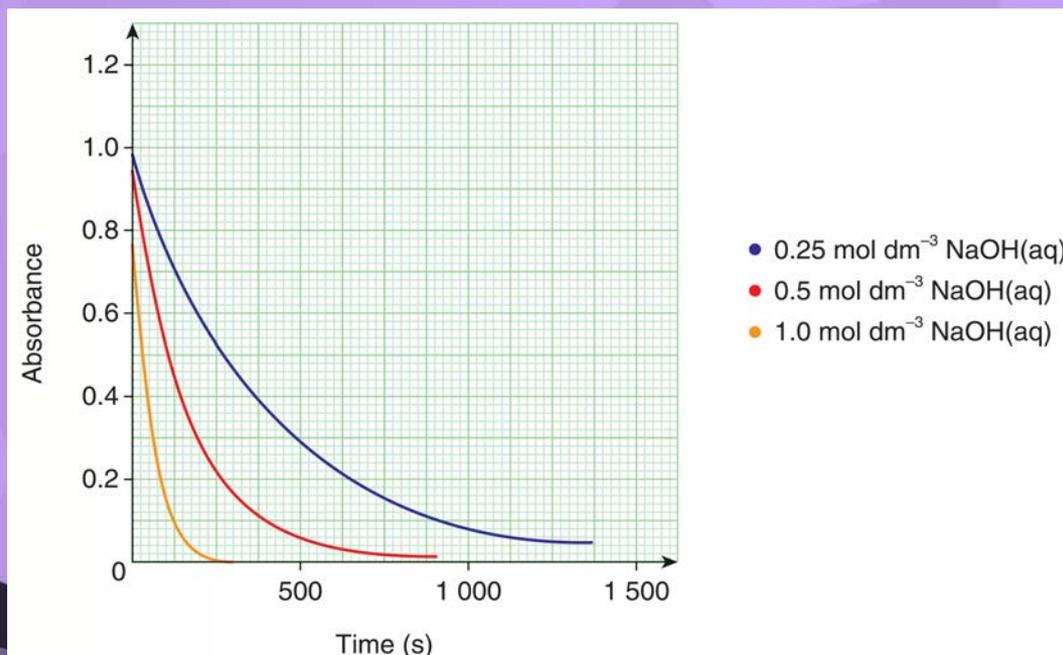
43.6 Determining the order of reaction — method of initial rate (p.17)

The absorbance is proportional to the concentration of phenolphthalein in the mixture.

Use the experimental results obtained to determine the order of reaction with respect to hydroxide ion.

43.6 Determining the order of reaction — method of initial rate (p.18)

A

In each trial, the −slope of the tangent to the absorbance-time curve at t = 0 s is proportional to the initial rate of discolouration of phenolphthalein.

Concentration of NaOH(aq) (mol dm^{-3})	−(slope of absorbance-time curve at t = 0 s)
0.25	0.0024
0.50	0.0050
1.00	0.010

43.6 Determining the order of reaction — method of initial rate (p.18)

The initial rate of decolourisation of phenolphthalein doubled when the concentration of NaOH(aq) doubled.

Hence the order of reaction with respect to hydroxide ion is one.

43.6 Determining the order of reaction — method of initial rate (p.18)

Practice 43.1

Three trials of an experiment were performed at the same temperature for the study of the chemical kinetics of the following reaction in the absence of air. $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(l)$
The table below shows the data obtained. Deduce the order of reaction with respect to $NO(g)$ and that to $H_2(g)$.

Trial	Initial concentration (mol dm^{-3})		Initial rate with respect to N$_2$(g) (mol dm^{-3} s^{-1})
	NO(g)	H$_2$(g)	
1	2.50×10^{-2}	1.00×10^{-2}	2.40×10^{-6}
2	5.00×10^{-2}	1.00×10^{-2}	9.60×10^{-6}
3	5.00×10^{-2}	2.00×10^{-2}	1.92×10^{-5}

43.6 Determining the order of reaction — method of initial rate (p.18)

Compare *Trials 1* and *2*.
The initial rate quadrupled when the initial concentration of NO(g) doubled, with the initial concentration of H_2(g) remaining the same. Thus, the order of reaction with respect to NO(g) is two.

Compare *Trials 2* and *3*.
The initial rate doubled when the initial concentration of H_2(g) doubled, with the initial concentrationof NO(g) remaining the same. Thus, the order of reaction with respect to H_2(g) is one.

43.7 Rate equations (p.19)

◆ The rate equation is an expression showing how the rate of a reaction is linked to the concentrations of the reagents involved.

◆ Consider the reaction:

nA + mB → products

Determining the rate equation for the reaction between sodium thiosulphate solution and dilute sulphuric acid using a microscale chemistry experiment *Ref.*

◆ The rate equation for this reaction is of the form:

rate = k [A]^p [B]^q

◆ Square brackets indicate concentrations, the exponents p and q are the individual orders of reaction with respect to the reagents A and B, and k is the proportionality constant called rate constant.

43.7 Rate equations (p.19)

◆ The sum of the individual orders, $p + q$, is known as the overall order of reaction.

◆ The rate constant, k, varies with the nature of the reaction, the temperature and the presence of any catalyst.

◆ The values of p, q and k have to be determined by experiments.

order of reaction with respect to A   order of reaction with respect to B

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

rate constant

concentration of B
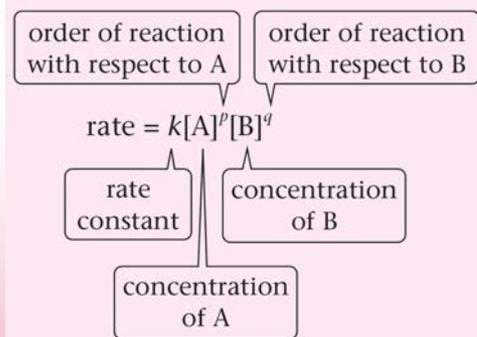
concentration of A

43.7 Rate equations (p.20)

Zero-order reactions

◆ Consider a zero-order reaction — the decomposition of dinitrogen monoxide on a hot platinum surface at constant temperature:

$$2N_2O(g) \xrightarrow{\text{Pt(s)}} 2N_2(g) + O_2(g)$$

◆ If you plot the graph of concentration of $N_2O(g)$ against time, you will get a straight line (Fig. 43.14a).

◆ The straight line indicates that the concentration of $N_2O(g)$ decreases at a constant rate in the above reaction.

◆ A straight line has a constant slope and indicates that the rate is independent of the concentration of $N_2O(g)$ (Fig. 43.14b).

43.7 Rate equations (p.20)
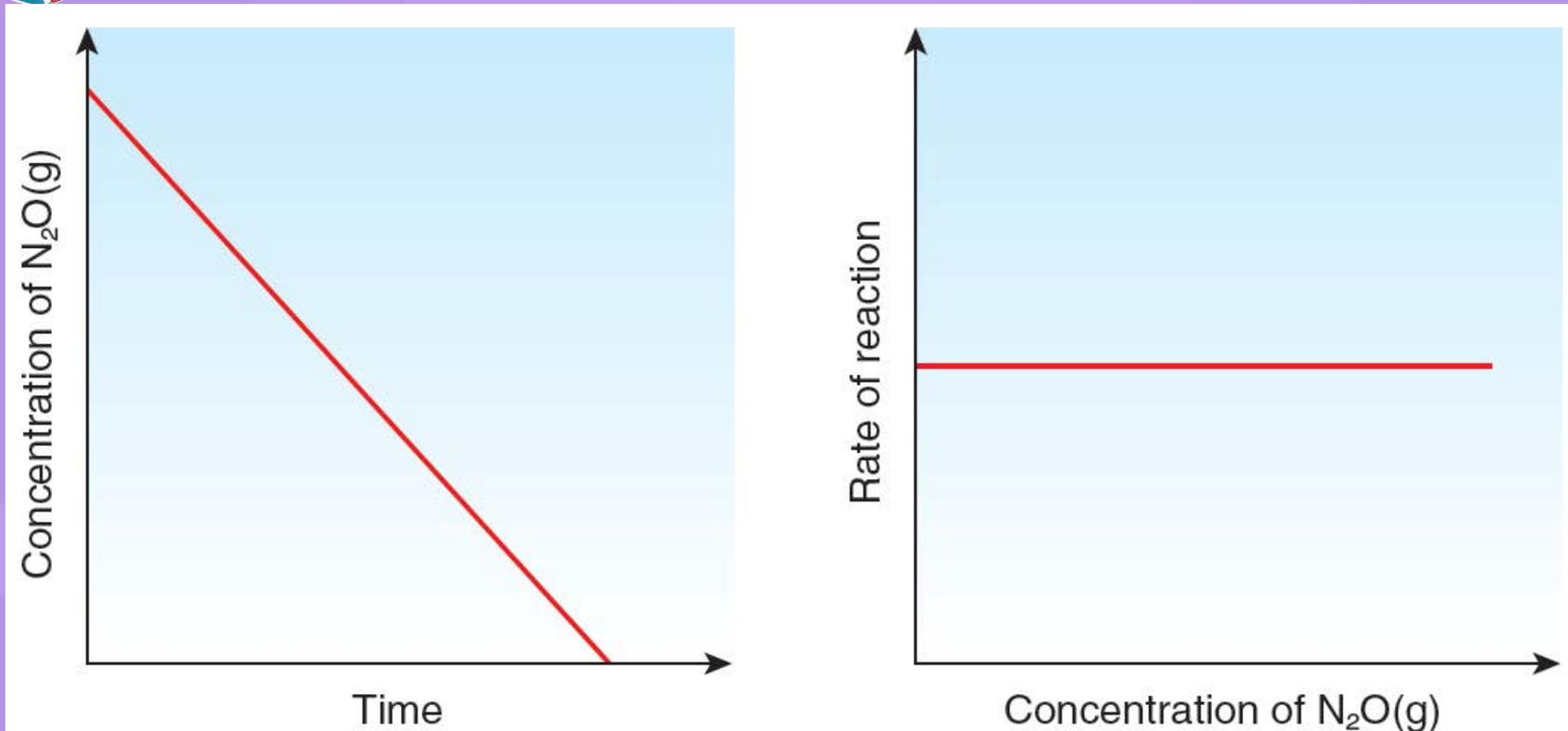
◆   The rate equation for this reaction is

rate = k [$N_2O(g)$]^0

= k

43.7 Rate equations (p.21)

First-order reactions

- Consider a first-order reaction — the decomposition of azomethane ($CH_3N=NCH_3$) at constant temperature:

  $CH_3N=NCH_3(g) \rightarrow C_2H_6(g) + N_2(g)$

- Fig. 43.15a shows how the concentration of $CH_3N=NCH_3(g)$ decreases with time.

- The rate of this reaction is directly proportional to the concentration of $CH_3N=NCH_3(g)$, as shown by the straight line through the origin in Fig. 43.15b..

43.7 Rate equations (p.21)
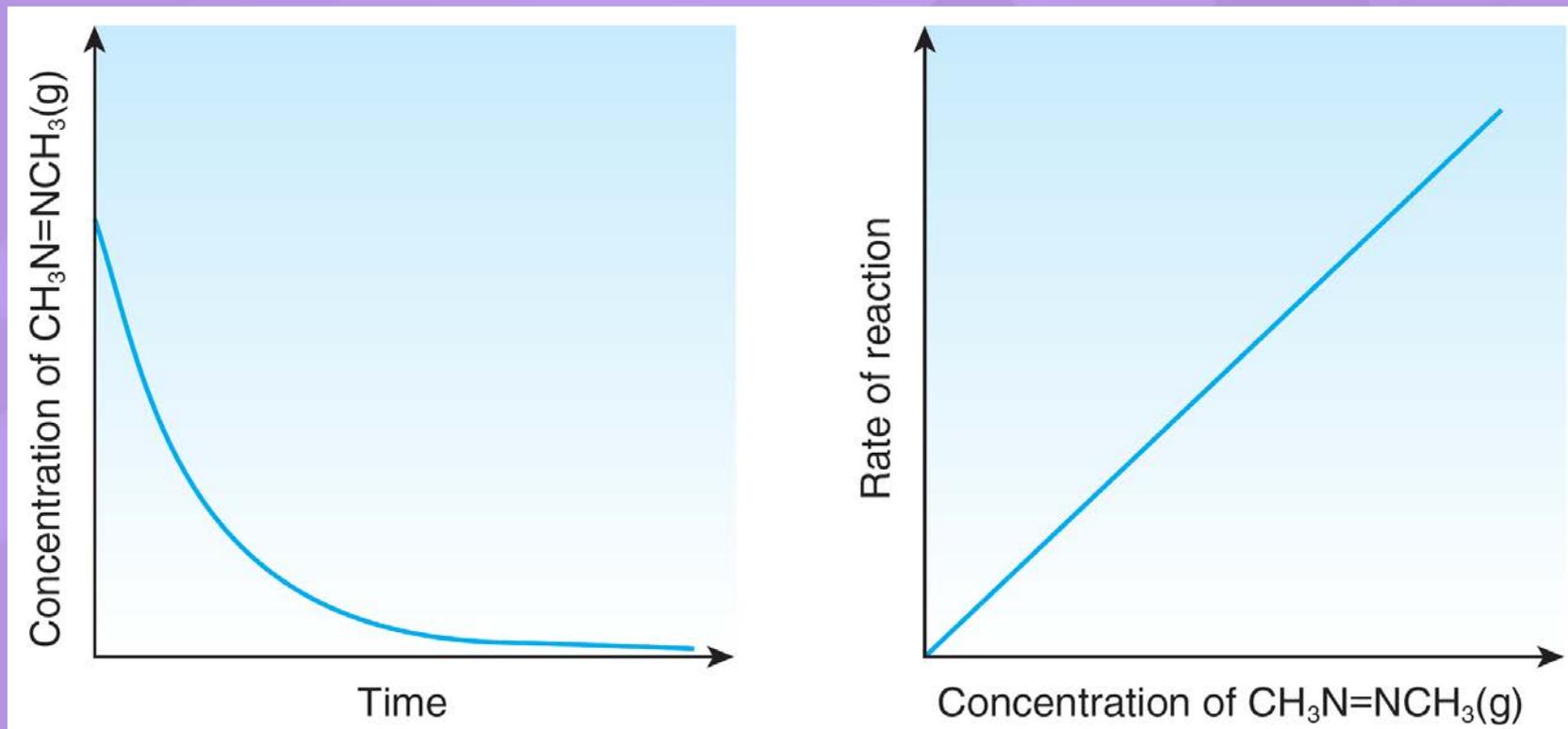
- The rate equation for this reaction is

  rate = k [CH$_3$N=NCH$_3$(g)]

- The slope of the straight line in Fig. 43.15b equals k.

43.7 Rate equations (p.22)

Second-order reactions

◆ Consider a second-order reaction — the decomposition of hydrogen iodide at constant temperature:

$2HI(g) \rightarrow H_2(g) + I_2(g)$
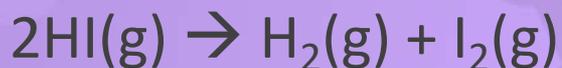
◆ Fig. 43.16a shows how the concentration of HI(g) decreases with time.

◆ Fig. 43.16b shows how the rate of the reaction varies with the concentration of HI(g).

◆ It can be proved that a reaction is second order (rather than third order, etc.) by plotting a graph of the rate of reaction against the square of concentration of HI(g) (Fig. 43.16c).

43.7 Rate equations (p.22)

◆ As the rate is proportional to $[HI(g)]^2$, this graph is a straight line through the origin.

43.7 Rate equations (p.22)
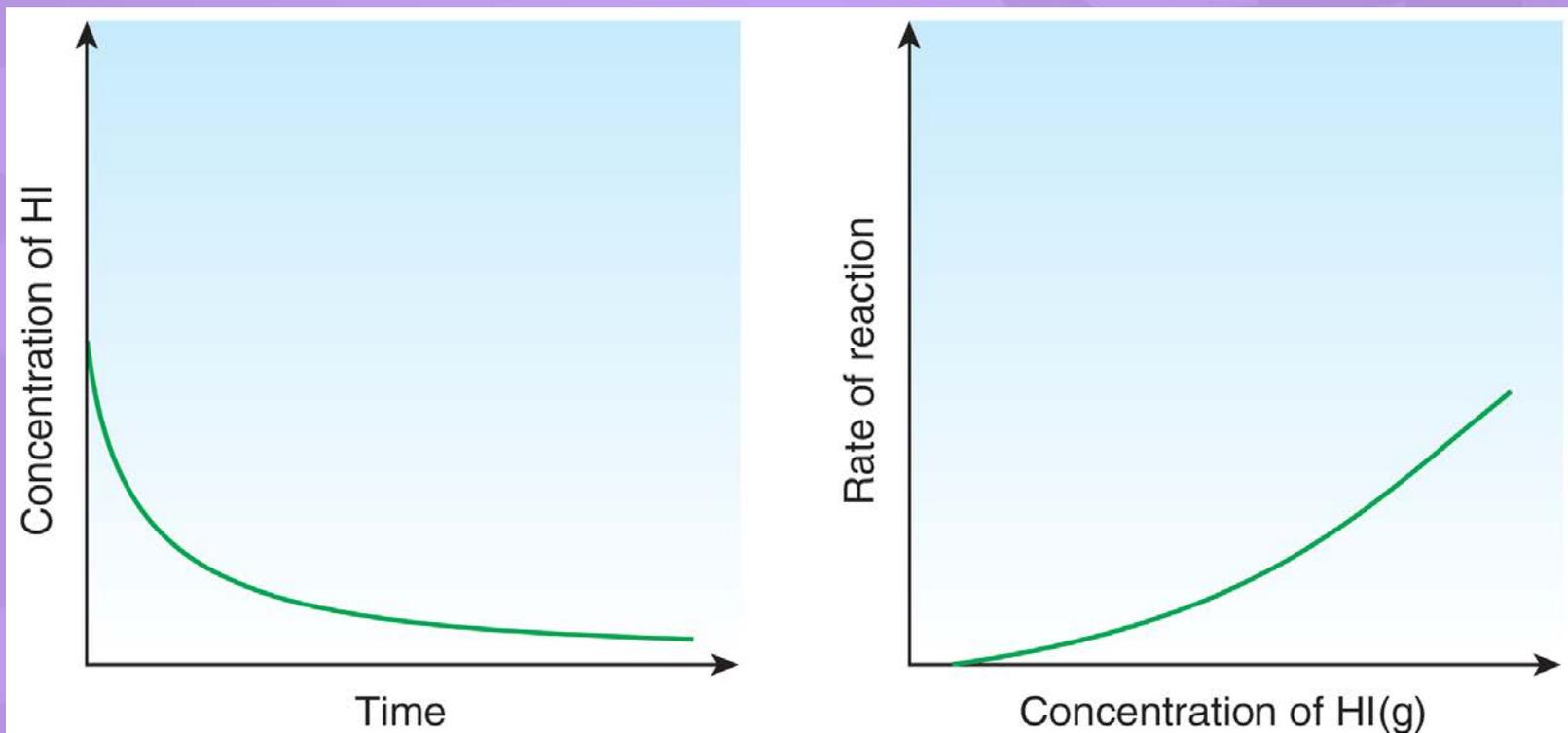
Rate of reaction vs $[HI(g)]^2$
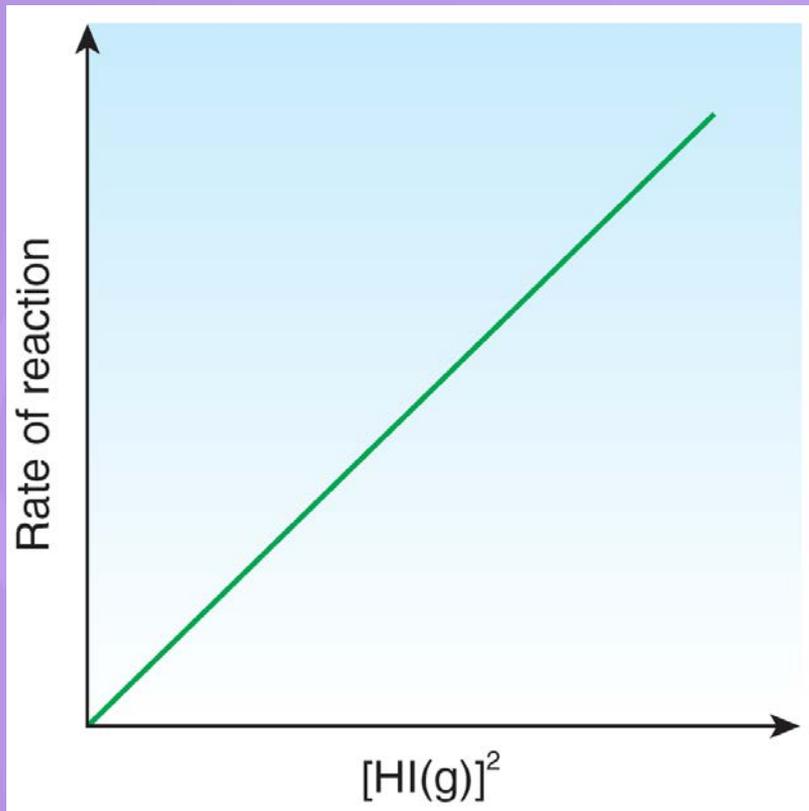
Determining the order of reaction of phenolphthalein in a highly alkaline solution

Determining the rate equation for the reaction between acidified propanone solution and iodine by colorimetry

◆ The rate equation for this reaction is

rate = $k\,[HI(g)]^2$

43.7 Rate equations (p.23)

Units of rate constant

◆ Rate usually has units of mol dm^{-3} s^{-1} and concentration has units of mol dm^{-3}.

◆ The units of the rate constant, k, depend on the overall order of reaction.

◆ For a zero-order reaction:

rate = k [reactant]^0 = k

The units of k are the same as those of rate, i.e. mol dm^{-3} s^{-1}.

Determining the rate equation for an iodine clock reaction

43.7 Rate equations (p.23)

◆ For a first-order reaction:

rate = k [reactant] and hence $k = \dfrac{\text{rate}}{\text{[reactant]}}$

The units of k are $\dfrac{\text{mol dm}^{-3}\ \text{s}^{-1}}{\text{mol dm}^{-3}}$, i.e. s^{-1}

◆ For a second-order reaction:

rate = k [reactant]^2 and hence $k = \dfrac{\text{rate}}{\text{[reactant]}^2}$

The units of k are $\dfrac{\text{mol dm}^{-3}\ \text{s}^{-1}}{(\text{mol dm}^{-3})^2}$ i.e. $dm^3\ mol^{-1}\ s^{-1}$

43.7 Rate equations (p.24)

◆ The different units of rate constant, k, for different overall orders of reaction are summarised in Table 43.4.

Table 43.4	Different units of rate constant, k, for different overall orders of reaction	
Overall order of reaction	Expression for rate constant k	Example of units
0	rate	$mol\ dm^{-3}\ s^{-1}$
1	$\dfrac{rate}{concentration}$	s^{-1}
2	$\dfrac{rate}{(concentration)^2}$	$dm^3\ mol^{-1}\ s^{-1}$

43.7 Rate equations (p.24)

Practice 43.2

Write a rate equation for each of the reactions below.

a) $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$
   The reaction is first order with respect to $N_2O_5(g)$.   rate = k [$N_2O_5(g)$]
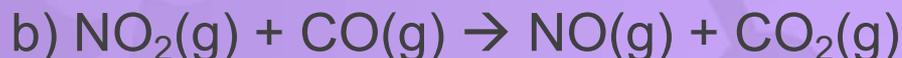
b) $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$
   The reaction is zeroth order with respect to $CO(g)$ and second order with respect to $NO_2(g)$.
   rate = k [$NO_2(g)$]^2

c) $C_{12}H_{22}O_{11}(aq) + H_2O(l)$ $\xrightarrow{\text{HCl(aq) as catalyst}}$ $2C_6H_{12}O_6(aq)$
   The reaction is zeroth order with respect to $H_2O(l)$ and first order with respect to both $C_{12}H_{22}O_{11}(aq)$ and $HCl(aq)$.   rate = k [$C_{12}H_{22}O_{11}(aq)$][$HCl(aq)$]

43.7 Rate equations (p.24)

Q (Example 43.3)

An experiment was devised to study the chemical kinetics of the following acid-catalysed reaction:

$$I_2(aq) + CH_3COCH_3(aq) \xrightarrow{\ H^+(aq)\ } CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$
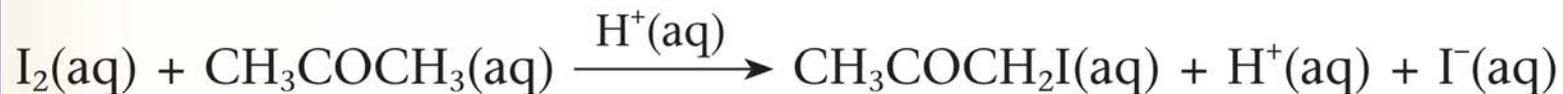
Three trials of the experiment were conducted at the same temperature, and the reaction mixtures used were prepared according to the table below:

Trial	Volume of reagents used (cm³)			
	0.02 mol dm^{-3} $I_2(aq)$	1.0 mol dm^{-3} $CH_3COCH_3(aq)$	$H_2O(l)$	1.0 mol dm^{-3} $H_2SO_4(aq)$
1	50.0	10.0	20.0	25.0
2	50.0	15.0	15.0	25.0
3	50.0	20.0	10.0	25.0

43.7 Rate equations (p.24)

In each trial, 10.0 cm^3 of the reaction mixture was withdrawn at regular time intervals and added to excess cold $NaHCO_3$(aq). When effervescence subsided, the resulting mixture was titrated against standard $Na_2S_2O_3$(aq).

I_2(aq) reacts with $Na_2S_2O_3$(aq) in the titration according to the equation below:

I_2(aq) + $2S_2O_3{}^{2-}$(aq) → $2I^-$(aq) + $S_4O_6{}^{2-}$(aq)

43.7 Rate equations (p.25)

The graph below shows the plot of the titre against time for each trial.
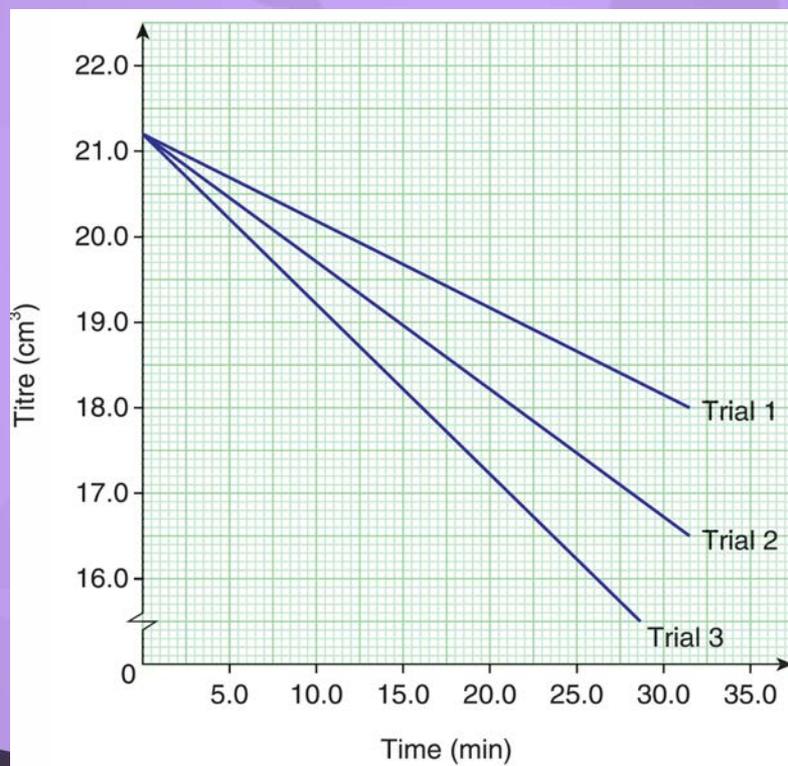
43.7 Rate equations (p.25)

a) What was the purpose of adding the reaction mixture to excess cold $NaHCO_3(aq)$ before each titration?

b) Deduce the order of the reaction with respect to iodine.

43.7 Rate equations (p.25)

c) For each trial, '–slope' of the line can represent the rate of the reaction. Rates in the trials are given in the table

Trial	Volume of 1.0 mol dm^{-3} $CH_3COCH_3(aq)$ (cm^3)	Rate of reaction (–slope) (cm^3 min^{-1})
1	10.0	0.100
2	15.0	0.150
3	20.0	0.200

Deduce the order of reaction with respect to $CH_3COCH_3(aq)$.

43.7 Rate equations (p.25)

A

a) As the reaction is catalysed by $H^+(aq)$, treating the reaction mixture with cold $NaHCO_3(aq)$ help remove the acid so as to quench the reaction.

b) The titre decreases with time linearly, i.e. the rate of the reaction is independent of the concentration of $I_2(aq)$. Thus, the order of reaction with respect to $I_2(aq)$ is zero.

c) The rate doubled when the concentration of $CH_3COCH_3(aq)$ was doubled. Hence the order of reaction with respect to $CH_3COCH_3(aq)$ is one.

43.7 Rate equations (p.26)

Q (Example 43.4)

An experiment was conducted to study the chemical kinetics of the reaction below at a certain temperature:

$2NO(g) + Br_2(g) \rightarrow 2NOBr(g)$

The table below lists the results obtained.

Trial	Initial concentration (mol dm^{-3})		Initial rate of reaction with respect to NOBr(g) (mol dm^{-3} s^{-1})
	NO(g)	Br$_2$(g)	
1	0.0150	0.0100	2.39 x 10^{-4}
2	0.0150	0.0200	4.78 x 10^{-4}
3	0.0600	0.00500	1.91 x 10^{-3}

43.7 Rate equations (p.26)

a) Deduce the rate equation for this reaction.

b) Based on the results in Trial 1, calculate the rate constant under the experimental conditions.

43.7 Rate equations (p.26)

A

a) Suppose the order of reaction with respect to $NO(g)$ is p and that with respect to $Br_2(g)$ is q.

The rate equation for the reaction is of the form:

$rate = k\,[NO(g)]^p\,[Br_2(g)]^q$

From Trials 1 and 2,

$$\frac{\text{Initial rate 1}}{\text{Initial rate 2}} = \frac{(0.0150)^p\,(0.0100)^q}{(0.0150)^p\,(0.0200)^q} = \frac{2.39 \times 10^{-4}}{4.78 \times 10^{-4}}$$

$q = 1$

43.7 Rate equations (p.26)

From Trials 1 and 3,

$$\frac{\text{Initial rate 1}}{\text{Initial rate 3}} = \frac{(0.0150)^p \,(0.0100)^q}{(0.0600)^p \,(0.00500)^q} = \frac{2.39 \times 10^{-4}}{1.91 \times 10^{-3}}$$

$p = 2$

The rate equation is:

rate = $k\,[NO(g)]^2\,[Br_2(g)]$

43.7 Rate equations (p.26)

Alternatively, compare Trials 1 and 2. The initial concentration of NO(g) remains the same, but the initial concentration of Br_2(g) is doubled. The initial rate also doubles. Thus, the order of reaction with respect to Br_2(g) is one.

Compare Trials 1 and 3, the initial concentration of NO(g) is quadrupled and that of Br_2(g) is decreased by one-half. This causes the initial rate to increase by a factor of 8. Thus, the order of reaction with respect to NO(g) is two.

43.7 Rate equations (p.27)

The rate equation is:

rate = k [NO(g)]^2 [Br$_2$(g)]

b) From the results of Trial 1,

2.39 x 10^{-4} mol dm^{-3} s^{-1} = k (0.0150 mol dm^{-3})^2 (0.0100 mol dm^{-3})

k = 106 dm^6 mol^{-2} s^{-1}

43.7 Rate equations (p.27)

Q (Example 43.5)

A student carried out two sets of experiments (one at T_1 and another at T_2) to study the chemical kinetics of the decomposition of $X_2(g)$.

$X_2(g) \rightarrow 2X(g)$

At each temperature, the student used different initial concentrations of $X_2(g)$ (in mol dm^{-3} s^{-1}) and found the initial rate of reaction (in mol dm^{-3} s^{-1}).

The variation of log (initial rate) with log $[X_2(g)]$ (where = initial concentration of $X_2(g)$) was plotted for the data obtained at each temperature.

43.7 Rate equations (p.27)
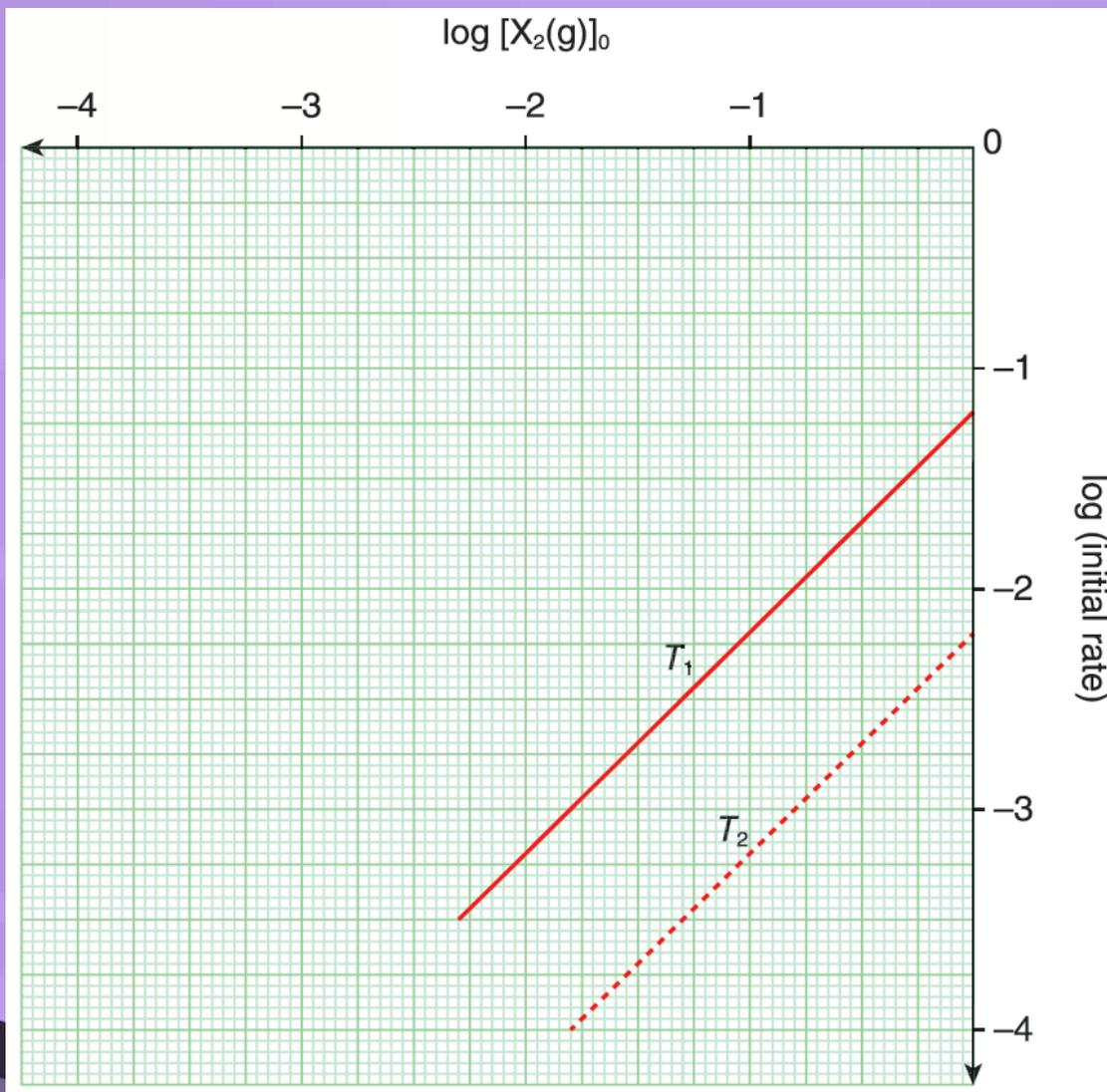
43.7 Rate equations (p.27)

The rate equation for the reaction is of the form:

rate = k [X$_2$(g)]^p

The rate equation can also be expressed as a logarithmic relationship:

log(rate) = log k + p log[X$_2$(g)]

A plot of log (initial rate) against log gives a straight line y = c + mx, where c is the y-intercept and m is the slope.

43.7 Rate equations (p.28)

a) Given that the line for T_1 and that for T_2 have the same slope, what can you deduce in terms of chemical kinetics?

b) From the line for T_1, deduce the order of reaction with respect to $X_2(g)$.

c) From the line for T_2, deduce the rate constant for the reaction at T_2.

43.7 Rate equations (p.28)

A

a) It can be deduced that the value of p is the same at T_1 and T_2. Hence the order of reaction is not affected by temperature change.

b) Slope of the line for $T_1 = \dfrac{-3.5 - (-1.2)}{-2.3 - 0}$

$$= 1$$

c) $\log k = -2.20$

$k = 6.3 \times 10^{-3} \text{ s}^{-1}$

43.7 Rate equations (p.28)

Q (Example 43.6)

The pyrolysis of ethanal gives methane and carbon monoxide.

$CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$

At a certain temperature, if the concentration of $CH_3CHO(g)$ is tripled, the new rate of reaction will become 5.20 times the original rate. Deduce the order of reaction with respect to $CH_3CHO(g)$.

43.7 Rate equations (p.28)

A

The rate equation for the reaction is of the form:

rate = k [CH$_3$CHO(g)]^p

When [CH$_3$CHO(g)] is tripled,

$$\frac{\text{new rate}}{\text{original rate}} = 5.20 = 3^p$$

log 5.20 = p log 3

0.716 = p (0.477)

p = 1.50

∴ the order of reaction with respect to CH$_3$CHO(g) is 1.50.

43.7 Rate equations (p.28)

Practice 43.3

The chemical kinetics of the following reaction at a certain temperature was studied: $5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$

In order to monitor this reaction, some small, fixed amounts of phenol and methyl orange indicator were added to the reaction mixture.

- At the start of the reaction, the phenol present reacted immediately with the bromine as it was produced, thus removing it from the reaction mixture.
- Once the bromine produced had reacted with all of the phenol present, then any further bromine produced would bleach the methyl orange indicator, providing a means to monitor the reaction rate.

43.7 Rate equations (p.28)

a) It was assumed that the initial rate of reaction was proportional to

$$\frac{1}{\text{time taken for the methyl orange indicator to be bleached}}$$

Explain why it is essential for the amount of phenol to be very small compared to the amounts of the reactants for this assumption to be valid.

Any one of the following:

• so that the phenol is used up / methyl orange is bleached during the initial rate period.

• so that the concentration of bromide / bromate / reactants does not fall significantly before all the phenol is used up / methyl orange is bleached.

• so that within this period the average rate of reaction approximates to the initial rate.

43.7 Rate equations (p.28)

b) Several trials of an experiment were attempted under the same experimental conditions except varying the initial concentration of $Br^-(aq)$ to measure the time (t) taken for the methyl orange indicator to be bleached. A plot of $1/t$ against the initial concentration of $Br^-(aq)$ is shown below. With reference to the graph, deduce the order of reaction with respect to $Br^-(aq)$.

The initial rate is directly proportional to $[Br^-(aq)]$.
Thus, the order of reaction with respect to $Br^-(aq)$ is one.
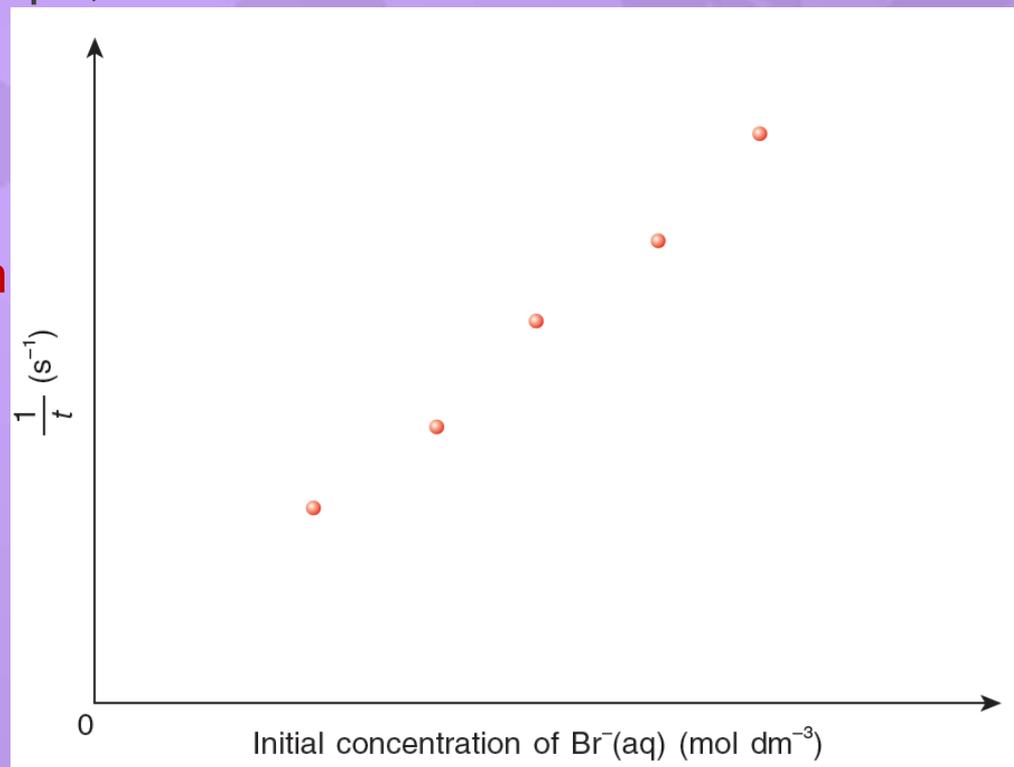
43.7 Rate equations (p.28)

c) The reaction is first order with respect to $BrO_3^-(aq)$ ion and second order with respect to $H^+(aq)$ ion.
Write the rate equation for the reaction.

rate $= k[Br^-(aq)][BrO_3^-(aq)][H^+(aq)]^2$

43.7 Rate equations (p.28)

2 The hydrolysis of maltose to form glucose can be represented by the equation below.

$$C_{12}H_{22}O_{11}(aq) + H_2O(l) \xrightarrow{\text{HCl(aq)}} 2C_6H_{12}O_6(aq)$$

maltose   glucose
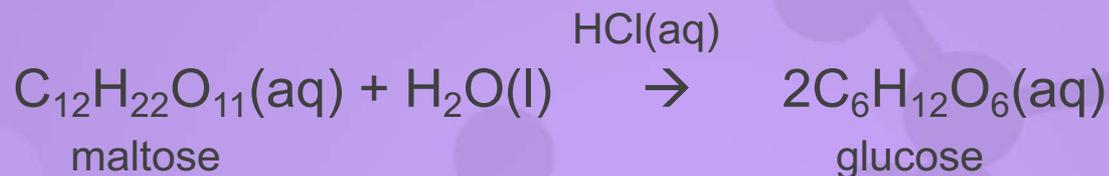
Three trials of an experiment were performed under the same experimental conditions to study the chemical kinetics of the hydrolysis. The table below showed the data obtained.

Trial	Initial concentration ($mol\ dm^{-3}$)		Initial rate of disappearance of $C_{12}H_{22}O_{11}(aq)$ ($mol\ dm^{-3}\ s^{-1}$)
	$C_{12}H_{22}O_{11}(aq)$	$HCl(aq)$	
1	0.020	0.10	5.0×10^{-4}
2	0.040	0.20	2.0×10^{-3}
3	0.060	0.20	3.0×10^{-3}

43.7 Rate equations (p.28)

a) Given that the order of reaction with respect to $H_2O(l)$ is zero, deduce the order of reaction with respect to $C_{12}H_{22}O_{11}(aq)$ and that to $HCl(aq)$.

Suppose the order of reaction with respect to $C_{12}H_{22}O_{11}(aq)$ is p and that with respect to $HCl(aq)$ is q.

The rate equation for the reaction is of the form:

$$rate = k[C_{12}H_{22}O_{11}(aq)]^p[HCl(aq)]^q$$

From *Trials 2* and *3*,

$$\frac{\text{initial rate 2}}{\text{initial rate 3}} = \frac{(0.040)^p(0.20)^q}{(0.060)^p(0.20)^q} = \frac{2.0 \times 10^{-3}}{3.0 \times 10^{-3}}$$

$$p = 1$$

From *Trials 1* and *2*,

$$\frac{\text{initial rate 1}}{\text{initial rate 2}} = \frac{(0.020)(0.10)^q}{(0.040)(0.20)^q} = \frac{5.0 \times 10^{-4}}{2.0 \times 10^{-3}}$$

$$q = 1$$

The rate equation is:

$$rate = k[C_{12}H_{22}O_{11}(aq)][HCl(aq)]$$

43.7 Rate equations (p.28)

b) What is the overall order of this reaction?

2

c) Deduce the initial rate of formation of glucose in *Trial 1*.

Initial rate of formation of glucose in *Trial 1*
= 2 x initial rate of disappearance of $C_{12}H_{22}O_{11}$(aq) in *Trial 1*
= 2 x 5.0 x 10^{-4} mol dm^{-3} s^{-1}
= 1.0 x 10^{-3} mol dm^{-3} s^{-1}

d) Based on the result in *Trial 2*, calculate the rate constant under the experimental conditions.

rate = k[$C^{12}H^{22}O_{11}$(aq)][HCl(aq)]
2.0 x 10^{-3} mol dm^{-3} s^{-1} = k(0.040 mol dm^{-3})(0.20 mol dm^{-3})
k = 0.25 dm^3 mol^{-1} s^{-1}

Key terms (p.31)

feedstock	供料	by-product	副產物
chemical kinetics	化學動力學	order of reaction	反應級數
light transmittance	透光度	rate equation	速率方程式
rate constant	速率常數	overall order of reaction	反應總級數

Summary (p.32)

1   The following diagram shows the steps in a chemical process.
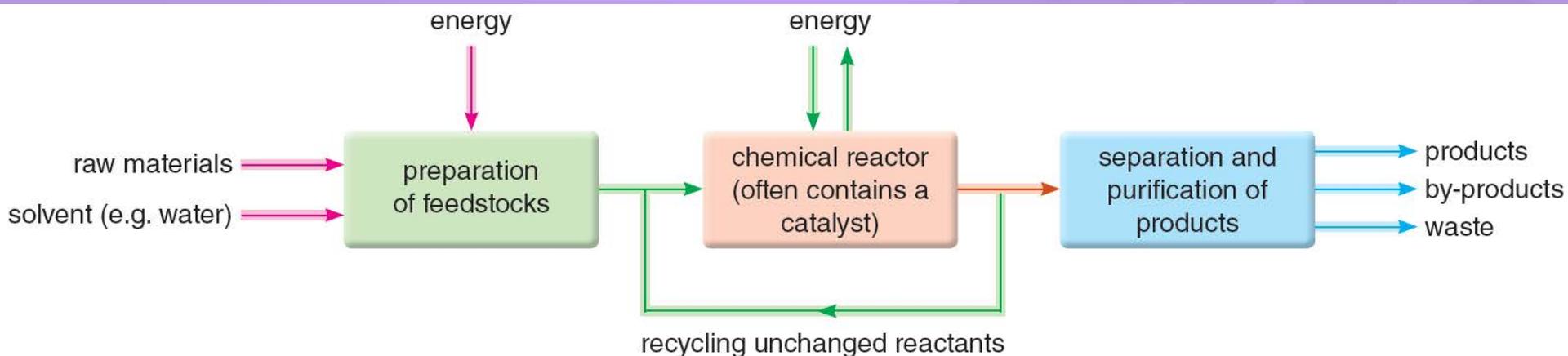
2   The rate of a chemical reaction depends on the concentrations of some or all of the reagents in the reaction vessel — reactants and catalysts.

Summary (p.32)

3 The initial rate of a reaction can be determined by measuring how long the reaction takes to produce a small, fixed amount of one of the products. The time taken is called the reaction time.

Initial rate of reaction $\propto \dfrac{1}{\text{reaction time}}$

Summary (p.32)

4   Consider the reaction:

nA + mB → products

The rate of equation for this reaction is of the form:

Rate = k [A]^p [B]^q where k is the rate constant;

p is the order of reaction with respect to the reactant A;

q is the order of reaction with respect to the reactant B.

The overall order of reaction is p + q.

Summary (p.32)

5. The concentration-time graphs and rate-concentration graphs of reactions of different orders are summarised below.
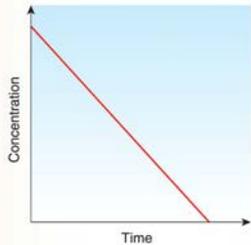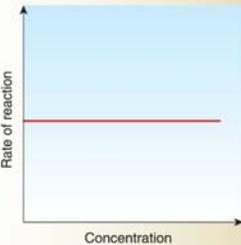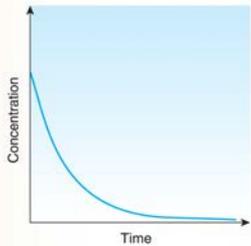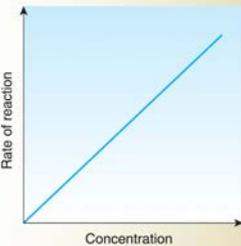
Unit Exercise (p. 34)

Note: Questions are rated according to ascending level of difficulty (from 1 to 5):

👍 **question targeted at level 3 and above;**
👍👍 **question targeted at level 4 and above;**
👍👍👍 **question targeted at level 5.**
**' * ' indicates 1 mark is given for effective communication.**

Unit Exercise (p. 34)

PART I KNOWLEDGE AND UNDERSTANDING

1 Complete the following concept map.

```
                    ┌─────────────────────────┐
                    │  rate equation for reaction │
                    └─────────────────────────┘
```
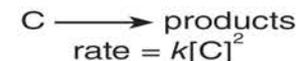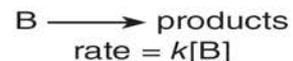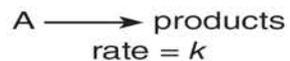
| A ⟶ products | B ⟶ products | C ⟶ products |
| rate = k | rate = $k[B]$ | rate = $k[C]^2$ |

| reaction is ___(a)___ order with respect to A | reaction is ___(d)___ order with respect to B | reaction is ___(g)___ order with respect to C |

concentration-time graph is | concentration-time graph is | concentration-time graph is

| (b) | (e) | (h) |

rate-concentration graph is | rate-concentration graph is | rate-concentration graph is

| (c) | (f) | (i) |

# Unit Exercise (p. 34)

a)   zeroth

b)

c)


d)   first

e)

f)

g)   second

h)

i)
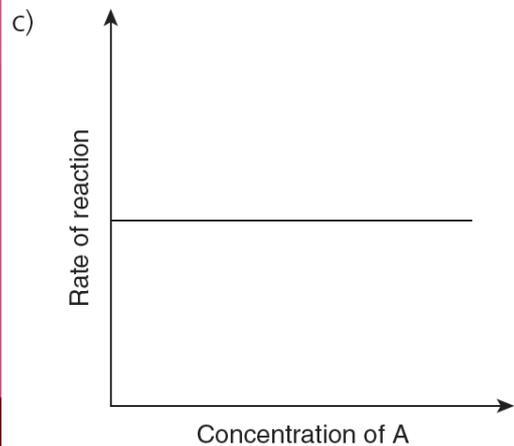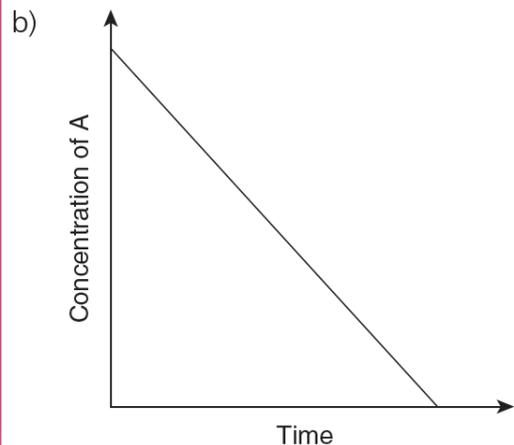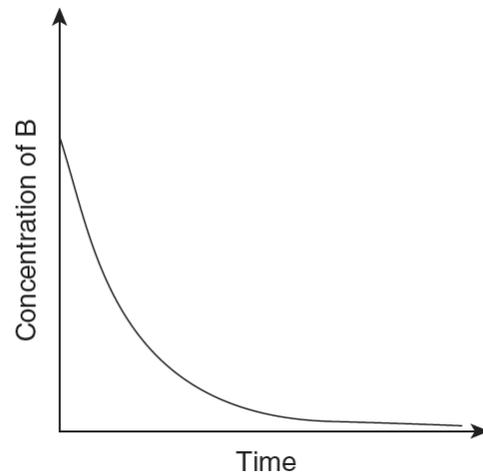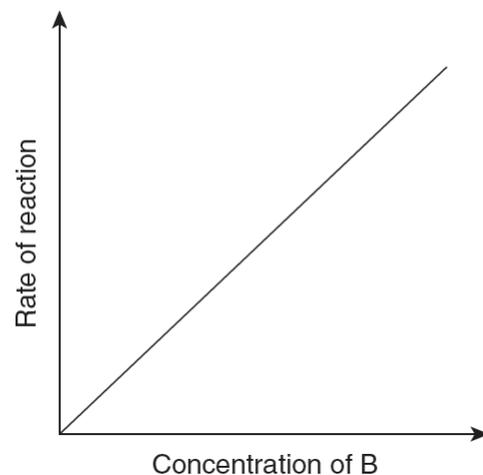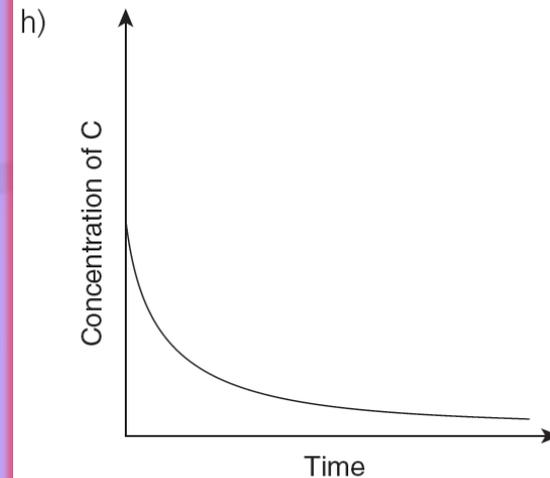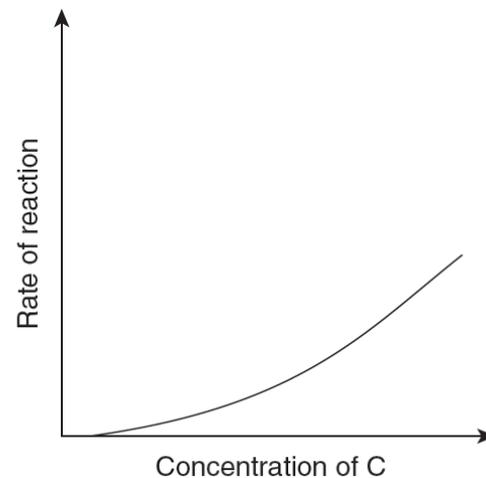
Unit Exercise (p. 34)

PART II **MULTIPLE CHOICE QUESTIONS**

2. Which of the following graphs shows a   reaction that is first order with respect to reactant X?
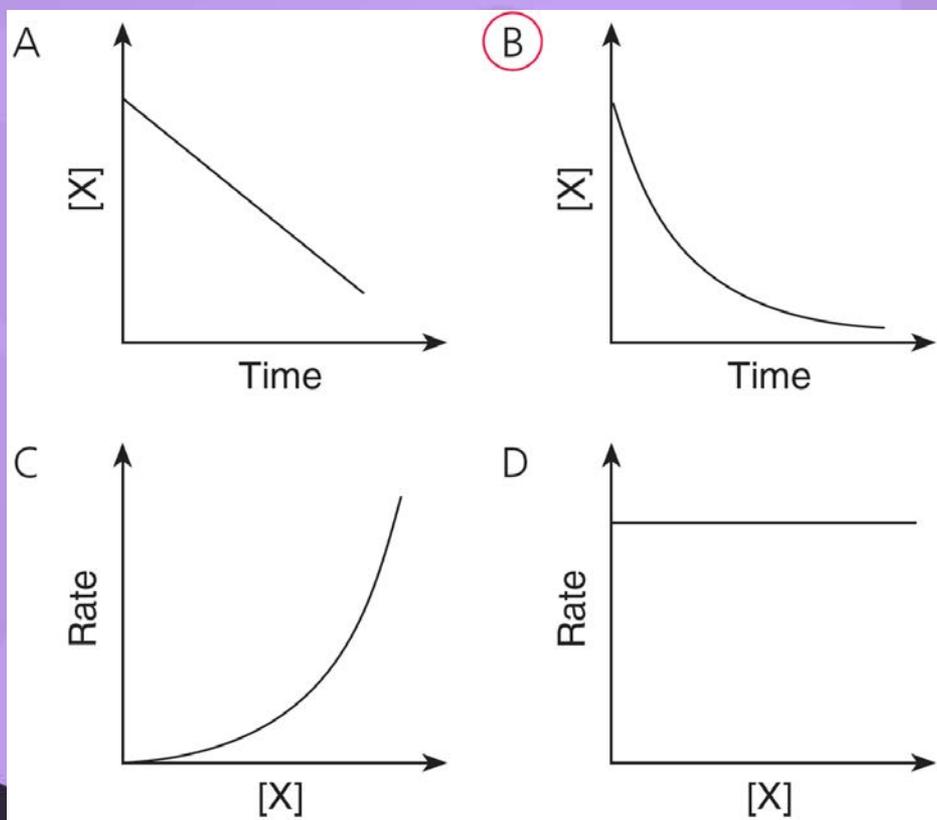
Unit Exercise (p. 34)

3. What is the overall order of a reaction if the rate constant has the units of dm^3 mol^{-1} s^{-1}?
   A Zero
   B First
   C Second
   D Third

Answer: C
Explanation: rate = $k[X]^2$

$$k = \frac{\text{rate}}{[X]^2}$$

Units of k are given by $\dfrac{mol\ dm^{-3}\ s^{-1}}{(mol\ dm^{-3})^2}$

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

Unit Exercise (p. 34)

4. The reaction between NO(g) and Br_2(g) to give NOBr(g) has a rate constant of 105 dm^6 mol^{-2} s^{-1} at a certain temperature.
   Which of the following is the most possible rate equation for this reaction?

   A Rate = $k[NO(g)]^2[Br_2(g)]^2$

   B Rate = $k[NO(g)]^2[Br_2(g)]$

   C Rate = $k[NO(g)][Br_2(g)]$

   D Rate = $k[NO(g)]$ Answer: B

   Explanation: rate = k $[NO(g)]^2$ $[Br_2(g)]$

   $$k = \frac{\text{rate}}{[NO(g)]2 \, [Br_2(g)]}$$

   Units of k are given by $\dfrac{\text{mol } dm^{-3} \, s^{-1}}{(\text{mol } dm^{-3})^2 \, (\text{mol } dm^{-3})}$

   = dm^6 mol^{-2} s^{-1}

Unit Exercise (p. 34)

5. Consider the following equation:

    A → products

    rate = k[A]

    If the initial concentration of A is doubled at the same

    temperature, then the value of k_{new} equals

    A   2k.

    B $\dfrac{k}{2}$

    C k.

    D   log (2k).   Answer: C

Unit Exercise (p. 34)

6. The following initial rate data were obtained at 60 °C for a reaction between an isomer of dibromoethane and potassium iodide in methanol. (In methanol, potassium iodide exists mainly as KI molecules.)
$$C_2H_4Br_2 + 3KI \rightarrow C_2H_4 + 2KBr + KI_3$$

Trial	Initial concentration (mol dm^{-3})		Initial rate (mol dm^{-3} s^{-1})
	$C_2H_4Br_2$	KI	
1	0.050	0.180	2.69×10^{-3}
2	0.050	0.720	1.08×10^{-2}
3	0.150	0.180	8.07×10^{-3}

Unit Exercise (p. 34)

What is the rate equation for this reaction?

A   Rate = $k[C_2H_4Br_2]$

B   Rate = $k[C_2H_4Br_2][KI]$

C   Rate = $k[C_2H_4Br_2]^2[KI]$

D   Rate = $k[C_2H_4Br_2]^2[KI]^2$

Answer: B

Compare Trials 1 and 2. The initial concentration of $C_2H_4Br_2$ remains the same, but the initial concentration of KI is quadrupled. The initial rate also quadruples. Thus, the order of reaction with respect to KI is one. Compare Trials 1 and 3. The initial concentration of KI remains the same, but the initial concentration of $C_2H_4Br_2$ is tripled. The initial rate also triples. Thus, the order of reaction with respect to $C_2H_4Br_2$ is one.

Unit Exercise (p. 34)

7. $H_2(g)$ and $Br_2(g)$ react to form $HBr(g)$. The rate equation for this reaction is:

rate $= k[H_2(g)] [Br_2(g)]^{\frac{1}{2}}$

If the concentration of both reactants is doubled at the same temperature, the rate will increase by a factor of

A   2.5.

B   2.8.

C   3.0.

D   3.5.

Unit Exercise (p. 34)

Answer: B

$$\text{rate}_1 = k[H_2(g)]\ [Br_2(g)]^{\frac{1}{2}}$$

$$\text{rate}_2 = k(2[H_2(g)] \times 2^{\frac{1}{2}}\ [Br_2(g)]^{\frac{1}{2}})$$

$$= k(2.8[H_2(g)]\ [Br_2(g)]^{\frac{1}{2}})$$

∴ the rate will increase by a factor of 2.8.

Unit Exercise (p. 34)
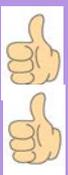
8. The table below shows the results of three trials to investigate the rate of reaction between X(g) and Y(g).

Trial	Initial concentration (mol dm^{-3})		Initial rate (mol dm^{-3} s^{-1})
	X(g)	Y(g)	
1	3.90×10^{-2}	9.60×10^{-2}	5.00×10^{-5}
2	7.80×10^{-2}	2.40×10^{-2}	5.00×10^{-5}
3	7.80×10^{-2}	1.20×10^{-2}	2.50×10^{-5}

Unit Exercise (p. 34)

What is the rate equation for this reaction?

A   Rate = $k[X(g)]$

B   Rate = $k[X(g)][Y(g)]$

C   Rate = $k[X(g)][Y(g)]^2$

D   Rate = $k[X(g)]^2[Y(g)]$ Answer: D

Compare Trials 2 and 3. The initial concentration of X(g) remains the same, but the initial concentration of Y(g) is decreased by one-half. The initial rate also decreased by one-half. Thus, the order of reaction with respect to Y(g) is one.

Compare Trials 1 and 2. The initial concentration of X(g) is doubled and that of Y(g) is decreased by a factor of 4. The initial rate remains the same. Thus, the order of reaction with respect to X(g) is two.

Unit Exercise (p. 34)

9. Consider the following reaction:

   A(g) + B(g) → products
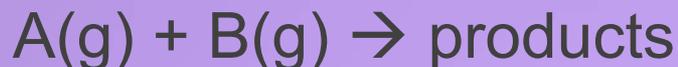
   It is observed that doubling the initial concentration of A(g) at the same temperature causes the initial rate of reaction to be four times as much, but doubling the initial concentration of B(g) does not affect the initial rate. The rate equation of the reaction is

   A   rate = $k[A(g)]^2$.

   B   rate = $k[B(g)]^2$.

   C   rate = $k[A(g)][B(g)]$.

   D   rate = $k[A(g)]^2[B(g)]^2$.

   Answer: A

Unit Exercise (p. 34)

10. The rate of the chemical reaction between substances A and B follows the rate equation:
rate = $k[A]^2[B]$ where k is a constant
If the initial concentration of A is halved, what should be done to the initial concentration of B to make the reaction go, initially, at 75% of its former rate at the same temperature?
The initial concentration of B should be

A   multiplied by $\dfrac{4}{3}$

B   doubled.

C   tripled.

D   halved.

Unit Exercise (p. 34)

Answer: C

Suppose the initial concentration of B in the second reaction is x mol dm^{-3}.

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{[A]2[B]}{[\frac{A}{2}]^2 \ x} = \frac{100}{75}$$

$$x = 4[B] \times \frac{75}{100}$$

$$= 3[B]$$

∴ the initial concentration of B should be tripled.

Unit Exercise (p. 34)

PART III STRUCTURED QUESTIONS

11. The rate equation for the reaction between compounds A and B is rate = k[A]^2[B].

    The graph below shows how, in an experiment, the concentration of A changes with time, t, in this reaction:
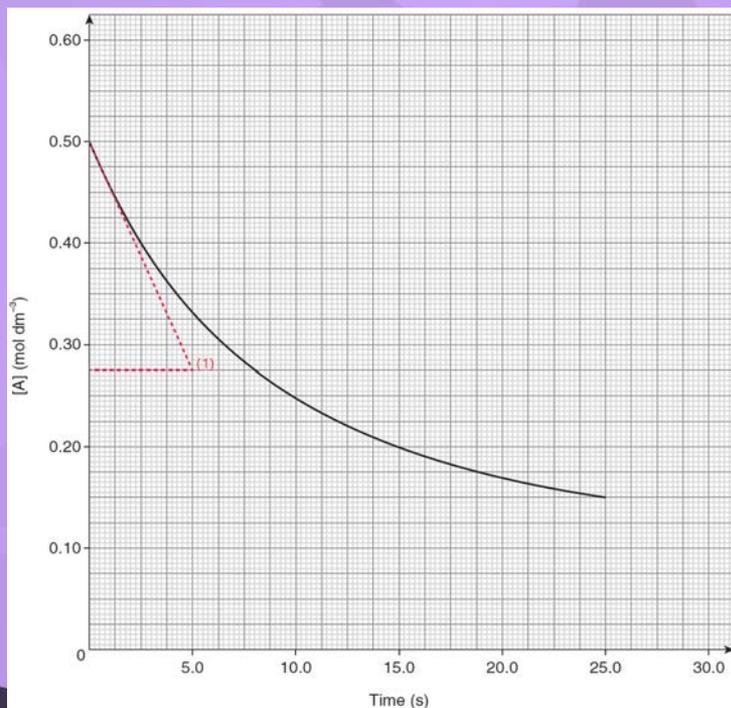
Unit Exercise (p. 34)

a) Draw a tangent to the curve at t = 0.

b) Use this tangent to deduce the initial rate of the reaction.

initial rate of reaction = $\dfrac{(0.275 - 0.50) \text{ mol dm}^{-3}}{5.0 \text{ s}}$

= 0.045 mol dm^{-3} s^{-1} (1)

c) The experiment was repeated at the same temperature and with the same initial concentration of B but with a different initial concentration of A. The new initial rate was 1.7 times greater than in the original experiment. Calculate the new initial concentration of A.

(AQA Advanced Level, Paper 2, Jun. 2017, 2)

Unit Exercise (p. 34)

$$\frac{\text{initial rate}_1}{\text{initial rate}_2} = \frac{[A_1]^2[B]}{[A_2]^2[B]}$$

$$\frac{1}{1.7} = \left(\frac{A_1}{A_2}\right)^2$$

$$\frac{A_1}{A_2} = \sqrt{\frac{1}{1.7}}$$

$$\frac{A_2}{A_1} = \sqrt{1.7} \ = 1.3 \hspace{4cm} (1)$$

$$A_2 = 1.3 \times A_1 \ = 1.3 \times 0.50 \text{ mol dm}^{-3}$$

$$= 0.65 \text{ mol dm}^{-3} \hspace{4cm} (1)$$

$\therefore$ the new initial concentration of A is 0.65 mol dm^{-3}.

Unit Exercise (p. 34)

12. Vitamin C can be obtained from fruits. Explain why it is still necessary to synthesise vitamin C industrially

.   (HKDSE, Paper 2, 2014, 1(a)(iii))

Unit Exercise (p. 34)

13. Chlorine dioxide (ClO_2) is a liquid at room temperature and pressure. In aqueous solution, chlorine dioxide reacts with hydroxide ions according to the following equation:

$2ClO_2(aq) + 2OH^-(aq) \rightarrow ClO_2^-(aq) + ClO_3^-(aq) + H_2O(l)$

The rate equation derived from experiments is:
rate = $k[ClO_2(aq)]^2[OH^-(aq)]$

The following data were obtained in an experiment conducted to study the chemical kinetics of the reaction at a certain temperature.

Unit Exercise (p. 34)

Trial	Initial concentration (mol dm^{-3})		Initial rate of reaction (mol dm^{-3} s^{-1})
	$ClO_2(aq)$	$OH^-(aq)$	
1	0.010	0.030	6.0 x 10^{-4}
2	0.040	0.075	?

a) Use the data from Trial 1 to calculate the rate constant at the temperature of the experiment.

6.0 x 10^{-4} mol dm^{-3} s^{-1} = k(0.010 mol dm^{-3})^2(0.030 mol dm^{-3})

k = 200 dm^6 mol^{-2} s^{-1} (1)

Unit Exercise (p. 34)

b) Calculate the initial rate of reaction in Trial 2.

Initial rate in Trial 2

$= (200 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1})(0.040 \text{ mol dm}^{-3})^2(0.075 \text{ mol dm}^{-3})$

$= 0.024 \text{ mol dm}^{-3} \text{ s}^{-1}$ (1)

Unit Exercise (p. 34)

14. The reaction between two substances A and B
    A + B → C + D
    has the following rate equation:
   rate = k[B]
    A solution with a certain amount of B and a solution with highly excess amount of A are mixed at constant temperature.

# Unit Exercise (p. 34)

Draw graphical representations of
a) [B] against time;
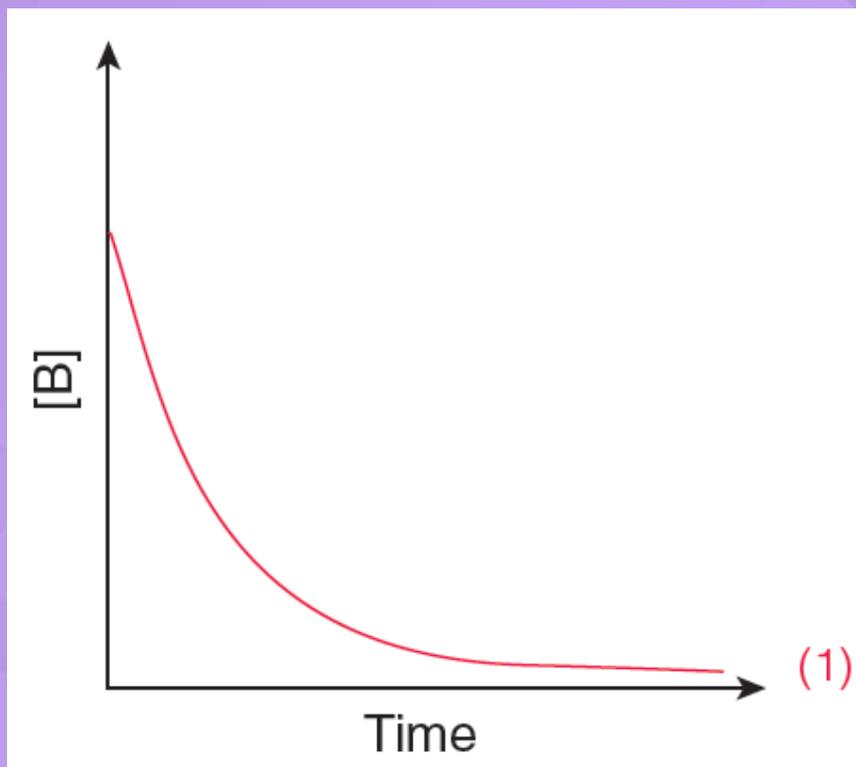
Unit Exercise (p. 34)

b) rate against [B].
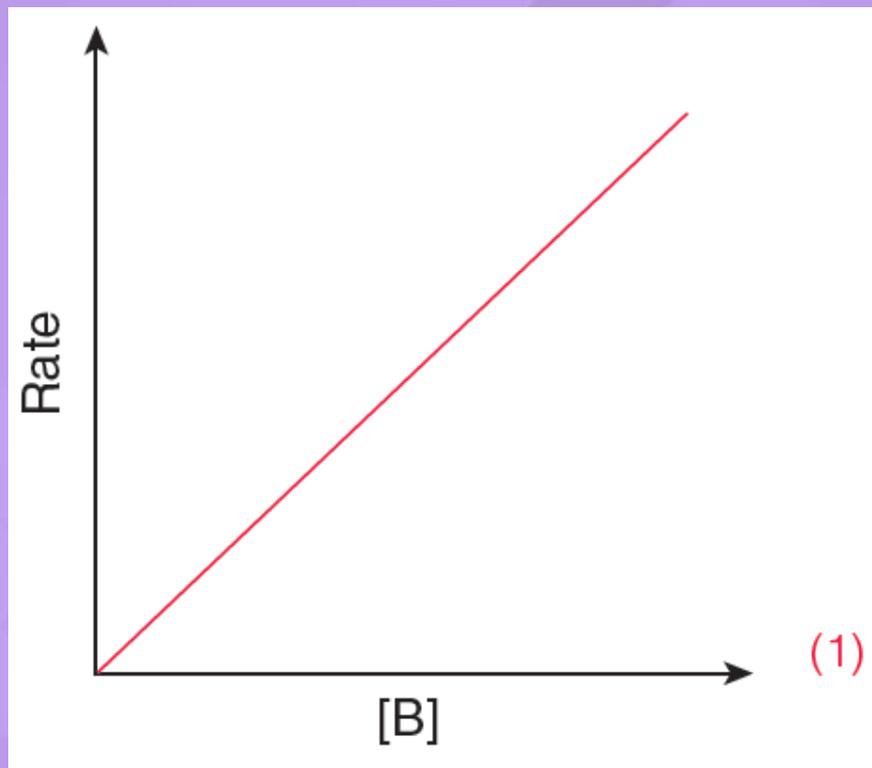
Unit Exercise (p. 34)

15. The following graph shows the variation of the concentration of reactant A(aq) in a certain reaction at a fixed temperature with time:
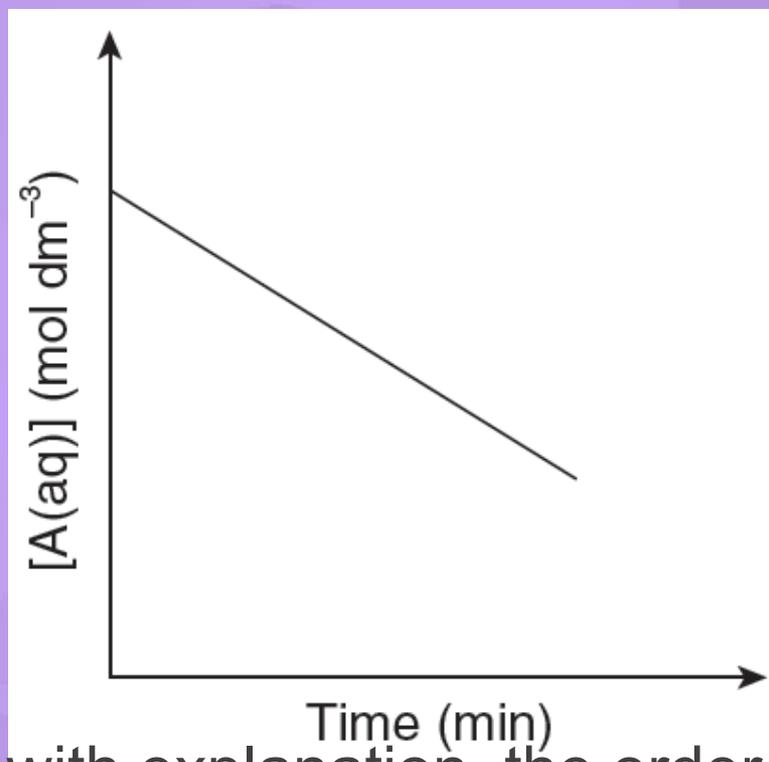
Suggest, with explanation, the order of reaction with respect to A(aq). (HKDSE, Paper 2, 2017, 1(a)(ii))

Unit Exercise (p. 34)

16. $C_6H_5N_2Cl(aq)$ decomposes in dilute aqueous solution according to the equation below.
$C_6H_5N_2Cl(aq) + H_2O(l) \rightarrow N_2(g) + HCl(aq) + C_6H_5OH(aq)$
A chemist investigated the rate of this decomposition. She used different initial concentrations but the same volume of $C_6H_5N_2Cl(aq)$ to start the decomposition at constant temperature, and collected the nitrogen gas. She measured the time (t) for 50 cm^3 of nitrogen to be collected. The following graph showed the experimental results obtained:
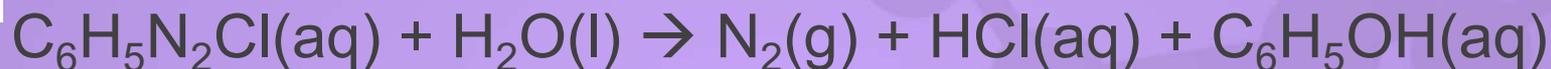
Unit Exercise (p. 34)

The graph shows $\frac{1}{t}$ (s^{-1}) on the y-axis against Initial concentration of $C_6H_5N_2Cl$(aq) (mol dm^{-3}) on the x-axis.
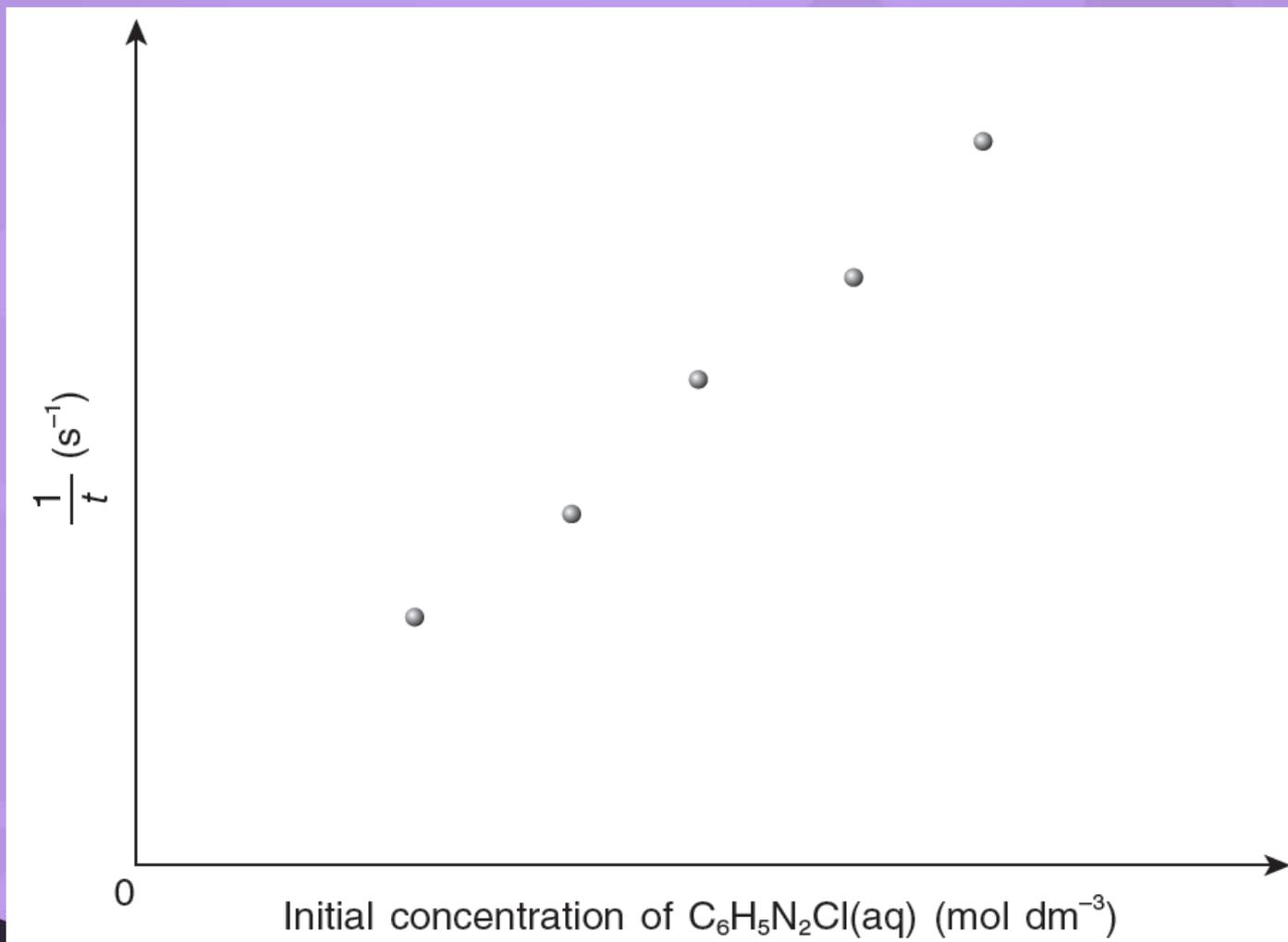
Unit Exercise (p. 34)

a) With reference to the graph above, deduce the order of reaction with respect to $C_6H_5N_2Cl(aq)$.
The initial rate is directly proportional to $[C_6H_5N_2Cl(aq)]$. Thus, the order of reaction with respect to $C_6H_5N_2Cl(aq)$ is one. (1)

b) The chemist could have measured the time to produce a much larger volume of nitrogen.

Suggest why it would have been INAPPROPRIATE to measure the time to collect larger volumes of gas, particularly in the experiments with lower concentrations of $C_6H_5N_2Cl(aq)$.

Only the initial concentration is known.

Collecting larger volumes would NOT give the initial rate. (1)

Unit Exercise (p. 34)

c) Besides gas collection, suggest ANOTHER method with which the chemist could follow the progress of the decomposition.
Any one of the following:

- Measuring the pH change   (1)

- Measuring the loss of mass   (1)

- Titrating HCl(aq) with a standard alkali   (1)

Unit Exercise (p. 34)

17. Hydrogen peroxide reacts with iodide ions in acidic condition according to the equation below.

$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$

The following data were obtained in an experiment conducted to study the chemical kinetics of the reaction at a certain temperature.

Trial	Initial concentration (mol dm^{-3})			Initial rate (mol dm^{-3} s^{-1})
	$H_2O_2(aq)$	$I^-(aq)$	$H^+(aq)$	
1	0.0050	0.020	0.20	2.85 x 10^{-6}
2	0.010	0.020	0.20	5.70 x 10^{-6}
3	0.010	0.020	0.30	5.70 x 10^{-6}
4	0.020	0.040	0.20	2.28 x 10^{-5}

The rate equation is:
rate = $k[H_2O_2(aq)][I^-(aq)]$

Unit Exercise (p. 34)

a) Show that the student's data support this rate equation.

Compare Trials 1 and 2. The initial concentrations of I^- (aq) and H^+(aq) remain the same, but the initial concentration of H_2O_2(aq) is doubled. The initial rate also doubles. Thus, the order of reaction with respect to H_2O_2(aq) is one. (1)

Compare Trials 2 and 3. The initial concentrations of H_2O_2(aq) and I^-(aq) remain the same, but the initial concentration of H^+(aq) is increased. The initial rate remains the same. Thus, the order of reaction with respect to H^+(aq) is zero. (1)

Compare Trials 3 and 4. The initial concentrations of both H_2O_2(aq) and I^-(aq) are doubled. The initial rate quadruples. Thus, the order of reaction with respect to I^-(aq) is one. (1)

Unit Exercise (p. 34)

b) Use the data from Trial 1 to calculate the rate constant, k, for this reaction. State the units of k.

$$2.85 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1} = k(0.0050 \text{ mol dm}^{-3})(0.020 \text{ mol dm}^{-3})$$

$$k = 0.0285 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Unit Exercise (p. 34)

18. Consider the acid-catalysed reaction between iodine and propanone:

$$I_2(aq) + CH_3COCH_3(aq) \xrightarrow{\quad H^+(aq) \quad} CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$
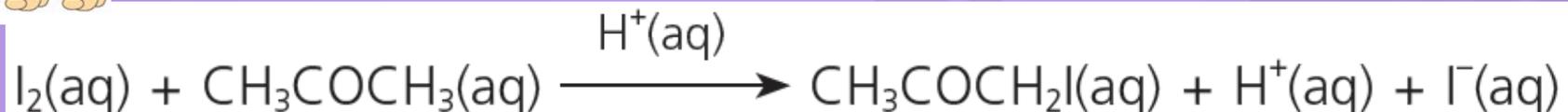
The reaction is zeroth order with respect to $I_2(aq)$ and first order with respect to both $CH_3COCH_3(aq)$ and $H^+(aq)$.

a) Write the rate equation for the reaction.

rate = $k[CH_3COCH_3(aq)][H^+(aq)]$ (1)

Unit Exercise (p. 34)

b) The graph of $[I_2(aq)]$ against time is a straight line, showing that the order of reaction with respect to iodine is zero.
Explain why propanone and hydrogen ion must be in large excess in this experiment in order to give this straight line.

Their concentrations do not change significantly over the course of the reaction. (1)
Only $[I_2(aq)]$ changes.

Unit Exercise (p. 34)

19. Trichloromethane reacts with chlorine according to the equation below at a certain temperature.
$CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$
If the concentration of $Cl_2(g)$ is doubled while the concentration of $CHCl_3(g)$ is kept unchanged, the new rate of reaction will become 1.41 times the original rate. Deduce the order of reaction with respect to $Cl_2(g)$.
(Note: The order of a reaction may NOT be an integer.)

Unit Exercise (p. 34)

Suppose the order of reaction with respect to $Cl_2(g)$ is *p*.

$$\frac{rate_1}{rate_2} = \frac{[Cl_2(g)]^p}{2^p \times [Cl_2(g)]^p} \qquad (1)$$

$$\frac{1}{1.41} = \frac{1}{2^p}$$

$$2^p = 1.41$$

$$p \log 2 = \log 1.41$$

$$p = 0.50 \qquad (1)$$

∴ the order of reaction with respect to $Cl_2(g)$ is 0.50.

Unit Exercise (p. 34)

20. Iodine monochloride ($ICl(g)$) can react with hydrogen to form iodine.
$2ICl(g) + H_2(g) \rightarrow 2HCl(g) + I_2(g)$
This reaction was carried out several times using different initial concentrations of $ICl(g)$ and $H_2(g)$. The table below lists the data obtained.

Trial	Initial concentration (mol dm^{-3})		Initial rate of formation of $I_2(g)$ (mol dm^{-3} s^{-1})
	$ICl(g)$	$H_2(g)$	
1	0.125	0.250	5.10×10^{-3}
2	0.250	0.250	1.02×10^{-2}
3	0.500	0.750	6.12×10^{-2}

Unit Exercise (p. 34)

a) Deduce the order of the reaction with respect to ICl(g) and that to H2(g).

Method 1
Suppose the order of reaction with respect to ICl(g) is p and that with respect to $H_2(g)$ is q.
The rate equation for the reaction is of the form:
rate = $k[ICl(g)]^p[H_2(g)]^q$
From Trials 1 and 2,
$$\frac{\text{initial rate 1}}{\text{initial rate 2}} = \frac{(0.125)^p(0.250)^q}{(0.250)^p(0.250)^q} = \frac{5.10 \times 10^{-3}}{1.02 \times 10^{-2}}$$
p = 1   (1)

Unit Exercise (p. 34)

From Trials 2 and 3,

$$\frac{\text{initial rate 2}}{\text{initial rate 3}} = \frac{(0.250)(0.250)^q}{(0.500)(0.750)^q} = \frac{1.02 \times 10^{-2}}{6.12 \times 10^{-2}}$$

$q = 1$ (1)

$\therefore$ the order of reaction with respect to $ICl(g)$ is one while that with respect to $H_2(g)$ is also one.

Unit Exercise (p. 34)

Method 2

Compare Trials 1 and 2. The initial concentration of $H_2(g)$ remains the same, but the initial concentration of ICl(g) is doubled. The initial rate also doubles. Thus, the order of reaction with respect to ICl(g) is one. (1)
Compare Trials 2 and 3. The initial concentration of ICl(g) is doubled and that of $H_2(g)$ is tripled. This causes the initial rate to increase by a factor of 6. Thus, the order of reaction with respect to $H_2(g)$ is one. (1)

Unit Exercise (p. 34)

b) Use the data from Trial 1 to calculate the rate constant, k, for this reaction. State the units of k..

5.10×10^{-3} mol dm^{-3} s^{-1} = k(0.125 mol dm^{-3})(0.250 mol dm^{-3})

$k = 0.163$ dm^3 mol^{-1} s^{-1} (1)

c) Calculate the initial rate of formation of $I_2(g)$ when ICl(g) has an initial concentration of 4.00 $\times 10^{-3}$ mol dm^{-3} and $H_2(g)$ has an initial concentration of 6.00 $\times 10^{-3}$ mol dm^{-3}.

Initial rate of formation of I_2

= 0.163(4.00 $\times 10^{-3}$)(6.00 $\times 10^{-3}$) mol dm^{-3} s^{-1}

= 3.91 $\times 10^{-6}$ mol dm^{-3} s^{-1} (1)

Unit Exercise (p. 34)

21. A bromoalkane has the molecular formula C_4H_9Br. The equation for the hydrolysis of this compound in sodium hydroxide solution is shown below.

$C_4H_9Br(aq) + OH^-(aq) \rightarrow C_4H_9OH(aq) + Br^-(aq)$

The rate of hydrolysis was investigated by mixing a large excess of the bromoalkane with sodium hydroxide solution, and measuring the time taken for all the hydroxide ions to be used up. This was carried out with different initial concentrations of bromoalkane and hydroxide ions. The results are shown in the table below.

Unit Exercise (p. 34)

Trial	Initial concentration (mol dm^{-3})		Time for hydroxide ions to be used up (s)	Initial rate (mol dm^{-3} s^{-1})
	[C$_4$H$_9$Br(l)]	[OH$^-$(aq)]		
1	0.010	0.0015	52	2.9×10^{-5}
2	0.020	0.0015	26	5.8×10^{-5}
3	0.020	0.0025	43	?

a) Complete the unknown value of the initial rate in the table.

Initial rate in Trial 3 = $\dfrac{0.0025 \text{ mol dm}^{-3}}{43 \text{ s}}$

$= 5.8 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$ (1)

Unit Exercise (p. 34)

b) Deduce the rate equation for the reaction.

Compare Trials 1 and 2. The initial concentration of $OH^-(aq)$ remains the same, but the initial concentration of $C_4H_9Br(l)$ is doubled. The initial rate also doubles. Thus, the order of reaction with respect to $C_4H_9Br(l)$ is one.   (1)

Compare Trials 2 and 3. The initial concentration of $C_4H_9Br(l)$ remains the same but the initial concentration of $OH^-(aq)$ is increased. The initial rate remains the same. Thus, the order of reaction with respect to $OH^-(aq)$ is zero.   (1)

$\therefore$ the rate equation for the reaction is rate = $k[C_4H_9Br(l)]$.   (1)

Unit Exercise (p. 34)

22. Bromine and propanone react according to the equation below.

$$Br_2(aq) + CH_3COCH_3(aq) \xrightarrow{H^+(aq)} CH_3COCH_2Br(aq) + HBr(aq)$$
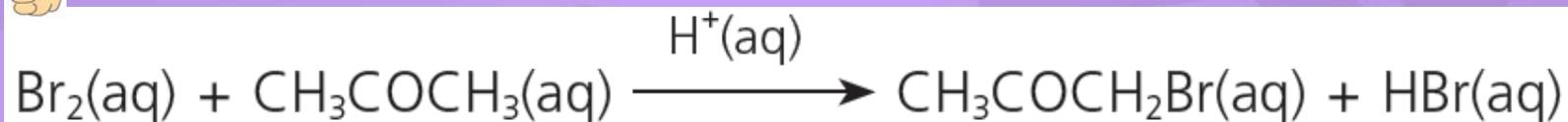
Unit Exercise (p. 34)

a) A colorimeter was used to follow the change in concentration of $Br_2(aq)$ in the reaction mixture. Explain why a colorimeter could be used in this experiment.

Bromine has a yellow-brown colour. As the reaction proceeds, the yellow-brown colour of the reaction mixture becomes less intense as the concentration of bromide decreases. (1)

Concentration of $Br_2(aq) \propto$ absorbance of reaction mixture (1)

Unit Exercise (p. 34)

b) The table below lists the experimental data obtained at a certain temperature.

Trial	Initial concentration (mol dm^{-3})			Initial rate for disappearance of Br_2(aq) (mol dm^{-3} s^{-1})
	Br_2(aq)	CH_3COCH_3(aq)	H^+(aq)	
1	0.060	0.040	0.032	4.80 x 10^{-6}
2	0.120	0.040	0.064	9.60 x 10^{-6}
3	0.060	0.080	0.064	1.92 x 10^{-5}

i)   How is the initial rate of disappearance of Br_2(aq) calculated from a concentration-time graph?
Determine the slope of the tangent to the concentration-time curve at time = 0.   (1)

Unit Exercise (p. 34)

ii) Given that the order of reaction with respect to $CH_3COCH_3(aq)$ is 1, deduce the rate equation for the reaction.

Suppose the order of reaction with respect to $Br_2(aq)$ is p and that with respect to $H^+(aq)$ is q.

The rate equation for the reaction is of the form:

rate $= k[Br_2(aq)]^p[CH_3COCH_3(aq)][H^+(aq)]^q$

From Trials 2 and 3,

$$\frac{\text{initial rate 2}}{\text{initial rate 3}} = \frac{(0.120)^p(0.040)(0.064)^q}{(0.060)^p(0.080)(0.064)^q} = \frac{9.60 \times 10^{-6}}{1.92 \times 10^{-5}}$$

$p = 0$ (1)

Unit Exercise (p. 34)

From Trials 1 and 2,

$$\frac{\text{initial rate 1}}{\text{initial rate 2}} = \frac{(0.060)^0(0.040)(0.032)^q}{(0.120)^0(0.040)(0.064)^q} = \frac{4.80 \times 10^{-6}}{9.60 \times 10^{-6}}$$

$q = 1$ (1)

∴ the rate equation for the reaction is:

rate = $k[CH_3COCH_3(aq)][H^+(aq)]$

iii) Based on Trial 1, calculate the rate constant and gives its units.

4.80 x 10^{-6} mol dm^{-3} s^{-1} = k(0.040 mol dm^{-3})(0.032 mol dm^{-3})

k = 3.75 x 10^{-3} dm^3 mol^{-1} s^{-1} (1)

Unit Exercise (p. 34)

23. Oxygen and nitrogen monoxide react together to form nitrogen dioxide.
    $$O_2(g) + 2NO(g) \rightarrow 2NO_2(g)$$
    Several trials of an experiment were attempted under the same experimental conditions except varying the initial concentration of $O_2(aq)$ to measure the initial rate of formation of $NO_2(g)$. The following graph shows the experimental results obtained from these trials:

Unit Exercise (p. 34)
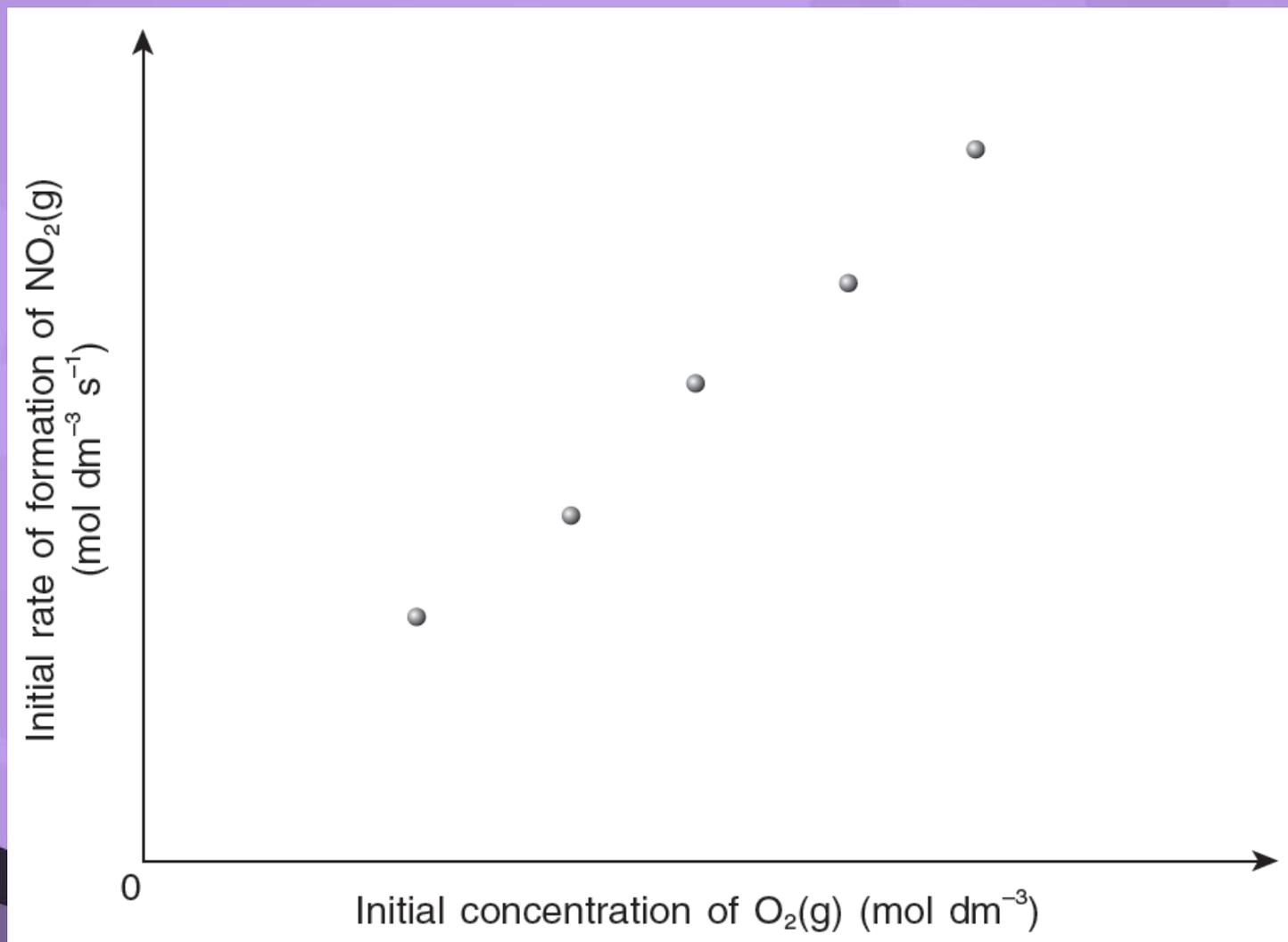
Unit Exercise (p. 34)

a) Explain why 'initial rate' is commonly used in the study of the chemical kinetics of a reaction.

Initial rate is used because the initial concentrations of reactants are known. (1)

b) With reference to the graph above, deduce the order of reaction with respect to $O_2(g)$.

The initial rate is directly proportional to $[O_2(g)]$.

Thus, the order of reaction with respect to $O_2(g)$ is one. (1)

Unit Exercise (p. 34)

c) Suggest how the order of reaction with respect to NO(g) can be determined.

Repeat the experiment using the same reagents, keeping the initial concentration of O_2(g) constant and varying the initial concentration of NO(g).　　(1)

d) Experimental results showed that the reaction was second order with respect to NO. Sketch a graph to show how the rate of reaction would change if the initial concentration of NO(g) was increased.

Unit Exercise (p. 34)
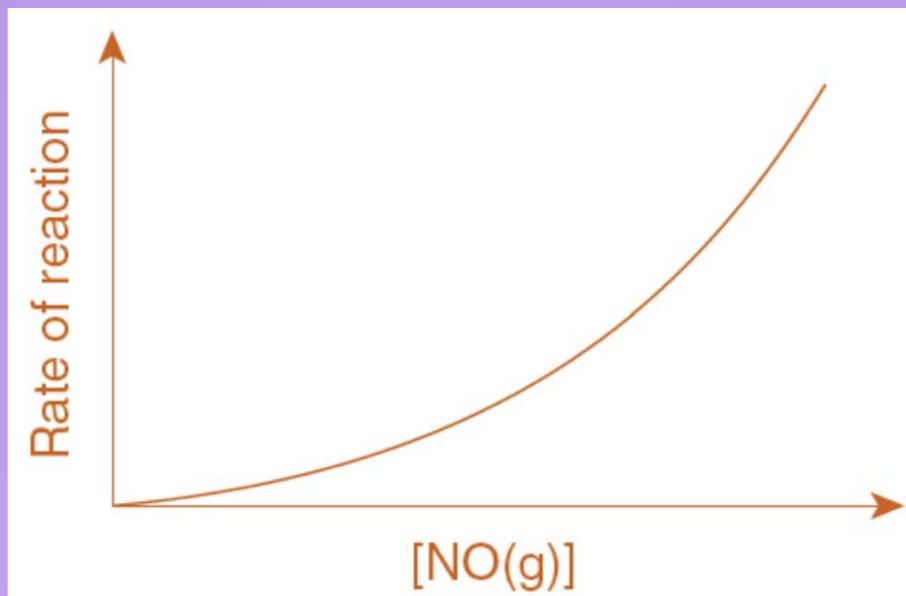
e) Deduce the overall order of this reaction..

Third order   (1)

Unit Exercise (p. 34)

f) State and explain what would happen to the intial rate of reaction if the initial concentration of NO(g) was doubled and that of O_2(g) was halved.

When the initial concentration of NO(g) was doubled, the initial rate of reaction quadrupled.

When the initial concentration of O_2(g) was halved, the initial rate of reaction became half.

∴ the initial rate of reaction would double.

(1)

Unit Exercise (p. 34)

24. 'Oust' is a common descalling treatment for kettles. Its main ingredient is the acid A, $C_3H_6O_3$.
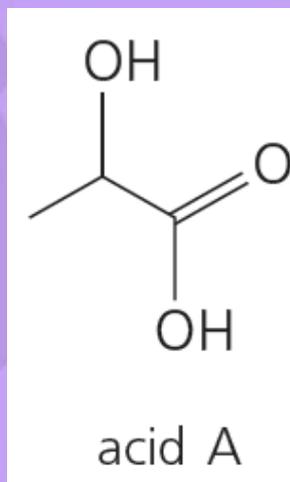
acid A

Unit Exercise (p. 34)

a) A sachet of Oust contains 25.0 g of a liquid. The information on the packet indicates that the only acid present is acid A and that its content is 30–50% by mass.
   Some students decide to investigate the percentage of acid A in Oust. They dilute the liquid from one sachet to 100.0 cm^3 with water. 25.00 cm^3 of this solution react exactly with 33.60 cm^3 of 1.00 mol dm^{-3} sodium hydroxide solution.
   Calculate the actual percentage by mass of acid A in Oust.
   (Relative molecular mass of acid A = 90.0).

Unit Exercise (p. 34)

Number of moles of NaOH

$$= 1.00 \text{ mol dm}^{-3} \times \frac{33.60}{1\,000} \text{ dm}^3$$

= 0.0336 mol   (1)

= number of moles of acid A in 25.00 cm^3

Number of moles of acid A in 100.0 cm^3

$$= 0.0336 \text{ mol} \times \frac{100.0}{25.00}$$

= 0.134 mol   (1)

Mass of acid A in Oust = 0.134 mol x 90.0 g mol^{-1}

= 12.1 g

Percentage by mass of acid A in Oust

$$= \frac{12.1 \text{ g}}{25.0 \text{ g}} \times 100\%$$

= 48.4%   (1)

Unit Exercise (p. 34)

b) The students use indicator B to determine the end point of their titration in (a).

They find that the indicator used for the titration is pink in very dilute alkali, but that the colour slowly fades in more concentrated alkali.

The slow reaction of indicator B in alkali can be represented as:

$B(aq) + OH^-(aq) \rightarrow BOH^-(aq)$

The students decide to follow this reaction by measuring the absorbance of the reaction mixture in a colorimeter.

Unit Exercise (p. 34)

They are provided with

● three aqueous solutions of sodium hydroxide with different concentrations;

● a suitable pink solution of indicator B.

They carry out experiments with the three sodium hydroxide solutions.

The results are shown on the graph and the magnitude of each initial gradient is given.

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Unit Exercise (p. 34)

Describe how the students could have carried out the experiments to obtain these results.
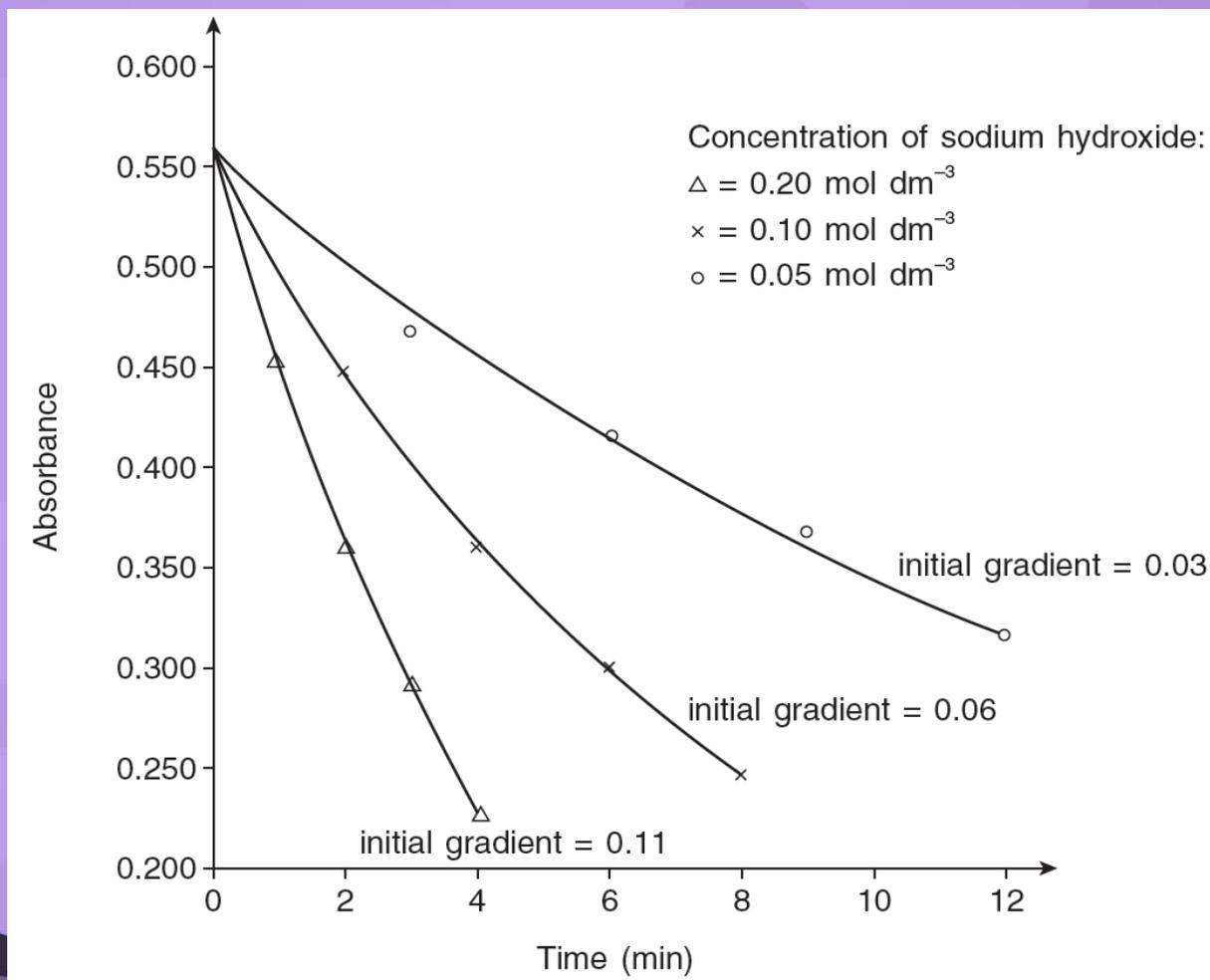
Unit Exercise (p. 34)

Mix a known volume of B with a known volume of each sodium hydroxide solution.   (1)
Measure the absorbance of each reaction mixture at regular time intervals.   (1)

c) The absorbance is proportional to the concentration of B.
   i)   Use the data on the graph to determine the order of reaction with respect to hydroxide ion.
         First order
         The initial gradient doubles as the concentration of NaOH(aq) doubles.   (1)

Unit Exercise (p.34)

ii) The students then set out to determine the order with respect to B.
How would the students do this?
Keep the initial concentration of NaOH(aq) constant.
Vary the initial concentration of B. (1)

(OCR Advanced GCE, Chem. B (Salters), F334,
Jun. 2014, 2(b)–(d)).