

## Chemistry (A-level)

### Reaction kinetics (Chapter 22)

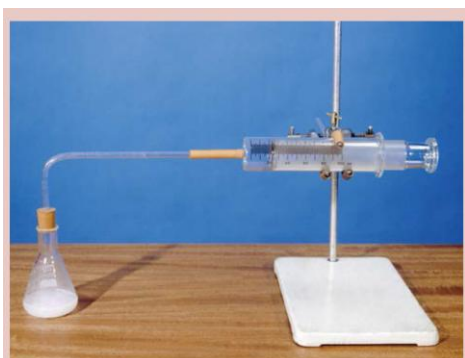
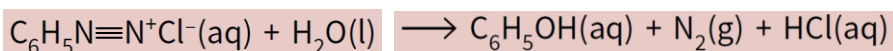
- **Rate of reaction** can be found by measuring the a decrease or an increase in a particular reactant or product over a period of time; unit:  $\text{mol dm}^{-3} \text{ s}^{-1}$

$$\text{rate of reaction} = \frac{\text{change in concentration}}{\text{time taken for this change}}$$

- Methods to find rate of reaction:
  - Colorimetry can be used to monitor colour changes of a particular reactant, e.g. iodine with propanone (fading colour of iodine):



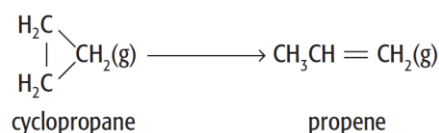
- Changes in gas volume or gas pressure, e.g. benzenediazonium chloride and water:



**Figure 22.3** Rate of reaction can be followed by measuring the change in volume of a gas given off in a reaction. In this experiment  $\text{CO}_2$  is being given off when  $\text{CaCO}_3$  reacts with  $\text{HCl}$ .

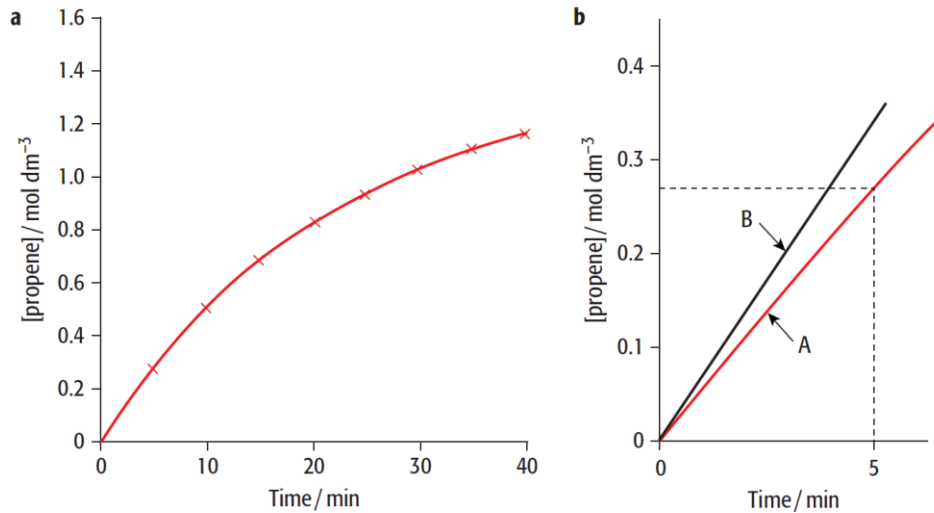
- Table 22.1 shows measurements taken at the same temperature:

Time / min	[cyclopropane] / $\text{mol dm}^{-3}$	[propene] / $\text{mol dm}^{-3}$
0	1.50	0.00
5	1.23	0.27
10	1.00	0.50
15	0.82	0.68
20	0.67	0.83
25	0.55	0.95
30	0.45	1.05
35	0.37	1.13
40	0.33	1.17



**Table 22.1** Concentrations of reactant (cyclopropane) and product (propene) at 5-minute intervals (temperature =  $500^\circ\text{C}$  (773 K)).

- [propene] means 'concentration of propene'
- Figure 22.5 showing the reaction graphically:

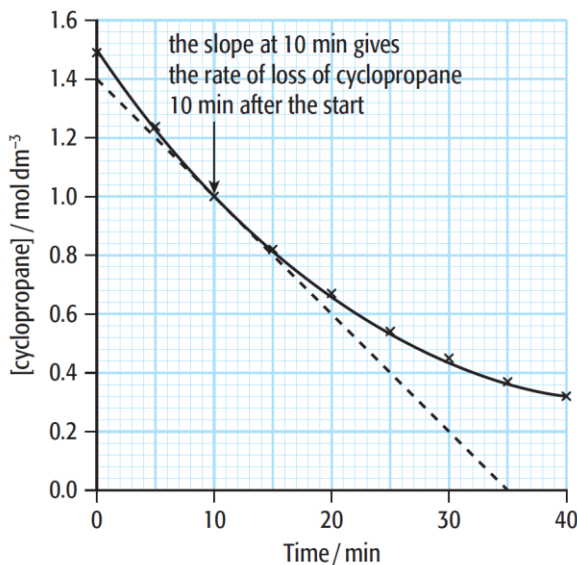


**Figure 22.5** How the concentration of propene changes with time in the reaction cyclopropane  $\longrightarrow$  propene: **a** the whole curve; **b** the first part of the curve magnified. Line A shows the average rate over the first 5 minutes. Line B shows the actual initial rate found by drawing a tangent at the start of the curve.

- Concentration of propene increases from 0.00 to 0.27 mol dm<sup>-3</sup> in the first 5 minutes, hence average rate of reaction:

$$\text{rate of reaction} = \frac{\Delta[\text{propene}]}{\Delta \text{time}} = \frac{0.27}{5} = 0.054 \text{ mol dm}^{-3} \text{ min}^{-1}$$

- To calculate the rate at a particular point on the curve:

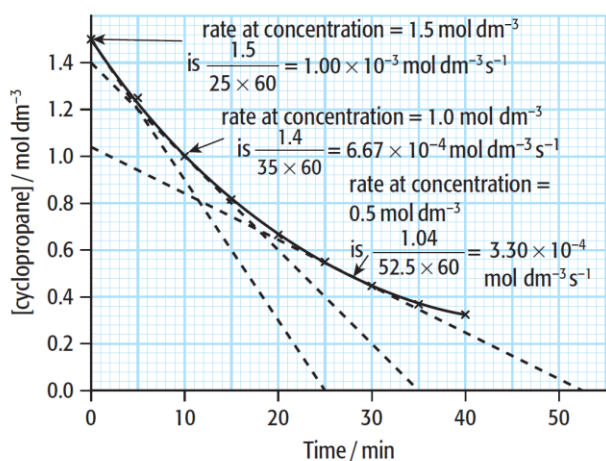


**Figure 22.6** The rate of decrease of cyclopropane concentration over times as the reaction proceeds. The rate of reaction at a given time can be found by drawing a tangent and measuring the gradient.

- Calculate the gradient of the tangent (rate of reaction):

$$\text{slope} = \frac{0.00 - 1.40}{35 \times 60} = -6.67 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$$

- The value of  $-6.67 \times 10^{-4}$  refers to the rate of change of cyclopropane concentration
- As time passes, concentration of cyclopropane falls; graph of [cyclopropane] against time:

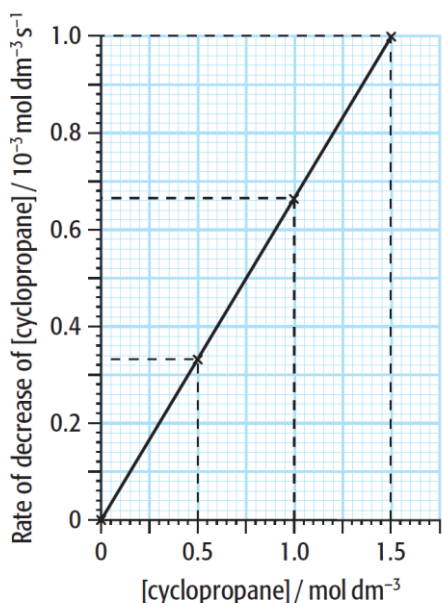


**Figure 22.7** Calculation of the rate of decrease of cyclopropane concentration, made at regular intervals.

[cyclopropane] / mol dm <sup>-3</sup>	Rate / mol dm <sup>-3</sup> s <sup>-1</sup>	Rate [cyclopropane] / s <sup>-1</sup>
1.50	1.00 × 10 <sup>-3</sup>	6.67 × 10 <sup>-4</sup>
1.00	6.67 × 10 <sup>-4</sup>	6.67 × 10 <sup>-4</sup>
0.50	3.30 × 10 <sup>-4</sup>	6.60 × 10 <sup>-4</sup>

**Table 22.2** Rates of decrease for cyclopropane at different concentrations, calculated from Figure 22.7.

- Table shows that the rate is directly proportional to the concentration of cyclopropane, hence:



**Figure 22.8** The rate of decrease of cyclopropane. Note how the gradient (rate/concentration) is constant.

- Rate of reaction given by:

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

- $K$  is the **rate constant**

Stoichiometric equation	Rate equation
1 $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \longrightarrow 2\text{HI}(\text{g})$	rate = $k[\text{H}_2][\text{I}_2]$
2 $\text{NO}(\text{g}) + \text{CO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow \text{NO}_2(\text{g}) + \text{CO}_2(\text{g})$	rate = $k[\text{NO}]^2$
3 $2\text{H}_2(\text{g}) + 2\text{NO}(\text{g}) \longrightarrow 2\text{H}_2\text{O}(\text{g}) + \text{N}_2(\text{g})$	rate = $k[\text{H}_2][\text{NO}]^2$
4 $\text{BrO}_3^-(\text{aq}) + 5\text{Br}^-(\text{aq}) + \text{H}^+(\text{aq}) \longrightarrow 3\text{Br}_2(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$	rate = $k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$

**Table 22.3** Rate equations for some reactions.

- Finding the rate of reaction through experiments (e.g. equation 3):
  - Find the effect of  $\text{H}_2$  (g) on the rate by varying the concentration of  $\text{H}_2$  (g), while keeping the concentration of  $\text{NO}$  (g) constant
  - Results show that the rate is proportional to the concentration of hydrogen (rate =  $k_1 [\text{H}_2]$ )
  - Find the effect of  $\text{NO}$  (g) on the rate by varying the concentration of  $\text{NO}$  (g), while keeping the concentration of  $\text{H}_2$  (g) constant
  - Results show that the rate is proportional to the square of the concentration of  $\text{NO}$  (rate =  $k_2 [\text{NO}]^2$ )
  - Combining gives: rate =  $k_1 [\text{H}_2] [\text{NO}]^2$
- The **order of reaction** with respect to a particular reactant is the power to which the concentration of that reactant is raised in the rate equation
  - E.g. equation 3, first-order with respect to  $\text{H}_2$ , second-order with respect to  $\text{NO}$ , third-order overall (as the sum of the powers is  $1 + 2 = 3$ )
- For a reaction that is  $\text{A} + \text{B} \rightarrow \text{products}$ , rate of reaction given by:

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

- $[\text{A}]$  and  $[\text{B}]$  are the concentrations of the reactants
- $m$  and  $n$  are the orders of the reaction
- The values of  $m$  and  $n$  can be 0, 1, 2, 3 or rarely higher
- When the value of  $m$  or  $n$  is 0 we can ignore the concentration term because any number to the power of zero = 1.

From equation 1 in Table 22.3.

**Step 1** Write the rate equation

$$\text{rate} = k[\text{H}_2][\text{I}_2]$$

**Step 2** Rearrange the equation in terms of  $k$ .

$$k = \frac{\text{rate}}{[\text{H}_2][\text{I}_2]}$$

**Step 3** Substitute the units.

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

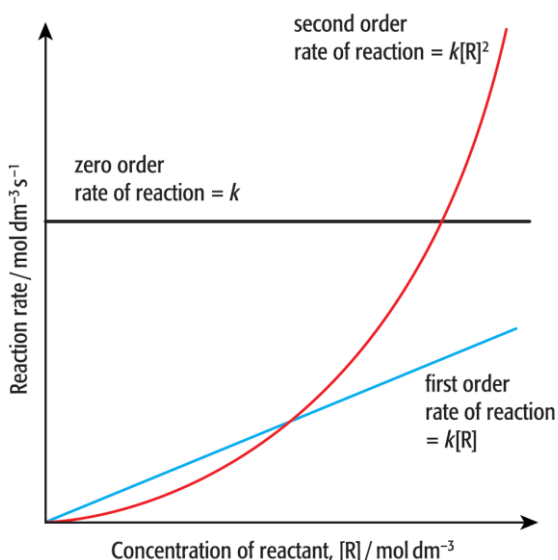
**Step 4** Cancel  $\text{mol dm}^{-3}$ .

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

**Step 5** Units of  $k$ .

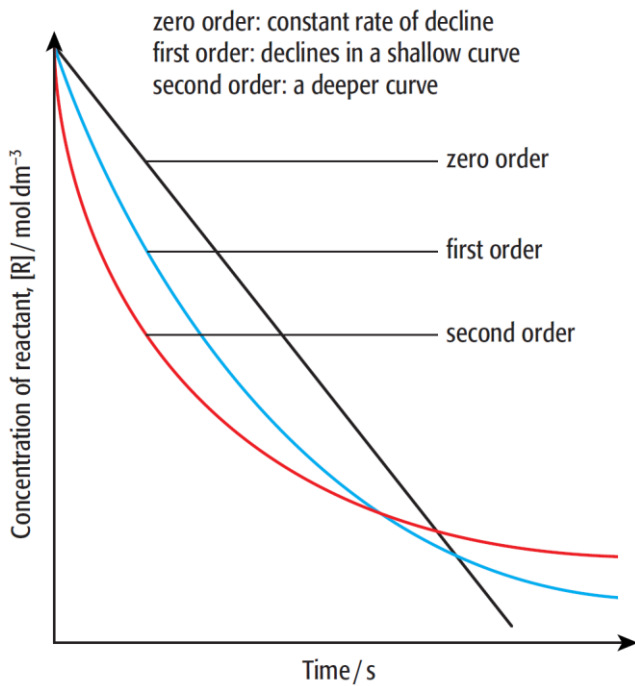
$$\text{units of } k = \text{s}^{-1} \text{ mol}^{-1} \text{ dm}^3 = \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

- when writing the units on one line, the indices on the bottom change sign
- we usually put the unit with the positive index first
- don't forget the  $\text{s}^{-1}$  arising from the units of rate.



Graph of reaction rate against concentration

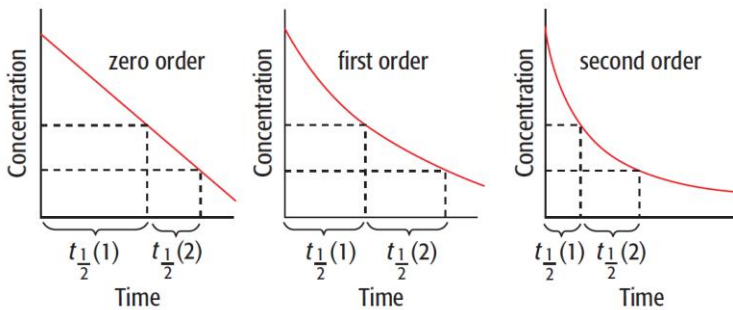
**Figure 22.9** Zero-, first- and second-order reactions: how changes in the concentration of a reactant affect the reaction rate.



Graph of concentration of reactant against time

**Figure 22.10** Zero-, first- and second-order reactions: how changes in the concentration of a reactant affect the time taken for a reaction to proceed.

- For first- and second-order reactions, the graph is a curve – distinguished by determining successive half-lives of the reaction
- **Half-life**,  $t_{1/2}$ , is the time taken for the concentration of a reactant to fall to half its original value



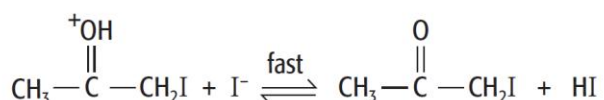
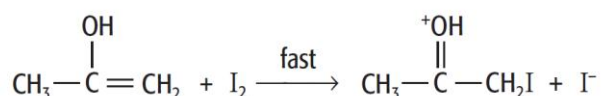
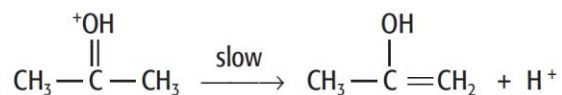
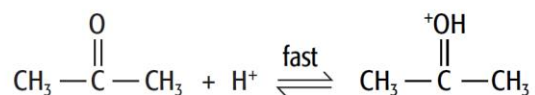
**Figure 22.12** The half-life of zero-, first- and second-order reactions can be determined from graphs of concentration against time.

- Zero-order reaction has successive half-lives which decrease with time
- First-order reaction has a constant half-life, where half-life is independent to the concentration
- Second-order reaction has successive half-lives which increase with time
- Calculating  $k$  from half-life (first-order reactions):

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

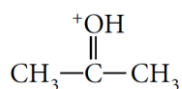
- $t_{1/2}$  is the half-life, units: s
- **Rate-determining step**: the slowest step in a reaction mechanism

- E.g. to find the rate-determining step:

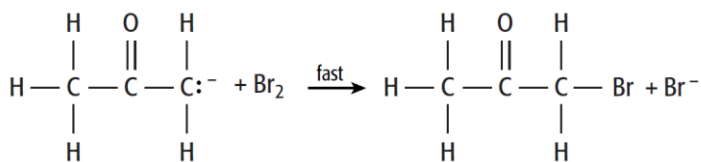
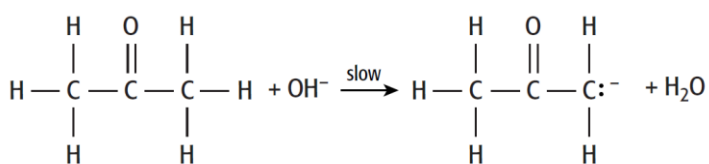
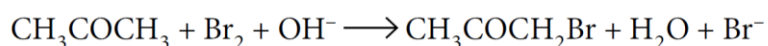


**Figure 22.17** Propanone molecules rapidly accept hydrogen ions to form an intermediate that slowly forms propen-2-ol. This reacts rapidly with iodine to give the products.

- Rate =  $k[\text{CH}_3\text{COCH}_3][\text{H}^+]$
- Where the slow step (rate-determining step) does not involve propanone or hydrogen ion directly, however the intermediate with the formula:



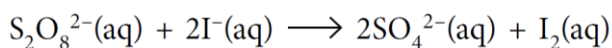
- Is derived from substances that react together to form it, hence propanone and hydrogen ion appear in the rate equation
- E.g. propanone and bromine in alkaline solution:



**Figure 22.19** The reaction mechanism for the bromination of propanone in alkaline conditions.

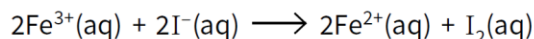
- Rate =  $k[\text{CH}_3\text{COCH}_3][\text{OH}^-]$
- **Catalysis** provides alternative pathway for the reaction with lower activation energy, hence increasing the rate of reaction
- **Homogeneous catalysis** occurs when the catalyst is in the same phase as the reaction mixture

- Often involves changes in oxidation number of the ions involved in catalysis
- The catalytic role of  $\text{Fe}^{3+}$  in the  $\text{I}^-/\text{S}_2\text{O}_8^{2-}$  reaction:

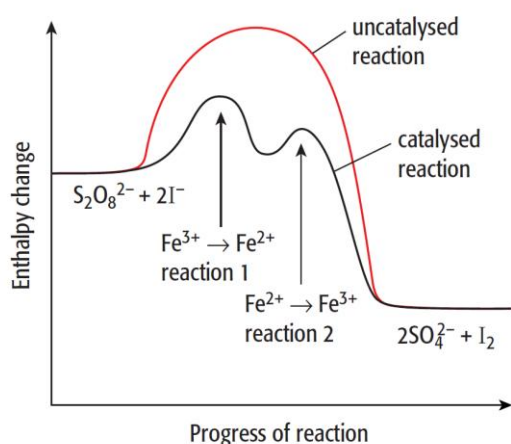
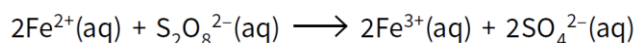


- $\text{Fe}^{3+}(\text{aq})$  catalyses this reaction involving two redox reactions:

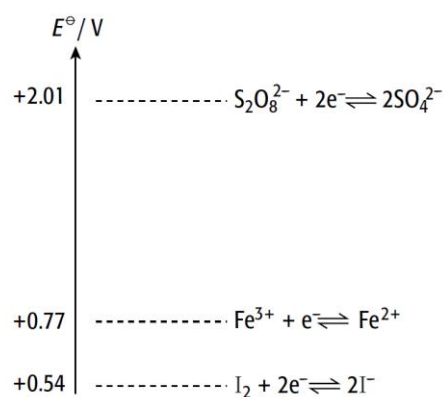
- Reaction 1: reduction of  $\text{Fe}^{3+}$  ions to  $\text{Fe}^{2+}$  ions by  $\text{I}^-$  ions:



- Reaction 2: oxidation of  $\text{Fe}^{2+}$  ions back to  $\text{Fe}^{3+}$  by  $\text{S}_2\text{O}_8^{2-}$  ions:

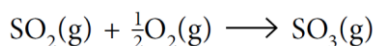


**Figure 22.21** Energy level profiles for the catalysed and uncatalysed reactions of peroxodisulfate ions with iodide ions.

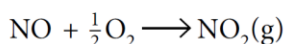
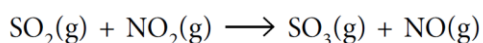


**Figure 22.22** The electrode potential diagram for the catalysis of the reaction  $\text{S}_2\text{O}_8^{2-} + 2\text{I}^- \longrightarrow 2\text{SO}_4^{2-} + \text{I}_2$ .

- The catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide:
  - One of the steps in the formation of acid rain is the oxidation of sulfur dioxide to sulfur trioxide:



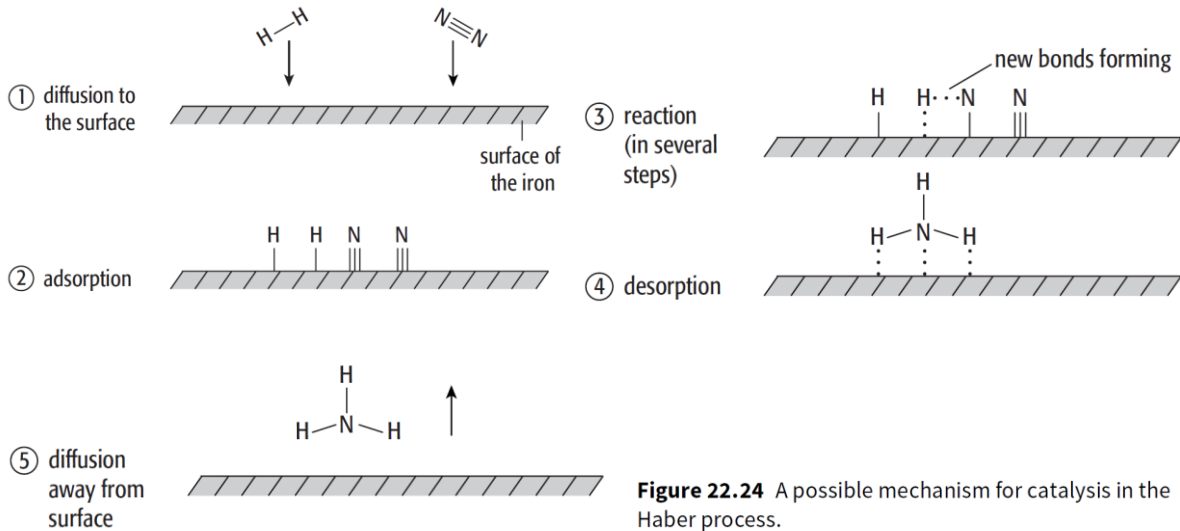
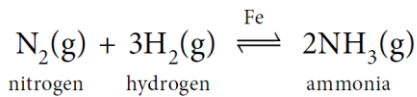
- Catalysed by nitrogen(IV) oxide



- **Heterogeneous catalysis** occurs when the catalyst is in a different phase to the reaction mixture
  - Often involves gaseous molecules reacting at the surface of a solid catalyst
  - Can be explained using the theory of adsorption onto the catalyst's surface
    - Adsorb means to bond to the surface
    - Absorb means to move right into the substance

➤ Iron in the Haber process (Fe catalyst):

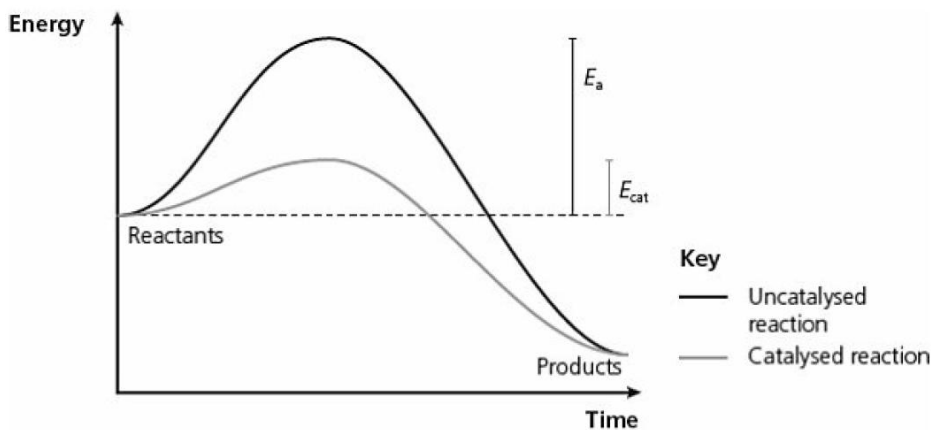
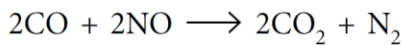
- Diffusion, adsorption, reaction and desorption



**Figure 22.24** A possible mechanism for catalysis in the Haber process.

➤ The catalytic removal of oxides of nitrogen from the exhaust gases of car engines:

- Adsorption, weakening of covalent bonds, formation of new bonds and desorption
- Small beads coated with platinum catalysts



**Figure 8.10** A reaction with and without an enzyme catalyst

- Example questions:

**3** By using iron and its compounds as examples, outline the different modes of action of homogeneous and heterogeneous catalysis.

Choose two examples, and for each example you should

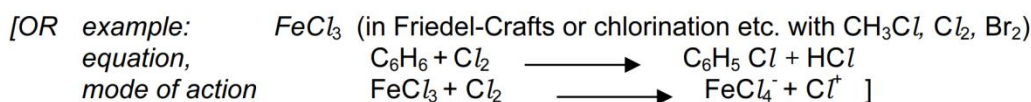
- state what the catalyst is, and whether it is acting as a homogeneous or a heterogeneous catalyst,
- write a balanced equation for the reaction.

.....



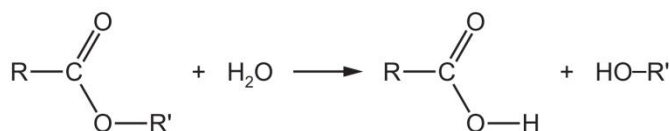
3

- heterogeneous: different phases/states or homogeneous: same phase/state
- (heterogeneous): adsorption onto the surface
- the correct allocation of the terms *heterogeneous* and *homogeneous* to the two exemplar
- example of heterogeneous, e.g.  $\text{Fe}$  (in the Haber process)
- equation, e.g.  $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$
- example of homogeneous, e.g.  $\text{Fe}^{3+}$  (in  $\text{S}_2\text{O}_8^{2-} + \text{I}^-$ )
- equation, e.g.  $\text{S}_2\text{O}_8^{2-} + 2\text{I}^- \longrightarrow 2\text{SO}_4^{2-} + \text{I}_2$
- how catalyst works, e.g.  $\text{Fe}^{3+} + \text{I}^- \longrightarrow \text{Fe}^{2+} + \frac{1}{2}\text{I}_2$



Total = [8]

6 Esterases are enzymes that hydrolyse esters.



Enzymes can be quite specific in the structures of the substrates they act upon. For example, an esterase isolated from the mould *Aspergillus niger* will hydrolyse phenyl ethanoate,  $\text{CH}_3\text{CO}_2\text{C}_6\text{H}_5$ , but not its isomer methyl benzoate,  $\text{C}_6\text{H}_5\text{CO}_2\text{CH}_3$ .

- (a) Outline how enzymes catalyse reactions, and explain their specificity. Use diagrams in your answer where appropriate.

6 (a)

essential mark

M1 the reactants/substrate has a **shape** complementary/**specific** to **active site** – can be awarded from a labelled diagram as below or diagrams showing this specificity clearly

any two of

M2: reactants/substrate binds to/fits into the **active site** of the enzyme

M3: (Interaction with site) causes a specific bond to be weakened, (which breaks) or lowers activation energy

M4: forms an E-S complex

M5: products released from enzyme/active site

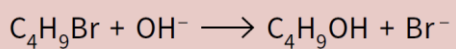
labelled diagrams



3

- Another method of finding the rate of reaction:
  - Sampling followed by titration can be used where small amounts of the reaction mixture are withdrawn by pipette at regular intervals; further reaction in this

sample is prevented or slowed down, e.g. by cooling the sample in ice; the concentration of one of the reactants or products is then determined by titration of the samples; common examples are the formation of an acid and an iodination reaction



(ii) Describe a suitable method for studying the rate of this reaction at a temperature of 40 °C, using the following.

- an electrical conductance meter which measures the electrical conductivity of solutions
  - solutions of known concentrations of 2-chlorobutane in propanone and sodium iodide in propanone
  - stopclock
  - access to standard laboratory equipment
- .....

2(b)(ii)

(Equilibrate) solutions at 40 °C / with a water bath (cannot be after mixing)

mix **known volumes and** start the clock / timing clearly mentioned/implied

measure conductance / conductivity at regular intervals / every measured time [method A]

OR measure the time for conductance to go to zero / a specific value / to be constant [method B]

prepare a curve of conductance vs. time [related to method A]

OR prepare a curve of conductance vs. concentration [related to method A]

OR repeating the experiment at different concentrations [related to method A and B]

any 3 points

3