Cambridge A2 Chemistry

(Code: 9701)

Chapter 22
Reaction kinetics

Factors affecting reaction rate

Why reaction rate is increased when:

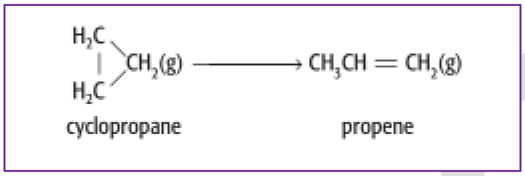
- The concentrations of the reactants are increased
- The temperature is increased
- A catalyst is added to the reaction mixture

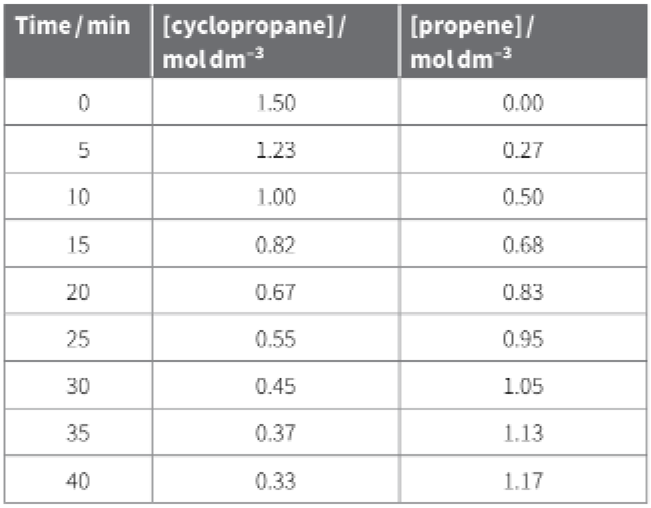
Rate of reaction

Defining rate of reaction

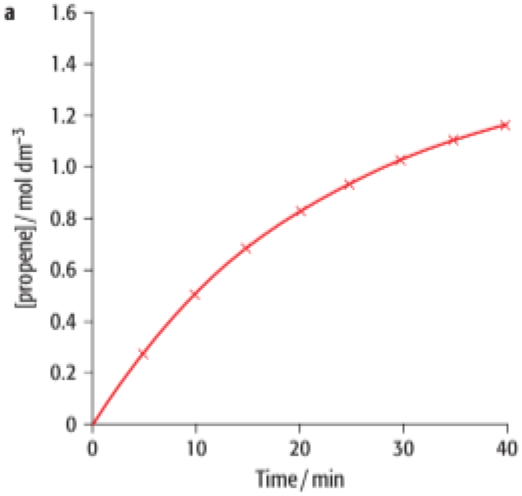
$$\boxed{rate\ of\ reaction\ = \frac{change\ in\ concentration}{time\ taken\ for\ this\ change}}$$

Calculating rate of reaction graphically





Time / min	[cyclopropane] / mol dm^{-3}	[propene] / 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

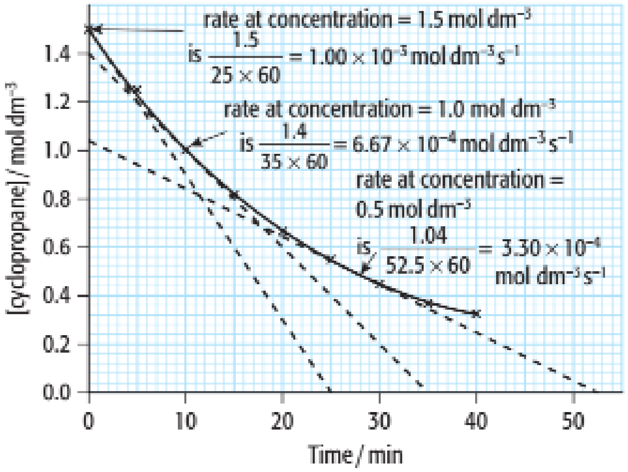


Note:

- we convert the minutes to seconds by multiplying by 60
- the sign of the slope is negative because the reactant concentration is decreasing
- the value of -6.67×10^{-4}moldm^{-3} s^{-1} refers to the rate of change of cyclopropane concentration
- This is the rate of reaction when the cyclopropane concentration is 1.00moldm^{-3}.

Changes in rate as the reaction proceeds

[cyclopropane] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}	$\frac{\text{Rate}}{\text{[cyclopropane]}}$ /s^{-1}
1.50	1.00×10^{-3}	6.67×10^{-4}
1.00	6.67×10^{-4}	6.67×10^{-4}
0.50	3.30×10^{-4}	6.60×10^{-4}



Rate equations

The rate constant and rate equations

$$\boxed{\text{rate of reaction} = k\,[x]}$$

The proportionality constant, k, is called the rate constant. The overall is the rate equation for this particular reaction.

Stoichiometric equation	Rate equation
1 $H_2(g) + I_2(g) \longrightarrow 2HI(g)$	rate = $k[H_2][I_2]$
2 $NO(g) + CO(g) + O_2(g) \longrightarrow NO_2(g) + CO_2(g)$	rate = $k[NO]^2$
3 $2H_2(g) + 2NO(g) \longrightarrow 2H_2O(g) + N_2(g)$	rate = $k[H_2][NO]^2$
4 $BrO_3^-(aq) + 5Br^-(aq) + H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$	rate = $k[BrO_3^-][Br^-][H^+]^2$

Order of reaction

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.

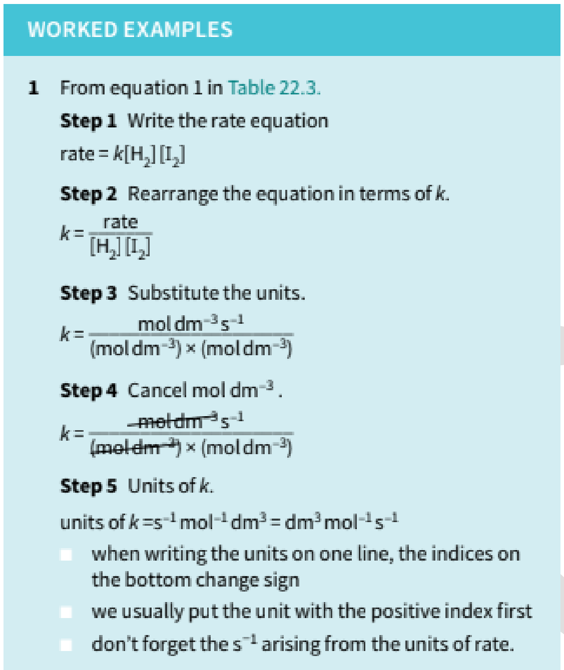
In general terms, for a reaction A + B products, the rate equation can be written in the form:

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

In this equation:

- [A] and [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.

Units of k



WORKED EXAMPLES

1 From equation 1 in Table 22.3.

Step 1 Write the rate equation

rate = $k[H_2][I_2]$

Step 2 Rearrange the equation in terms of k.

$$k = \frac{\text{rate}}{[H_2][I_2]}$$

Step 3 Substitute the units.

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

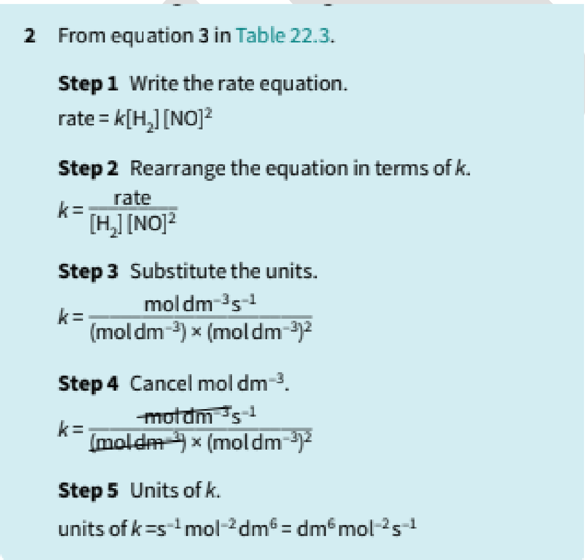
Step 4 Cancel mol dm^{-3}.

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

Step 5 Units of k.

units of k = s^{-1} mol^{-1} dm^{3} = dm^{3} mol^{-1} 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 s^{-1} arising from the units of rate.



2 From equation 3 in Table 22.3.

Step 1 Write the rate equation.

rate = $k[H_2][NO]^2$

Step 2 Rearrange the equation in terms of k.

$$k = \frac{\text{rate}}{[H_2][NO]^2}$$

Step 3 Substitute the units.

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

Step 4 Cancel mol dm^{-3}.

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

Step 5 Units of k.

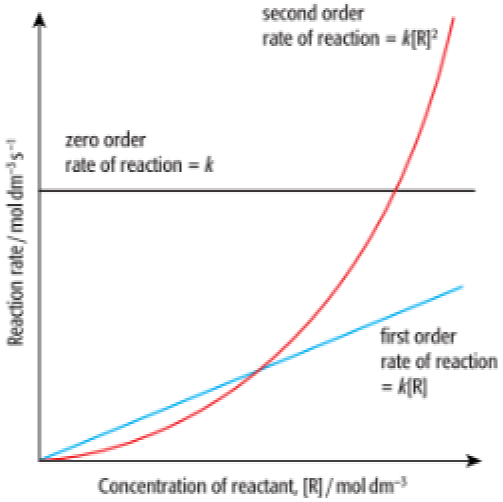
units of k = s^{-1} mol^{-2} dm^{6} = dm^{6} mol^{-2} s^{-1}

Which order of reaction?

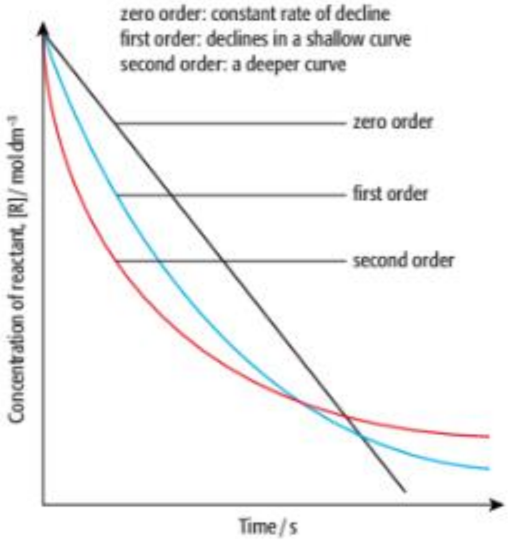
We can identify the order of a reaction in three ways:

- plot a graph of reaction rate against concentration of reactant
- plot a graph of concentration of reactant against time
- Deduce successive half-lives from graphs of concentration against time.

Graphs of reaction rate against concentration

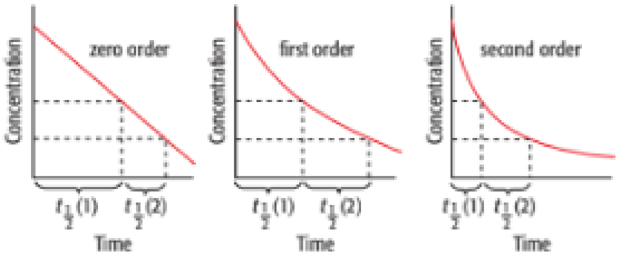


Graphs of concentration of reactant against time



Half-life and reaction rates

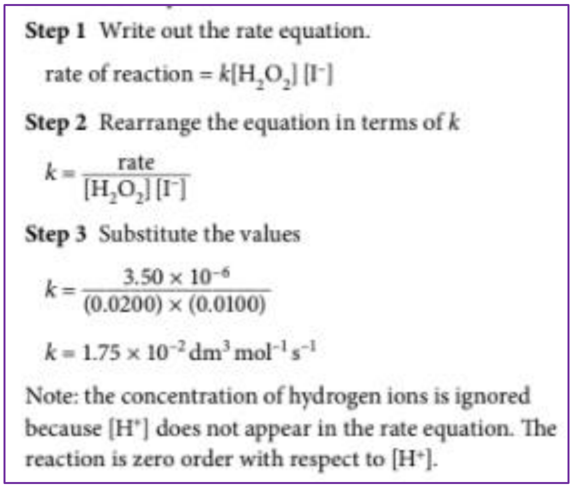
Half-life, $t_{\frac{1}{2}}$, is the time taken for the concentration of a reactant to fall to half of its original value.



1. A zero-order reaction has successive half-lives which decrease with time.
2. A first-order reaction has a half-life which is constant.
3. Second-order reactions have successive half-lives which increase with time. (This also applies to reactions with a higher order for particular reagent but we will not be discussing these.)

Calculations involving the rate constant, k

Calculating k from initial concentrations and initial rate



Step 1 Write out the rate equation.

rate of reaction = $k[H_2O_2][I^-]$

Step 2 Rearrange the equation in terms of k

$$k = \frac{\text{rate}}{[H_2O_2][I^-]}$$

Step 3 Substitute the values

$$k = \frac{3.50 \times 10^{-6}}{(0.0200) \times (0.0100)}$$

$$k = 1.75 \times 10^{-2}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$$

Note: the concentration of hydrogen ions is ignored because $[H^+]$ does not appear in the rate equation. The reaction is zero order with respect to $[H^+]$.

Deducing order of reaction from raw data

Using data from the course of a reaction

Step 1 Plot a graph to show how the concentration of a particular reactant (or product) changes with time.

Step 2 Take tangents at various points along the curve which correspond to particular concentrations of the reactant.

Step 3 Calculate the slope (gradient) at each concentration selected. The rate of reaction is calculated from the slope of the graph.

Step 4 Plot a graph of rate of reaction against concentration.

Using initial rates

The initial rates method is often used when the rate of reaction is slow.

- Carry out several experiments with different known initial concentrations of each reactant.
- Measure the initial rates of reaction by either:

  – taking the tangent of the curve at the start of each experiment or

  – measuring the concentration of a reactant or product soon after the experiment has started.

- For each reactant, plot a graph of initial rate against concentration of that particular reactant.

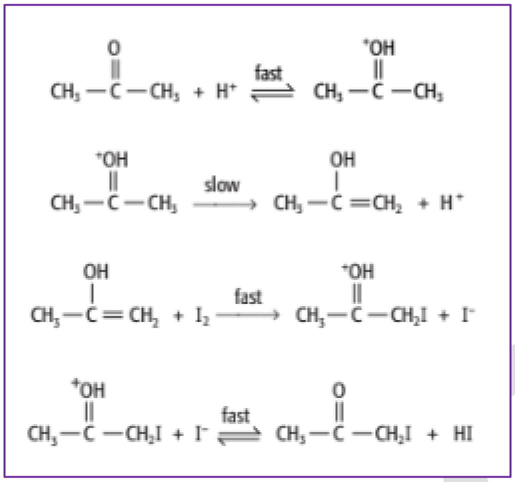
Kinetics and reaction mechanisms

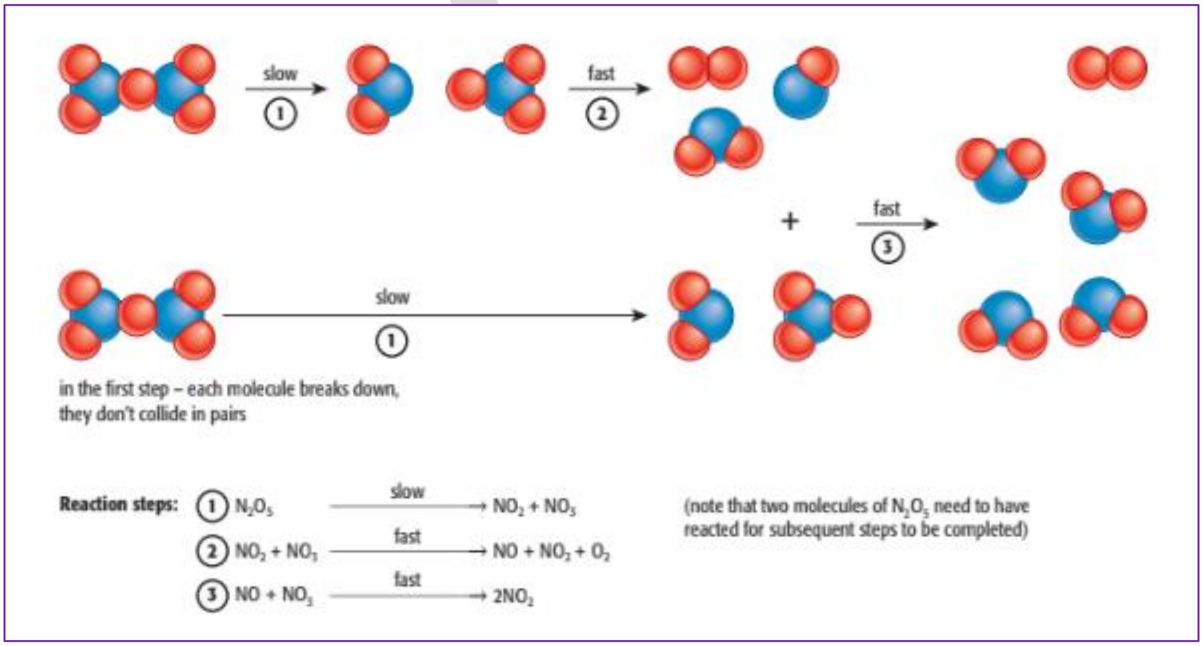
The rate-determining step

- A reactant that appears in the chemical equation may have no affect on reaction rate.
- A substance that is not a reactant in the chemical equation can affect reaction rate.

The overall rate of reaction depends on the slowest step. We call this the rate-determining step.

Verifying possible reaction mechanisms

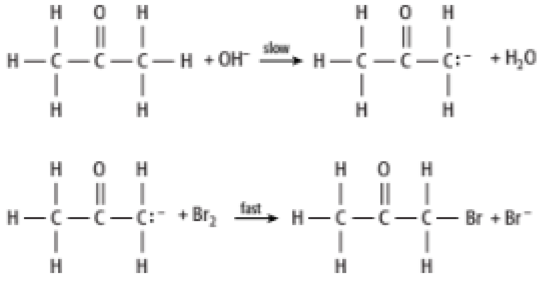




Predicting the order of a reaction from reaction mechanisms

$$CH_3COCH_3 + Br_2 + OH^- \longrightarrow CH_3COCH_2Br + H_2O + Br^-$$

The reaction mechanism is shown in Figure 22.19.



Catalysis

We can divide catalysts into two main classes.

1. Homogeneous catalysis occurs when the catalyst is in the same phase as the reaction mixture. For example: hydrogen ions catalyse the hydrolysis of esters.

$$CH_3COOC_2H_5(aq) + H_2O(l) \overset{H^+(aq)}{\rightleftharpoons} CH_3COOH(aq) + C_2H_5OH(aq)$$

In this reaction the reactants, products and catalyst are all in the aqueous phase.

2. Heterogeneous catalysis occurs when the catalyst is in a different phase to the reaction mixture. For example, the decomposition of aqueous hydrogen peroxide catalysed by manganese(IV) oxide.

$$2H_2O_2(aq) \xrightarrow{MnO_2(s)} 2H_2O(l) + O_2(g)$$

Homogeneous catalysis

The iodine–peroxodisulfate reaction

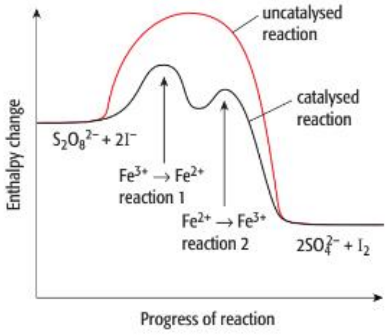


Figure 22.21 Energy level profiles for the catalysed and uncatalysed reactions of peroxodisulfate ions with iodide ions.

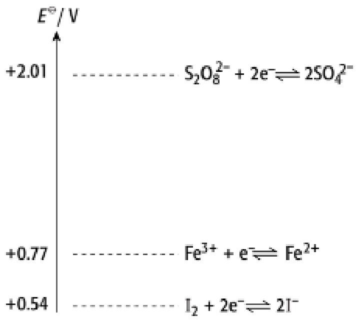


Figure 22.22 The electrode potential diagram for the catalysis of the reaction $S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$.

Oxides of nitrogen and acid rain

One of the steps in the formation of acid rain is the oxidation of sulfur dioxide to sulfur trioxide.

$$SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g)$$

This oxidation is catalysed by a wide variety of mechanisms. Nitrogen(IV) oxide present in the atmosphere from a variety of sources can catalyse the oxidation of sulfur dioxide. The nitrogen(IV) oxide is reformed by reaction with atmospheric oxygen.

$$SO_2(g) + NO_2(g) \rightarrow SO_3(g) + NO(g)$$

$$NO + \frac{1}{2}O_2 \rightarrow NO_2(g)$$

Heterogeneous catalysis

The mechanism of this catalysis can be explained using the theory of adsorption. Chemical adsorption (also called chemisorption) occurs when molecules become bonded to atoms on the surface of a solid.

Adsorb
means to bond to the surface of a substance.

Absorb
means to move right into the substance – rather like a sponge absorbs water.

The stages in adsorption of hydrogen onto nickel are:

- hydrogen gas diffuses to the surface of the nickel
- the hydrogen is physically adsorbed onto the surface – weak van der Waals' forces link the hydrogen molecules to the nickel
- the hydrogen becomes chemically adsorbed onto the surface – this causes stronger bonds to form between the hydrogen and the nickel
- this causes weakening of the hydrogen–hydrogen covalent bond.

Examples of heterogeneous catalysis

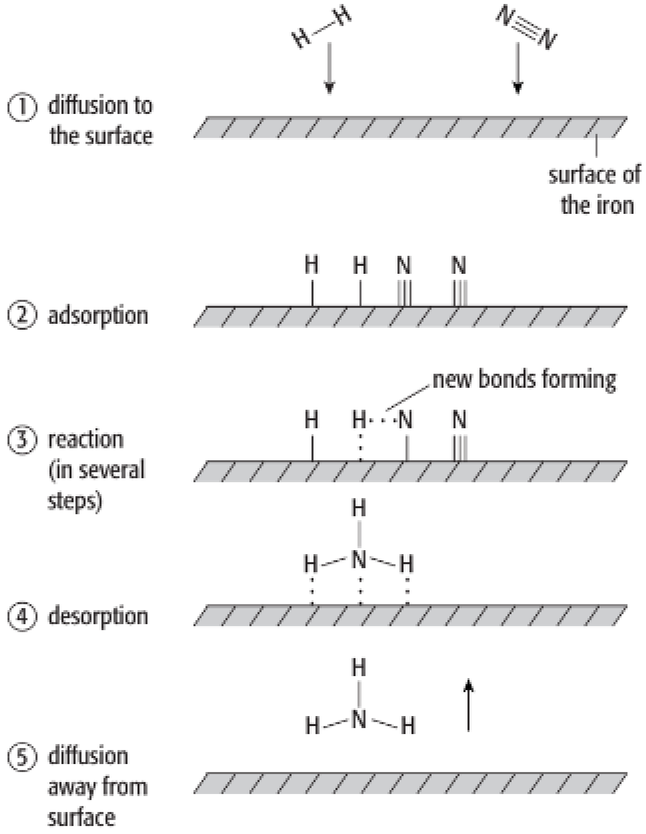
Iron in the Haber process

1. Diffusion: nitrogen gas and hydrogen gas diffuse to the surface of the iron.
2. Adsorption: the reactant molecules are chemically adsorbed onto the surface of the iron. The bonds formed between the reactant molecules and the iron are:

   – strong enough to weaken the covalent bonds within the nitrogen and hydrogen molecules so the atoms can react with each other

   – weak enough to break and allow the products to leave the surface.

3. Reaction: the adsorbed nitrogen and hydrogen atoms react on the surface of the iron to form ammonia.
4. Desorption: the bonds between the ammonia and the surface of the iron weaken and are eventually broken.
5. Diffusion: ammonia diffuses away from the surface of the iron.



Transition elements in catalytic converters

Possible steps in the catalytic process include:

- adsorption of nitrogen oxides and carbon monoxide onto the catalyst surface
- weakening of the covalent bonds within the nitrogen oxides and carbon monoxide
- formation of new bonds between
    - – adjacent nitrogen atoms (to form nitrogen molecules)
    - – carbon monoxide and oxygen atoms to form carbon dioxide
- desorption of nitrogen molecules and carbon dioxide molecules from the surface of the catalyst.

EXCERSISE

1.

a. Fig. 1.1 below shows, for a given temperature T, a Boltzmann distribution of the kinetic energy of the molecules of a mixture of two gases that will react together.
The activation energy for the reaction, E_a, is marked.

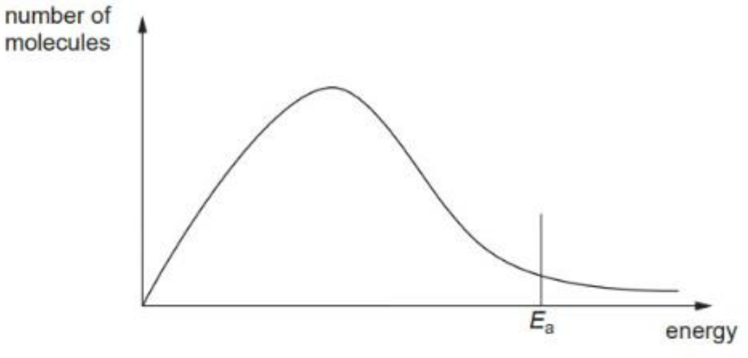


Fig. 1.1

On Fig. 1.1 above,

i. draw a new distribution curve, clearly labelled T_2, for the same mixture of gases at a lower temperature, T_2.

ii. mark clearly, as H, the position of the activation energy of the reaction at the lower temperature, T_2.

b. Explain the meaning of the term activation energy.

c.

i. On the energy axis in Fig. 1.1, mark the position, clearly labelled C, of the activation energy of the reaction when a catalyst is used.

ii. Use your answer to (i) to explain how the use of a catalyst results in reactions occurring at a faster rate.

d. Two reactions involving aqueous NaOH are given below.

$CH_3CHBrCH_3 + NaOH \rightarrow CH_3CH(OH)CH_3 + NaBr$ reaction 1

$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$ reaction 2

The reagents in reaction 1 must be heated together for some time for the reaction to occur. Whereas, reaction 2 is almost instantaneous at room temperature.
Suggest brief explanations why the rates of these two reactions are very different.

2.

a. A platinum-rhodium catalyst used in the reaction forming nitrogen(II) oxide from ammonia.

$$4NH_3\,(g) + 5O_2\,(g) \rightleftharpoons 4NO(g) + 6H_2O\,(g)$$

i. State what is meant by the term heterogeneous catalyst.

ii. Explain why a catalyst has no effect on the yield of the products in the reaction.

b. A group of students were completing a practical, investigating the factors which affect the rate of the following chemical reaction.

$$A\ (s) + B\ (aq) \rightarrow C\ (g)$$

The students collected the gas produced and plotted the graph shown in Fig. 1.1.

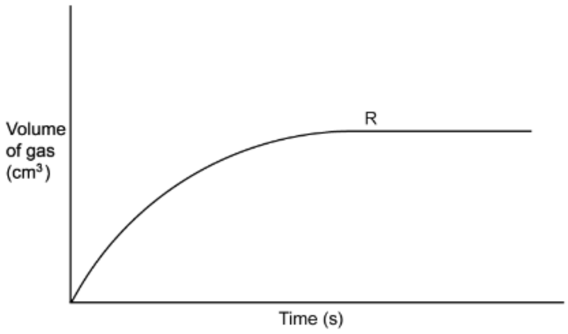


Fig. 1.1

i. State and explain what the letter R represents on the student's graph.
ii. In the original reaction above, the students used 0.5 g of A and 50 cm^3 of 1.0 mol dm^{-3} of B. Sketch a curve on the graph in Fig 1.1 to show how the total volume of gas collected would change if the students still used 0.5 g of A, but used 50 cm^3 of 2.0 mol dm^{-3} of B.

c. Explain why the gradient of the curve in part (b) decreases as the time of the reaction progresses.

d. Another way to increase the rate of reaction is to increase the temperature.
Explain why a small increase in temperature has a large effect on the initial rate of a chemical reaction.

3.

a. This question is about how different factors affect the rate of a chemical reaction.
A reaction between reactant molecules can only occur when collisions between the reactant molecules are effective.
i. Explain what is meant by the term effective collision.
ii. State two factors that could cause an ineffective collision.

b. A student made the following statement about factors that affect the rate of a chemical reaction.
'The rate of a reaction increases with temperature as there are more collisions'
Discuss why this statement is only true to an extent and what other factors need to be considered to fully explain how the rate of a reaction is affected by temperature.

c. Hydrogen and oxygen can react to form water in an exothermic reaction.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

The rate of this reaction depends on the pressure as well as the temperature.
Describe and explain the effect of increasing the pressure on this reaction.

d. If the rate of reaction increases suddenly, an explosion can occur.
A highly exothermic reaction, such as the reaction in (c), is at more risk of exploding than a less exothermic reaction.
Suggest why.

4.

a. Ammonia can be produced by the reaction of nitrogen and hydrogen.

$N_2\,(g) + 3H_2(g)\ 2NH_3\,(g) \qquad \Delta H = -92\ kJ\ mol^{-1}$

The reaction can be catalysed and the activation energy for this catalysed reaction is +109 kJ mol^{-1}

Complete the reaction pathway diagram in Fig. 1.1 for the uncatalysed and the catalysed reaction between nitrogen and hydrogen.

You should label the following:

- Products
- the enthalpy change of reaction, ΔH
- the activation energy of the forward, uncatalysed reaction, E_a
- the activation energy of the forward, catalysed reaction, E_c

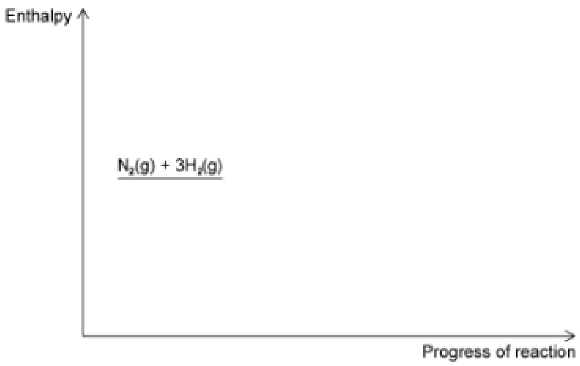


Fig. 1.1

b. Calculate the value of the activation energy of the catalysed decomposition of ammonia into nitrogen and hydrogen.

Show your working.

c. Catalysts, such as iron used in the production of ammonia, increase the rate of reaction. Explain why. Use a labelled Boltzmann distribution to explain your answer.

Platinum is used as a catalyst in catalytic converters which are fitted to vehicle exhaust systems to remove nitrogen oxide from the exhaust gases.

$2NO(g) + 2CO\,(g) \rightarrow N_2\,(g) + 2CO_2(g)$

i. State the type of catalyst that platinum is in a catalytic converter

ii. Explain, using oxidation numbers, if nitrogen is being oxidised or reduced in this reaction.

5.

a. Reaction rates can be affected by a range of factors including changes in pressure and temperature.

Fig 1.1

- i. Sketch one Maxwell-Boltzmann distribution labelled T, and a second Maxwell-Boltzmann distribution at a higher temperature labelled T_2.
- ii. State how the mean energy of the molecules would be at T_2 compared to T_1.

b. Hydrogen iodide can be used in the manufacturing of pharmaceuticals and can be broken down back into its elements in standard form, iodine and hydrogen.

$2HI(g) \rightarrow H_2(g) + I2(g) \qquad \Delta H = -52 \text{ kJ mol}^{-1}$

The activation energy when uncatalysed is +183 kJ mol-1 and when catalysed with gold it is +105 kJ mol^{-1}.

- i. Sketch a reaction profile for the reaction, including the curves for the activation energies for both the catalysed and uncatalysed reactions.
- ii. Calculate the activation energy for the reverse reaction in both the uncatalysed and catalysed reactions.
- iii. Explain why increasing the concentration of hydrogen iodide gas results in a faster reaction rate.

c. Catalysts are often used in industrial processes and can be used in a variety of forms.

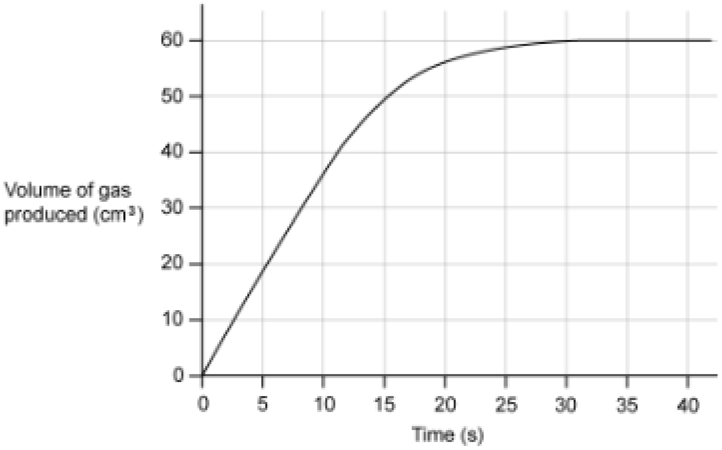
- i. Explain why it is likely that the solid gold catalyst was used in powder form to catalyse the reaction mentioned in part (c).
- ii. Gold is a heterogeneous catalyst used in the formation of hydrogen iodide. State the difference between a homogenous and heterogenous catalyst.
- iii. State how, if at all, the area under the curve of a Maxwell-Boltzmann distribution curve, changes as a catalyst is introduced without changing the temperature or the total number of molecules.

d. The Contact process is an important industrial process, contributing to the production of sulfuric acid. In the Contact process, solid vanadium (V) oxide, a heterogeneous catalyst, is used to make sulfur trioxide from sulfur dioxide and oxygen. This process is reversible.

- i. Write a balanced symbol equation for this reaction. Include state symbols in your
- ii. Explain why the use of the catalyst in the Contact process, reduces energy demand and benefits the environment.

6.

a. 0.5 g of magnesium reacts with 50 cm3 of 0.01 moldm-3 nitric acid. Magnesium is in excess. A graph monitoring the volume of hydrogen gas produced is shown below:



i. Calculate the mean rate of reaction over the first 15 seconds of the reaction

ii. Calculate the actual rate of reaction at 15 seconds

iii. Explain the difference in values for rate

b. Compare the expected rate and progress of the reaction if 25 cm^3 of 0.2 mol dm^{-3} nitric acid was used instead of 50 cm^3 of 0.1 mol dm^{-3} nitric acid.

c. Suggest one change to the reaction that could be made to produce more hydrogen gas in total and explain your choice.

d. Suggest why it is often better to study a slower reaction instead of a faster one.

7.

a. A Maxwell-Boltzmann distribution curve is shown below in Fig 3.1

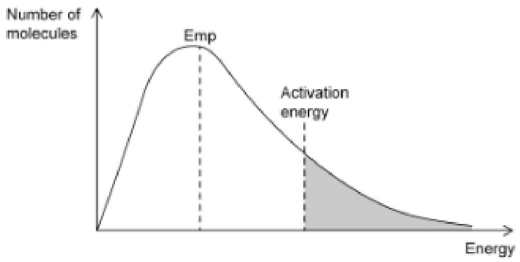


Fig 3.1

For the changes detailed in part (i) and (ii) state and explain the effect the change would have on:

- The area under the curve
- The value of the most probable energy of the molecules, E_{mp}
- The proportion of molecules with greater than or equal to E_a

i. The temperature of the original reaction is increased, but no other changes are made.

ii. A catalyst is added to the original reaction mixture, but no other changes are made.

b. A chemist performed a reaction at three different temperatures, 100K, 300 K and 700 K as shown by the Maxwell-Boltzmann distribution graph in Fig 3.2.

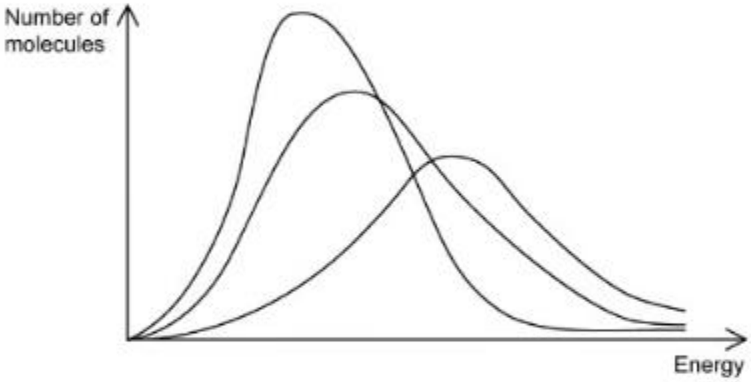


Fig 3.2

i. Label each curve in Fig 3.2 ith the correct temperature values, 100 K, 300 K and 700K.

ii. Consider the following statement, 'All reacting molecules have higher kinetic energy at 700 K than they do at 300 K'.
State whether you agree this statement is correct and justify your reasons.

c. Hydrogen will react with chlorine to form the hydrogen halide, hydrogen chloride, a colourless gas.

$$H_2(g) + Cl_2(g) \rightarrow 2HCl\ (g)$$

i. Give one reason why most collisions between hydrogen and chlorine molecules do not lead to the formation of hydrogen chloride.

ii. Apart from changing the temperature, state and explain two ways of speeding up the formation of hydrogen chloride.