Week 38

A-Level Chemistry

Homework bundle for this week

本周作业合集

exercises.lol

Contents 目录

A-Level Chemistry Name: _____ Score: _____

1. The rate equation of a reaction:
   - ☐ can only be found by experiment, not from the balanced equation
   - ☐ is read straight off the balanced equation
   - ☐ never includes a rate constant
   - ☐ is always second order
2. A reaction whose half-life stays the same as it proceeds is:
   - ☐ first order
   - ☐ zero order
   - ☐ second order
   - ☐ not happening
3. The rate-determining step is:
   - ☐ the slowest step, which controls the overall rate
   - ☐ the fastest step
   - ☐ always the first step
   - ☐ the step with no intermediate
4. A heterogeneous catalyst:
   - ☐ is in a different physical state from the reactants and works by adsorption and desorption
   - ☐ is in the same state as the reactants
   - ☐ is used up permanently
   - ☐ changes the enthalpy change
5. If doubling [A] doubles the rate, the order with respect to A is:
   - ☐ 1 (first order)
   - ☐ 0 (zero order)
   - ☐ 2 (second order)
   - ☐ 3
6. A first-order reaction has a half-life of 100 s. What is k? ($k = 0.693/t_{½}$)

   _____

7. A constant half-life can be used to identify a first-order reaction.

   ☐ True ☐ False

8. A heterogeneous catalyst is in a different physical state from the reactants.

   ☐ True ☐ False

9. The power to which a reactant's concentration is raised in the rate equation is its _____.

   _____

10. A first-order reaction has a constant half-life.

    ☐ True ☐ False

26. Reaction kinetics

Answers · 答案

A-Level Chemistry

1. **can only be found by experiment, not from the balanced equation**

   Orders must be measured experimentally; they cannot be deduced from the stoichiometric equation.

2. **first order**

   A constant half-life (independent of concentration) is the signature of a first-order reaction.

3. **the slowest step, which controls the overall rate**

   The slowest step is the bottleneck, so it determines the overall rate.

4. **is in a different physical state from the reactants and works by adsorption and desorption**

   Heterogeneous = different state (e.g. solid + gases); reactants adsorb, react, then products desorb.

5. **1 (first order)**

   Rate $\propto [A]^1$, so doubling [A] doubles the rate — first order.

6. **0.00693**

   k = 0.693 / 100 = 0.00693 (per second).

7. **True**

   Only first-order reactions have a half-life that is independent of the concentration.

8. **True**

   e.g. a solid catalyst with gaseous reactants.

9. **order**

   The orders are found experimentally.

10. **True**

    The half-life is independent of concentration.

A-LEVEL CHEMISTRY • EXERCISE SHEET

26.1 Rate equations, orders of reaction and rate constants

Name: _____ Class: _____ Date: _____ **Total: 31 marks**

KEY WORDS rate equation 速率方程 • initial rate 初始速率 • rate constant 速率常数 • order of reaction 反应级数 • half-life 半衰期

Objective

Build the skills to answer exam questions on **rate equations** 速率方程 — **order of reaction** 反应级数, the **rate constant** 速率常数, **half-life** 半衰期, and the **rate-determining step** 决速步.

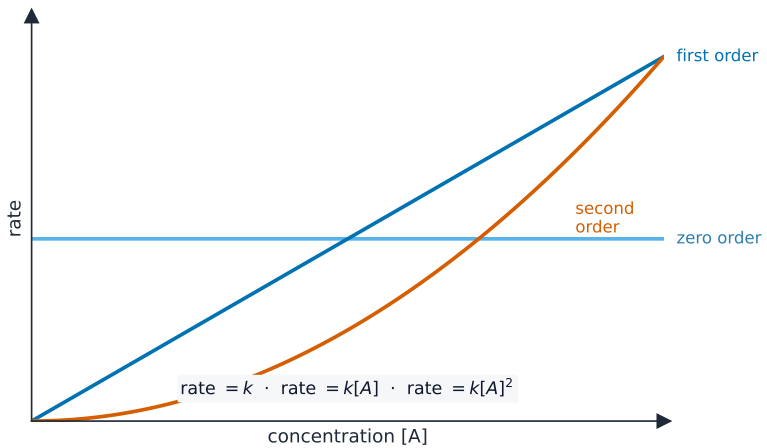
You must be able to:

- deduce orders from initial-rates data or concentration–time graphs and construct a rate equation
- use first-order half-life and calculate the rate constant
- deduce a rate equation from a mechanism and identify the rate-determining step

1 Worked examples

■ Rate equation and order

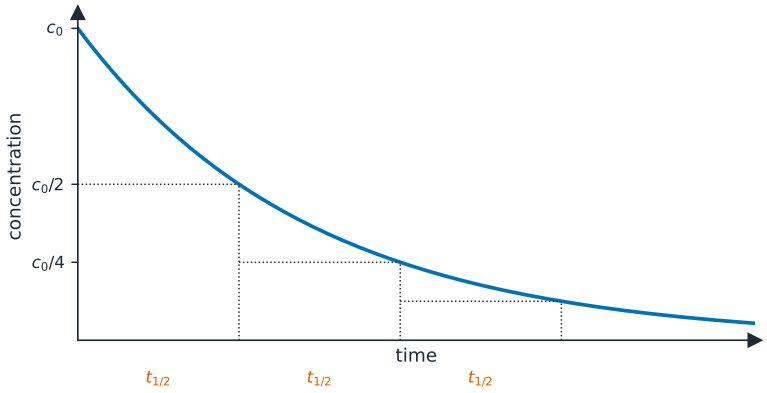
rate = $k[\mathrm{A}]^m[\mathrm{B}]^n$ — found only by **experiment**. Order m/n = 0, 1 or 2; overall order = $m + n$.



Deduce the order from the shape of the graphs, or from initial-rates data

Initial rates: if doubling [A] doubles the rate → 1st order; if it quadruples → 2nd order; no change → 0 order.

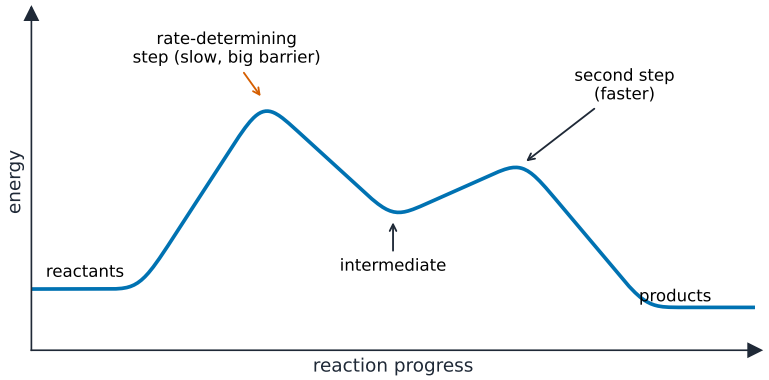
■ Half-life and rate constant



$$t_{1/2} = \frac{\ln 2}{k} \quad \text{(constant for 1st order)}$$

*A first-order reaction has a **constant** half-life (independent of concentration):* $k = 0.693/t_{1/2}$

Mechanism and rate-determining step



rate-determining step = highest E_a barrier (slowest elementary step)

*The rate equation reflects the species in the **rate-determining (slowest) step**; an intermediate is made then used up*

Finding the orders, and what each graph tells you

The rate equation is rate $= k[\mathrm{A}]^m[\mathrm{B}]^n$, where m and n are the **orders** with respect to each reactant. They are found **experimentally** — never from the stoichiometric equation. The **overall order** is $m + n$, and it fixes the units of k:

Overall order	Units of k
0	$\mathrm{mol\ dm^{-3}\ s^{-1}}$
1	$\mathrm{s^{-1}}$
2	$\mathrm{mol^{-1}\ dm^{3}\ s^{-1}}$
3	$\mathrm{mol^{-2}\ dm^{6}\ s^{-1}}$

Derive them rather than memorising: rearrange the rate equation for k and cancel.

From initial-rate data. Compare two experiments in which only ONE concentration changes:

- concentration $\times 2$, rate unchanged $\rightarrow$ **zero order**;
- concentration $\times 2$, rate $\times 2$ $\rightarrow$ **first order**;
- concentration $\times 2$, rate $\times 4$ $\rightarrow$ **second order**.

From graphs, which the exam asks you to recognise:

Graph	Zero order	First order	Second order
concentration against time	straight line, constant gradient	curve with a **constant half-life**	curve, half-life doubles each time
rate against concentration	horizontal line	straight line through the origin	upward curve

The **constant half-life** is the single most useful signal: measure $t_{1/2}$ from the first half of the decay and again from the next, and if they agree the reaction is first order in that reactant.

Worked example. In three experiments, doubling [A] doubles the rate; tripling [B] multiplies the rate by nine. Give the rate equation, the overall order and the units of k.

1. [A]: rate $\propto [\mathrm{A}]^1$, so first order.
2. [B]: $3^n = 9$, so $n = 2$, second order.
3. rate $= k[\mathrm{A}][\mathrm{B}]^2$; overall order $= 3$.
4. $k = \dfrac{\text{rate}}{[\mathrm{A}][\mathrm{B}]^2} = \dfrac{\mathrm{mol\ dm^{-3}\ s^{-1}}}{(\mathrm{mol\ dm^{-3}})^3} = \mathrm{mol^{-2}\ dm^{6}\ s^{-1}}$.

The rate-determining step. The orders give the composition of the slowest step: an order of 1 in A and 2 in B means the rate-determining step involves one A and two B. A species that appears in the equation but NOT in the rate equation enters after the rate-determining step — a catalyst, or a fast subsequent step.

2 Practice

2.1 State what is meant by the **overall order** of a reaction. [1]

2.2 State how the half-life of a first-order reaction changes as the reaction proceeds. [1]

2.3 State the units of k for a reaction that is first order overall, and show how you obtained them. [2]

2.4 A concentration–time graph is a straight line. State the order and explain how you know. [2]

2.5 Explain why the orders cannot be deduced from the stoichiometric equation. [2]

3 Exam-style questions

3.1 A reaction is first order in A and second order in B. Its overall order is: [1]

- **A** 1
- **B** 2
- **C** 3
- **D** 0

3.2 A first-order reaction has a half-life of 50 s. Its rate constant is ($k = 0.693/t_{1/2}$): [1]

- **A** 0.014 s^{-1}
- **B** 0.0139 s^{-1}
- **C** 36 s^{-1}
- **D** 50 s^{-1}

3.3 Experiment data for A + B → products:

[A]	[B]	initial rate
0.10	0.10	2.0×10^{-3}
0.20	0.10	4.0×10^{-3}
0.20	0.20	1.6×10^{-2}

(a) Deduce the order with respect to A and to B. [2]

(b) Write the rate equation and calculate the rate constant k (with units). [3]

3.4 The rate equation for a reaction is rate = k[X]. A proposed mechanism has two steps. State which step must be rate-determining and why. [2]

3.5 The reaction P + 2Q → R was investigated at constant temperature. The initial rates are shown.

experiment	[P] / mol dm^{-3}	[Q] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.10	0.10	2.0×10^{-4}
2	0.20	0.10	4.0×10^{-4}
3	0.20	0.30	3.6×10^{-3}

(a) Deduce the order with respect to P, showing which experiments you used. [2]

(b) Deduce the order with respect to Q, showing your reasoning. [2]

(c) Write the rate equation and state the overall order. [2]

(d) Calculate the value of k and give its units. [3]

(e) The accepted mechanism has a rate-determining step involving one P and two Q. Explain how your rate equation supports this. [2]

(f) A concentration–time graph for a different reactant, S, shows successive half-lives of 40 s, 40 s and 41 s. Deduce the order with respect to S and explain your reasoning. [3]

Solutions

2.1 the sum of the orders with respect to each reactant ($m + n$).

2.2 it stays constant (independent of concentration).

2.3 Rearranging, $k = \dfrac{\text{rate}}{[\text{A}]}$, so the units are $\dfrac{\text{mol dm}^{-3}\,\text{s}^{-1}}{\text{mol dm}^{-3}} = \text{s}^{-1}$.

2.4 Zero order; the rate is independent of concentration, so the concentration falls at a constant rate and the graph has a constant gradient.

2.5 The orders depend on the mechanism, specifically on the species in the rate-determining step; the stoichiometric equation only gives the overall ratio of reactants to products, and says nothing about the steps.

3.1 C. Overall order = 1 + 2 = 3.

3.2 B. $k = 0.693/50 = 0.0139\ \text{s}^{-1}$.

3.3 (a) A: doubling [A] (rows 1→2) doubles the rate → first order; B: doubling [B] (rows 2→3) makes the rate ×4 → second order.
(b) rate = $k[\text{A}][\text{B}]^2$; $k = \dfrac{2.0 \times 10^{-3}}{(0.10)(0.10)^2} = 2.0\ \text{mol}^{-2}\text{dm}^6\text{s}^{-1}$.

3.4 the first step (or whichever contains only X) must be rate-determining; because only X appears in the rate equation, so the slow step involves X.

3.5 (a) Experiments 1 and 2: [Q] is constant, [P] doubles and the rate doubles; so the reaction is first order in P.
(b) Experiments 2 and 3: [P] is constant, [Q] trebles and the rate rises by a factor of 9; since $3^2 = 9$, the reaction is second order in Q.
(c) rate = $k[\text{P}][\text{Q}]^2$; overall order 3.
(d) Using experiment 1: $k = \dfrac{2.0 \times 10^{-4}}{(0.10)(0.10)^2} = 2.0$; units $\text{mol}^{-2}\,\text{dm}^6\,\text{s}^{-1}$.
(e) The rate equation is first order in P and second order in Q, and the orders give the number of each species in the rate-determining step, so one P and two Q is exactly what the equation predicts.
(f) First order in S; the half-life is constant within experimental error, and a constant half-life is the characteristic of a first-order decay.

3 **(a)** Solid manganese(IV) oxide, MnO_2, catalyses the decomposition of hydrogen peroxide.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

State the type of catalysis for this reaction. Explain your answer.

.....

..... [1]

(b) Hydrogen peroxide reacts with iodide ions in acidic conditions as shown.

$$H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$$

The initial rate of this reaction is investigated with different concentrations of H_2O_2, I^- and H^+. The results obtained are shown in Table 3.1.

Table 3.1

experiment	$[H_2O_2]$ / mol dm^{-3}	$[I^-]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.0450	0.0300	0.0125	2.42×10^{-3}
2	0.0225	0.0600	0.0125	2.42×10^{-3}
3	0.0225	0.120	0.0125	4.84×10^{-3}
4	0.0450	0.120	0.0500	9.68×10^{-3}

(i) Use the information in Table 3.1 to deduce the rate equation for this reaction.

Explain your reasoning.

.....

.....

.....

.....

.....

.....

..... [4]

(ii) Use your rate equation from **(b)(i)** and the data from Experiment 1 to calculate the rate constant, *k*, for this reaction. Include the units of *k*.

k = ... units ..... [2]

(c) The rate of the thermal decomposition of azomethane, $CH_3N{=}NCH_3$, is investigated.

$$CH_3N{=}NCH_3 \rightarrow N_2 + C_2H_6$$

Fig. 3.1 shows the results obtained. The reaction is first order with respect to $CH_3N{=}NCH_3$.

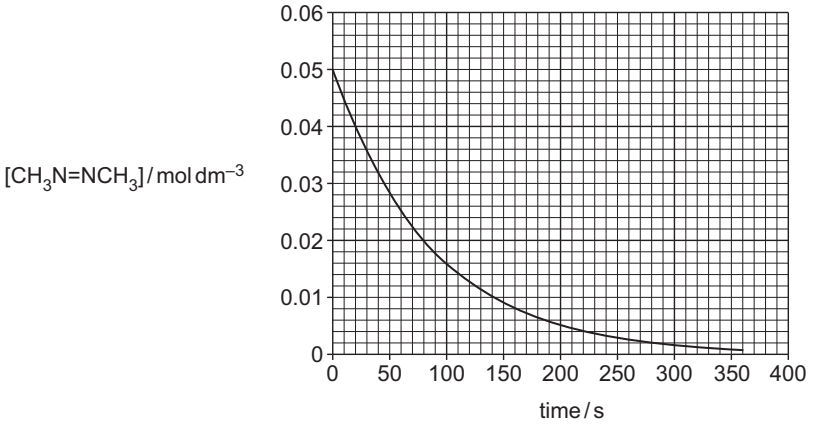


Fig. 3.1

(i) Use Fig. 3.1 to calculate **two** half-lives, $t_{\frac{1}{2}}$, to show that the reaction is first order.

.....

.....

.....

..... [2]

(ii) Use your answer to **(c)(i)** to calculate the rate constant, *k*, for the decomposition of azomethane.

k = ... s^{-1} [1]

(d) Describe the effect of increasing temperature on the rate constant and on the rate of a reaction.

.....

.....

..... [1]

[Total: 11]

2 Ethanal, CH_3CHO, reacts with nitrogen dioxide, NO_2. The products of the first step of this reaction are a $CH_3\dot{C}{=}O$ radical and a molecule of nitrous acid, HNO_2.

$$CH_3CHO + NO_2 \rightarrow CH_3\dot{C}{=}O + HNO_2$$

(a) (i) Use **two** words to complete the sentence.

This reaction involves .... of the single covalent bond between a hydrogen atom and a carbon atom in CH_3CHO.

[1]

(ii) The hydrogen atom mentioned in **(a)(i)** forms a covalent bond with one of the oxygen atoms of an NO_2 molecule. An NO_2 molecule has a single, unpaired electron on the nitrogen atom. All electrons are paired in an HNO_2 molecule.

Draw dot-and-cross diagrams of NO_2 and HNO_2 in the boxes. Show outer shell electrons only.

NO_2

HNO_2

[1]

(iii) Use VSEPR theory to predict the bond angle at the nitrogen atom in an HNO_2 molecule.

bond angle = ... [1]

(b) The rate equation for the reaction between CH_3CHO and NO_2 is shown.

$$\text{rate} = k[CH_3CHO][NO_2]$$

Under certain conditions, when the concentrations of both CH_3CHO and NO_2 are $0.200\,\text{mol dm}^{-3}$, the rate of the reaction is $1.53 \times 10^{-4}\,\text{mol dm}^{-3}\,\text{s}^{-1}$.

Calculate the value of the rate constant, k, under these conditions. Give the units of k.

k = ... units ..... [2]

(c) The reaction mixture described in **(b)** is monitored over a period of time.

Predict whether the graph of $[NO_2]$ against time shows a constant half-life.

Explain your answer.

prediction .....

explanation .....

.....

[1]

(d) NO_2 also reacts with ozone, O_3.

The rate equation is shown.

$$\text{rate} = k_1[NO_2]$$

Under certain conditions, the value of k_1 is $0.0848\,\text{s}^{-1}$.

The reaction has a constant half-life under these conditions.

Calculate the half-life in seconds.

half-life = ... s [1]

(e) NO_2 is present in the exhaust gases of cars. It can react with carbon monoxide, CO, on the surface of a heterogeneous catalyst in the car's catalytic converter.

Describe the mode of action of this heterogeneous catalyst.

.....

.....

.....

.....

.....

..... [2]

[Total: 9]

4 **(a)** Nitrogen monoxide, NO, reacts with hydrogen, as shown in reaction 3.

reaction 3 $2NO + 2H_2 \rightarrow N_2 + 2H_2O$

(i) The rate equation for reaction 3 is shown.

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

Complete Table 4.1.

Table 4.1

the order of reaction with respect to $[H_2]$	
the order of reaction with respect to [NO]	
the overall order of the reaction	

[1]

(ii) Predict how the initial rate for reaction 3 changes when the concentration of NO is halved.

..... [1]

(iii) Predict how the initial rate for reaction 3 changes when the concentrations of NO and H_2 are both increased **three** times.

..... [1]

(iv) Suggest why reaction 3 is unlikely to proceed by a mechanism involving only a single step.

.....

..... [1]

(v) Suggest equations for the **three** steps of the reaction mechanism for reaction 3.

Each step involves a reaction between **two** molecules.

step 1 ..... $\rightarrow$ .....

step 2 ..... + ... $\rightarrow N_2O +$ .....

step 3 $N_2O +$ ..... $\rightarrow$ ..... + ...

[2]

(vi) Suggest the role of N_2O in this mechanism.

Explain your reasoning.

.....

.... [1]

(b) Iodine, I_2, reacts with thiosulfate ions, $S_2O_3^{2-}$, as shown in reaction 4.

reaction 4 $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

Reaction 4 is carried out in the presence of a large excess of I_2. Under these conditions, the reaction is first order with respect to $[S_2O_3^{2-}]$ and zero order with respect to $[I_2]$.

The half-life, $t_{\frac{1}{2}}$, for reaction 4 is 720 s under certain conditions.

Calculate the value of the rate constant, k, for reaction 4. Include the units of k.

k = ... units ..... [1]

(c) The reaction between iodide ions, $I^-(aq)$, and peroxydisulfate ions, $S_2O_8^{2-}(aq)$, is catalysed by $Co^{3+}(aq)$. The mechanism is similar to the mechanism of this reaction when $Fe^{3+}(aq)$ is used as the catalyst.

(i) State the type of catalysis that occurs in this reaction.

Explain your reasoning.

.....

..... [1]

(ii) Write **two** equations to show how $Co^{3+}(aq)$ catalyses this reaction.

equation 1 .....

equation 2 .....

[2]

(iii) Suggest why this reaction is slow in the absence of $Co^{3+}(aq)$.

.....

..... [1]

[Total: 12]

2 A student uses the following method to investigate the kinetics of the reaction between iodine and tin to produce tin(IV) iodide, SnI_4.

step 1 Rinse a block of tin with distilled water and then rinse it with propanone.

step 2 Place 50 cm^3 of a 0.400 mol dm^{-3} solution of iodine dissolved in methylbenzene in a 100 cm^3 beaker.

step 3 Suspend the block of tin from a three decimal place balance as shown in Fig. 2.1. Start a timer.

step 4 Record the balance reading every 100 seconds.

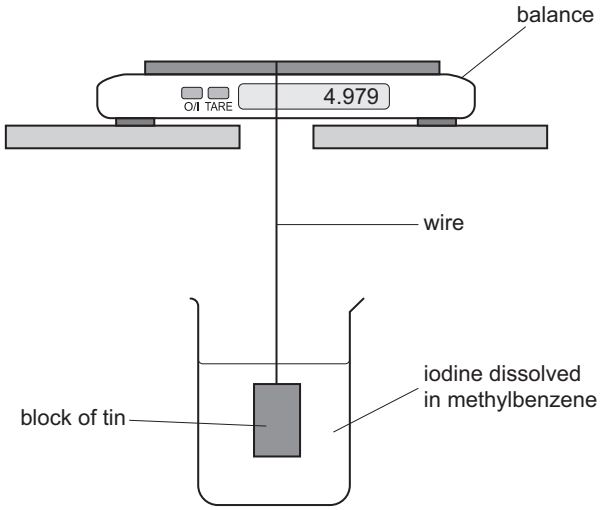


Fig. 2.1

(a) (i) Suggest why the student rinses the block of tin with propanone after rinsing it with distilled water in step 1.

.....

..... [1]

(ii) Suggest why water is **not** used as the solvent for iodine.

.....

..... [1]

(iii) Suggest why a three decimal place balance is more suitable than a two decimal place balance for this experiment.

..... [1]

(iv) Suggest a control experiment that could be used to verify that the loss in mass of tin is caused by reaction with iodine and **not** any other factor.

.....

..... [1]

(b) The student's results are shown in Table 2.1.

Complete Table 2.1.

Table 2.1

time / s	balance reading / g	total mass of tin reacted / g
0	4.979	0.000
100	4.910	
200	4.859	
300	4.761	
400	4.688	
500	4.620	

[1]

(c) (i) Use the results from Table 2.1 to plot a graph on the grid in Fig. 2.2 to show the relationship between total mass of tin reacted and time.

Use a cross (×) to plot each data point. Draw a straight line of best fit.

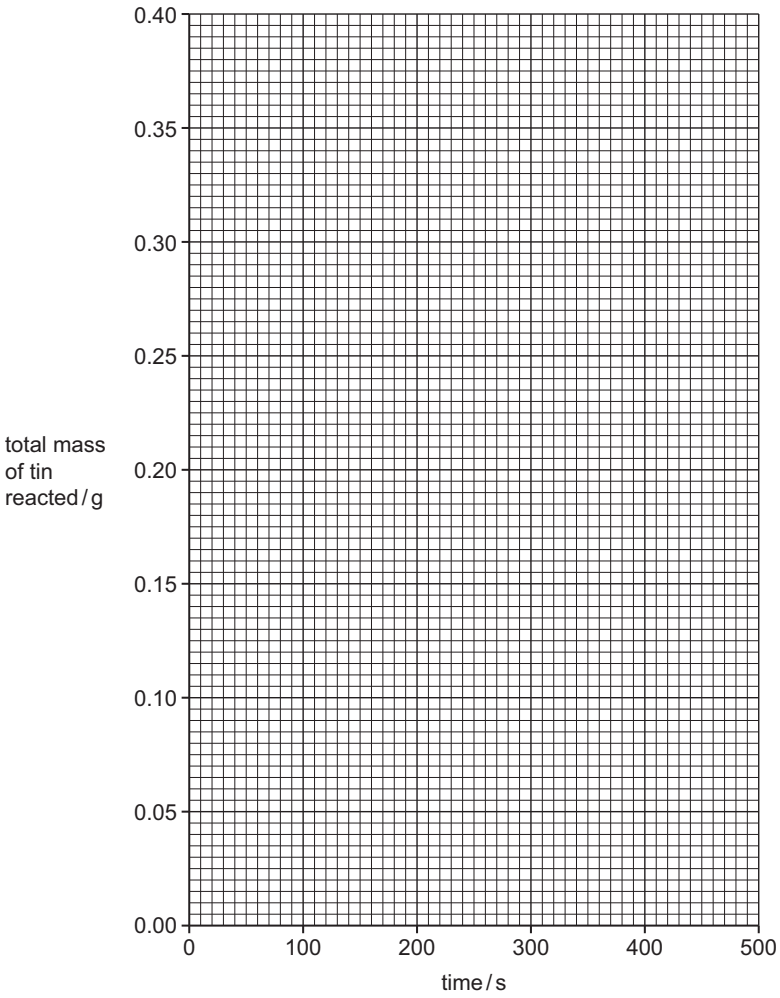


Fig. 2.2

[2]

(ii) Circle the point on the graph in Fig. 2.2 that you consider to be most anomalous.

Suggest **one** reason why this anomaly may have occurred during this experimental procedure.

Assume all measurements of mass are accurate.

.....

.... [1]

(d) Use your graph in Fig. 2.2 to determine the gradient of the line of best fit.

State the coordinates of both points you used in your calculation. These must be selected from your line of best fit.

Give your gradient to **three** significant figures.

coordinates 1 ..... coordinates 2 .....

gradient = ...
[2]

(e) Another student makes various concentrations of solutions of iodine dissolved in methylbenzene by dilution of the 0.400 mol dm^{-3} I_2 solution.

The student repeats the experiment at a different temperature using these solutions.

Table 2.2

volume of 0.400 mol dm^{-3} I_2 solution used / cm^3	volume of methylbenzene used / cm^3	$[I_2]$ / mol dm^{-3}	relative rate of reaction
100.0	0.0	0.400	4.76
		0.300	3.57
		0.200	2.35
		0.100	1.15

(i) Complete Table 2.2 by adding the volumes of solutions that are mixed to make 100.0 cm^3 of a solution of iodine dissolved in methylbenzene for each required concentration.

[1]

(ii) Identify the independent variable in this experiment.

..... [1]

(iii) The student concludes that the rate equation for the reaction between iodine and tin is as follows.

$$\text{rate} = k\,[I_2]^2$$

State whether the results support the student's conclusion.

Explain your answer using values from Table 2.2.

.....

.....

.....

.....

.....

..... [2]

[Total: 14]

Important values, constants and standards

molar gas constant	$R = 8.31\,\text{J K}^{-1}\,\text{mol}^{-1}$
Faraday constant	$F = 9.65 \times 10^4\,\text{C mol}^{-1}$
Avogadro constant	$L = 6.02 \times 10^{23}\,\text{mol}^{-1}$
electronic charge	$e = -1.60 \times 10^{-19}\,\text{C}$
molar volume of gas	$V_m = 22.4\,\text{dm}^3\,\text{mol}^{-1}$ at s.t.p. (101 kPa and 273 K) $V_m = 24.0\,\text{dm}^3\,\text{mol}^{-1}$ at room conditions
ionic product of water	$K_w = 1.00 \times$ [illegible] $\text{mol}^2\,\text{dm}^{-6}$ (at 298 K (25 °C))
specific heat capacity of water	$c = 4.18\,\text{kJ kg}^{-1}\,\text{K}^{-1}$ ($4.18\,\text{J g}^{-1}\,\text{K}^{-1}$)

The Periodic Table of Elements

Group 1	2												13	14	15	16	17	18
																		2 He helium 4.0
								1 H hydrogen 1.0					5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0	10 Ne neon 20.2
													13 Al aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 Cl chlorine 35.5	18 Ar argon 39.9
3 Li lithium 6.9	4 Be beryllium 9.0										29 Cu copper 63.5	30 Zn zinc 65.4	31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8
11 Na sodium 23.0	12 Mg magnesium 24.3										47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
19 K potassium 39.1	20 Ca calcium 40.1	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	46 Pd palladium 106.4	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium –	85 At astatine –	86 Rn radon –
37 Rb rubidium 85.5	38 Sr strontium 87.6	39 Y yttrium 88.9	40 Zr zirconium 91.2	41 Nb niobium 92.9	42 Mo molybdenum 95.9	43 Tc technetium –	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	78 Pt platinum 195.1	111 Rg roentgenium –	112 Cn copernicium –	113 Nh nihonium –	114 Fl flerovium –	115 Mc moscovium –	116 Lv livermorium –	117 Ts tennessine –	118 Og oganesson –
55 Cs caesium 132.9	56 Ba barium 137.3	57–71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	110 Ds darmstadtium –	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium –	85 At astatine –	86 Rn radon –
87 Fr francium –	88 Ra radium –	89–103 actinoids	104 Rf rutherfordium –	105 Db dubnium –	106 Sg seaborgium –	107 Bh bohrium –	108 Hs hassium –	109 Mt meitnerium –	110 Ds darmstadtium –	111 Rg roentgenium –	112 Cn copernicium –	113 Nh nihonium –	114 Fl flerovium –	115 Mc moscovium –	116 Lv livermorium –	117 Ts tennessine –	118 Og oganesson –	

Key

atomic number
atomic symbol
name
relative atomic mass

lanthanoids	57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium –	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0
actinoids	89 Ac actinium –	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium –	94 Pu plutonium –	95 Am americium –	96 Cm curium –	97 Bk berkelium –	98 Cf californium –	99 Es einsteinium –	100 Fm fermium –	101 Md mendelevium –	102 No nobelium –	103 Lr lawrencium –

26.2 Homogeneous and heterogeneous catalysts

Name: _____ Class: _____ Date: _____ **Total: 23 marks**

KEY WORDS catalyst 催化剂 • heterogeneous 多相 • heterogeneous catalyst 多相催化剂 • homogeneous 均相 • homogeneous catalyst 均相催化剂

Objective

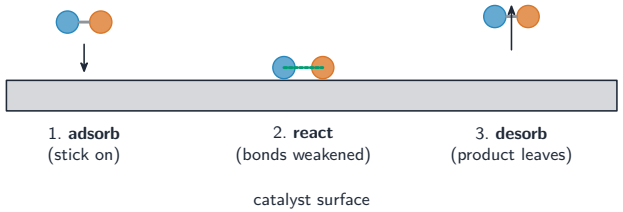
Build the skills to answer exam questions on the **mode of action of catalysts** 催化剂作用方式 — **heterogeneous** 多相 and **homogeneous** 均相 catalysis.

You must be able to:

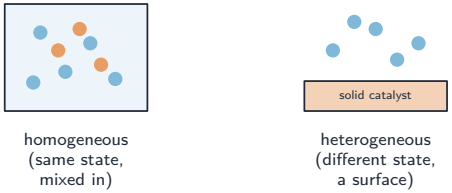
- describe heterogeneous catalysis (adsorption, bond weakening, desorption)
- describe homogeneous catalysis (used in one step, reformed in a later step)
- give the examples in the syllabus

1 Worked examples

Heterogeneous catalysis



A heterogeneous catalyst works at its surface: ***adsorption*** *of reactants →* ***bond weakening*** *→ reaction →* ***desorption*** *of products*



Homogeneous versus heterogeneous catalysis

Examples: **iron** in the Haber process; **Pt/Pd/Rh** in catalytic converters (removing NO_x).

Homogeneous catalysis

A homogeneous catalyst (same state as the reactants) is **used in one step and reformed in a later step**. Examples: oxides of nitrogen catalysing $SO_2 \rightarrow SO_3$ in the atmosphere; Fe^{2+}/Fe^{3+} catalysing the $I^-/S_2O_8^{2-}$ reaction (the Fe ion is regenerated, so it is a catalyst not a reactant).

2 Practice

2.1 State the three stages of heterogeneous catalysis. [3]

2.2 State what "homogeneous" means for a catalyst. [1]

3 Exam-style questions

3.1 In heterogeneous catalysis, the reactant molecules first: [1]

- **A** desorb from the surface
- **B** adsorb onto the catalyst surface
- **C** dissolve in the catalyst
- **D** evaporate

3.2 The iron catalyst in the Haber process is an example of a: [1]

- **A** homogeneous catalyst
- **B** heterogeneous catalyst
- **C** reactant
- **D** product

3.3 Explain how a heterogeneous catalyst speeds up a reaction at its surface. [3]

3.4 Fe^{2+} catalyses the reaction between iodide ions and peroxodisulfate ions. Explain why it is described as a homogeneous catalyst, not a reactant. [2]

3.5 Two industrial reactions use catalysts.

- Reaction 1: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ over solid iron.
- Reaction 2: $S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$, catalysed by $Fe^{3+}(aq)$.

(a) Classify each as homogeneous or heterogeneous, giving your reason. [2]

(b) Describe, in three stages, how the iron catalyst speeds up Reaction 1. [3]

(c) Write the two equations that show how Fe^{3+} catalyses Reaction 2, and state what the pair of equations shows about the catalyst. [4]

(d) Explain, with reference to the Boltzmann distribution, why a catalyst increases the rate but not the yield at equilibrium. [3]

Solutions

2.1 adsorption of the reactants onto the surface; reaction (bonds weakened); desorption of the products.

2.2 it is in the same physical state as the reactants.

3.1 B. Reactants first adsorb onto the catalyst surface.

3.2 B. Solid iron with gaseous reactants is a heterogeneous catalyst.

3.3 reactant molecules adsorb onto the catalyst surface; this weakens their bonds and holds them close together, lowering the activation energy; the products then desorb, freeing the surface.

3.4 the Fe^{2+} is used in one step but is regenerated (reformed) in a later step, so it is not used up overall — it is a catalyst, in the same (aqueous) state as the reactants.

3.5 (a) Reaction 1 is **heterogeneous** — the catalyst is a solid and the reactants are gases, so they are in different phases. Reaction 2 is **homogeneous** — catalyst and reactants are all in aqueous solution.
(b) The gases **adsorb** onto the iron surface at active sites, which weakens the strong N ≡ N and H–H bonds; the adsorbed species are held close together in the right orientation, so they react; the ammonia then **desorbs**, freeing the site for more reactant.
(c) $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$ and $2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$. Adding them gives the overall equation with no iron in it — the catalyst is used in the first step and **regenerated** in the second, so it is not consumed. It works because both reactants are negative ions, which repel each other; Fe^{3+} offers a route via oppositely charged species.
(d) The catalyst provides an alternative route of **lower activation energy**; on the Boltzmann distribution a larger fraction of molecules lies to the right of the new, lower E_a, so a greater proportion of collisions is successful; it lowers E_a for the forward and reverse reactions **equally**, so equilibrium is reached sooner but its position — and the yield — is unchanged.

3 **(a)** Solid manganese(IV) oxide, MnO_2, catalyses the decomposition of hydrogen peroxide.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

State the type of catalysis for this reaction. Explain your answer.

.....

..... [1]

(b) Hydrogen peroxide reacts with iodide ions in acidic conditions as shown.

$$H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$$

The initial rate of this reaction is investigated with different concentrations of H_2O_2, I^- and H^+. The results obtained are shown in Table 3.1.

Table 3.1

experiment	$[H_2O_2]$ / mol dm^{-3}	$[I^-]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.0450	0.0300	0.0125	2.42×10^{-3}
2	0.0225	0.0600	0.0125	2.42×10^{-3}
3	0.0225	0.120	0.0125	4.84×10^{-3}
4	0.0450	0.120	0.0500	9.68×10^{-3}

(i) Use the information in Table 3.1 to deduce the rate equation for this reaction.

Explain your reasoning.

.....

.....

.....

.....

.....

.....

..... [4]

(ii) Use your rate equation from **(b)(i)** and the data from Experiment 1 to calculate the rate constant, *k*, for this reaction. Include the units of *k*.

k = ... units ..... [2]

(c) The rate of the thermal decomposition of azomethane, $CH_3N{=}NCH_3$, is investigated.

$$CH_3N{=}NCH_3 \rightarrow N_2 + C_2H_6$$

Fig. 3.1 shows the results obtained. The reaction is first order with respect to $CH_3N{=}NCH_3$.

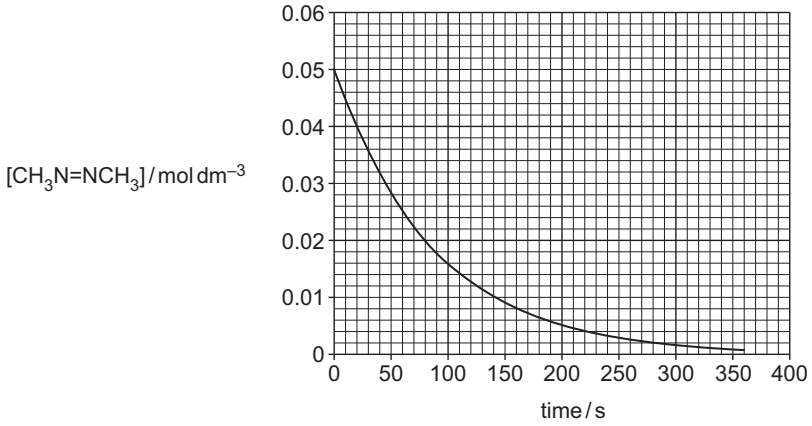


Fig. 3.1

(i) Use Fig. 3.1 to calculate **two** half-lives, $t_{\frac{1}{2}}$, to show that the reaction is first order.

.....

.....

.....

..... [2]

(ii) Use your answer to **(c)(i)** to calculate the rate constant, k, for the decomposition of azomethane.

k = ... s^{-1} [1]

(d) Describe the effect of increasing temperature on the rate constant and on the rate of a reaction.

.....

.....

..... [1]

[Total: 11]

2 Ethanal, CH_3CHO, reacts with nitrogen dioxide, NO_2. The products of the first step of this reaction are a $CH_3\dot{C}{=}O$ radical and a molecule of nitrous acid, HNO_2.

$$CH_3CHO + NO_2 \rightarrow CH_3\dot{C}{=}O + HNO_2$$

(a) (i) Use **two** words to complete the sentence.

This reaction involves .... of the single covalent bond between a hydrogen atom and a carbon atom in CH_3CHO.

[1]

(ii) The hydrogen atom mentioned in **(a)(i)** forms a covalent bond with one of the oxygen atoms of an NO_2 molecule. An NO_2 molecule has a single, unpaired electron on the nitrogen atom. All electrons are paired in an HNO_2 molecule.

Draw dot-and-cross diagrams of NO_2 and HNO_2 in the boxes. Show outer shell electrons only.

NO_2

HNO_2

[1]

(iii) Use VSEPR theory to predict the bond angle at the nitrogen atom in an HNO_2 molecule.

bond angle = ... [1]

(b) The rate equation for the reaction between CH_3CHO and NO_2 is shown.

$$\text{rate} = k[CH_3CHO][NO_2]$$

Under certain conditions, when the concentrations of both CH_3CHO and NO_2 are 0.200 mol dm^{-3}, the rate of the reaction is 1.53×10^{-4} mol dm^{-3} s^{-1}.

Calculate the value of the rate constant, k, under these conditions. Give the units of k.

k = ... units ..... [2]

(c) The reaction mixture described in **(b)** is monitored over a period of time.

Predict whether the graph of $[NO_2]$ against time shows a constant half-life.

Explain your answer.

prediction .....

explanation .....

.....

[1]

(d) NO_2 also reacts with ozone, O_3.

The rate equation is shown.

$$\text{rate} = k_1[NO_2]$$

Under certain conditions, the value of k_1 is $0.0848\,s^{-1}$.

The reaction has a constant half-life under these conditions.

Calculate the half-life in seconds.

half-life = ... s [1]

(e) NO_2 is present in the exhaust gases of cars. It can react with carbon monoxide, CO, on the surface of a heterogeneous catalyst in the car's catalytic converter.

Describe the mode of action of this heterogeneous catalyst.

.....

.....

.....

.....

.....

..... [2]

[Total: 9]

4 **(a)** Nitrogen monoxide, NO, reacts with hydrogen, as shown in reaction 3.

reaction 3 $2NO + 2H_2 \rightarrow N_2 + 2H_2O$

(i) The rate equation for reaction 3 is shown.

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

Complete Table 4.1.

Table 4.1

the order of reaction with respect to $[H_2]$	
the order of reaction with respect to [NO]	
the overall order of the reaction	

[1]

(ii) Predict how the initial rate for reaction 3 changes when the concentration of NO is halved.

..... [1]

(iii) Predict how the initial rate for reaction 3 changes when the concentrations of NO and H_2 are both increased **three** times.

..... [1]

(iv) Suggest why reaction 3 is unlikely to proceed by a mechanism involving only a single step.

.....

..... [1]

(v) Suggest equations for the **three** steps of the reaction mechanism for reaction 3.

Each step involves a reaction between **two** molecules.

step 1 ..... $\rightarrow$ .....

step 2 ..... + ... $\rightarrow N_2O$ + ...

step 3 N_2O + ... $\rightarrow$ ..... + ...

[2]

(vi) Suggest the role of N_2O in this mechanism.

Explain your reasoning.

.....

.... [1]

(b) Iodine, I_2, reacts with thiosulfate ions, $S_2O_3^{2-}$, as shown in reaction 4.

reaction 4 $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

Reaction 4 is carried out in the presence of a large excess of I_2. Under these conditions, the reaction is first order with respect to $[S_2O_3^{2-}]$ and zero order with respect to $[I_2]$.

The half-life, $t_{\frac{1}{2}}$, for reaction 4 is 720 s under certain conditions.

Calculate the value of the rate constant, *k*, for reaction 4. Include the units of *k*.

k = ... units ..... [1]

(c) The reaction between iodide ions, I^-(aq), and peroxydisulfate ions, $S_2O_8^{2-}$(aq), is catalysed by Co^{3+}(aq). The mechanism is similar to the mechanism of this reaction when Fe^{3+}(aq) is used as the catalyst.

(i) State the type of catalysis that occurs in this reaction.

Explain your reasoning.

.....

..... [1]

(ii) Write **two** equations to show how Co^{3+}(aq) catalyses this reaction.

equation 1 .....

equation 2 .....
[2]

(iii) Suggest why this reaction is slow in the absence of Co^{3+}(aq).

.....

..... [1]

[Total: 12]