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 $CH_3N{=}NCH_3$.

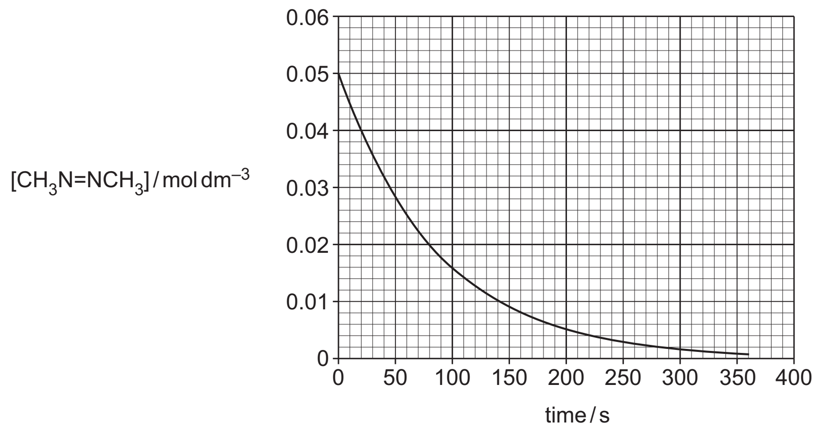

Fig. 3.1

(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 $1.53 \times 10^{-4}\,mol\,dm^{-3}\,s^{-1}$.

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 .... → ....

step 2 .... + ... → N_2O + ...

step 3 N_2O + ... → .... + ...

[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.

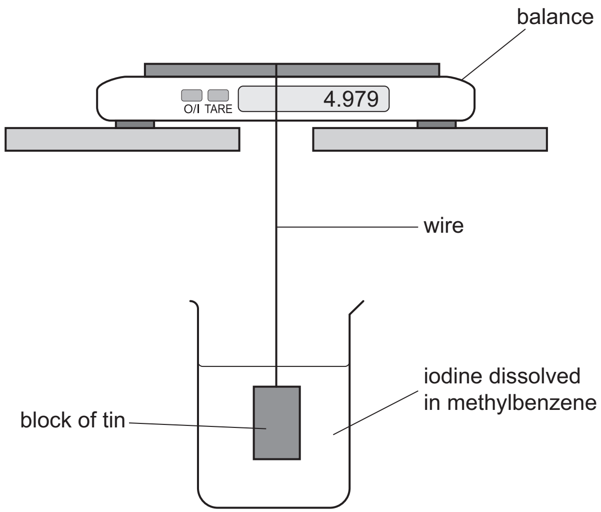

Fig. 2.1

(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.

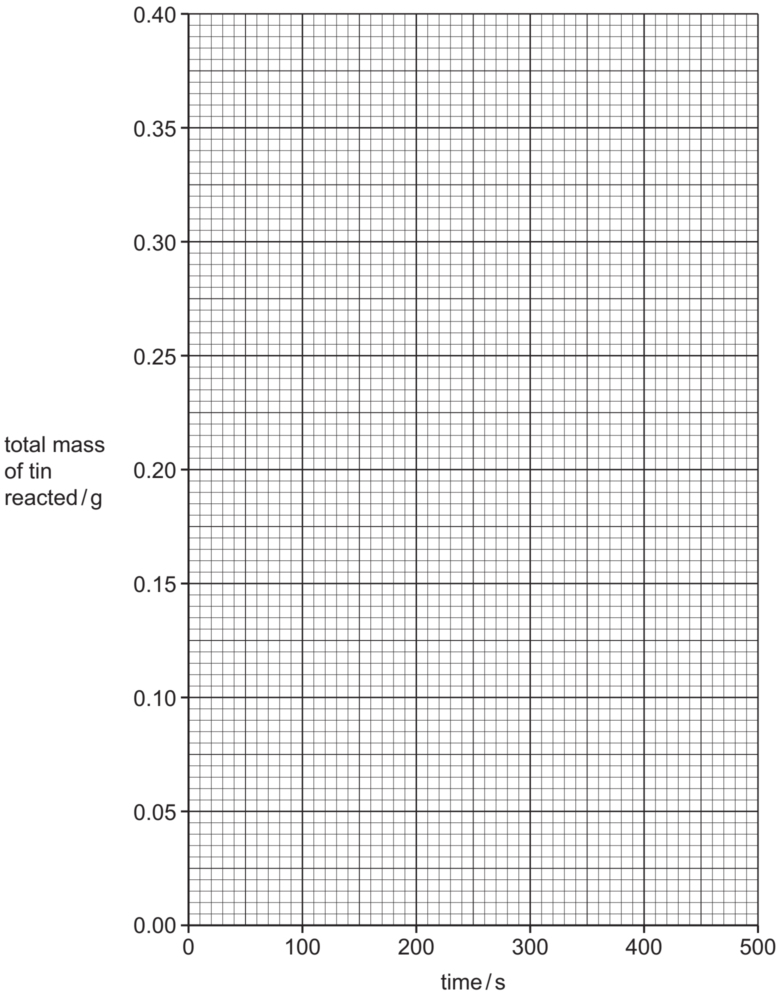

Fig. 2.2

[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	$K_w = 1.00 \times 10^{-14}\,\text{mol}^2\,\text{dm}^{-6}$ (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

Key: atomic number / **atomic symbol** / name / relative atomic mass

Group

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H hydrogen 1.0																	2 He helium 4.0
2	3 Li lithium 6.9	4 Be beryllium 9.0											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
3	11 Na sodium 23.0	12 Mg magnesium 24.3											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
4	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	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
5	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	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
6	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	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 –
7	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 –

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 –