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 $0.200\,\text{mol}\,\text{dm}^{-3}$, the rate of the reaction is $1.53 \times 10^{-4}\,\text{mol}\,\text{dm}^{-3}\,\text{s}^{-1}$.

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 $0.0848\,s^{-1}$.

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]

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 $CH_3N{=}NCH_3$.

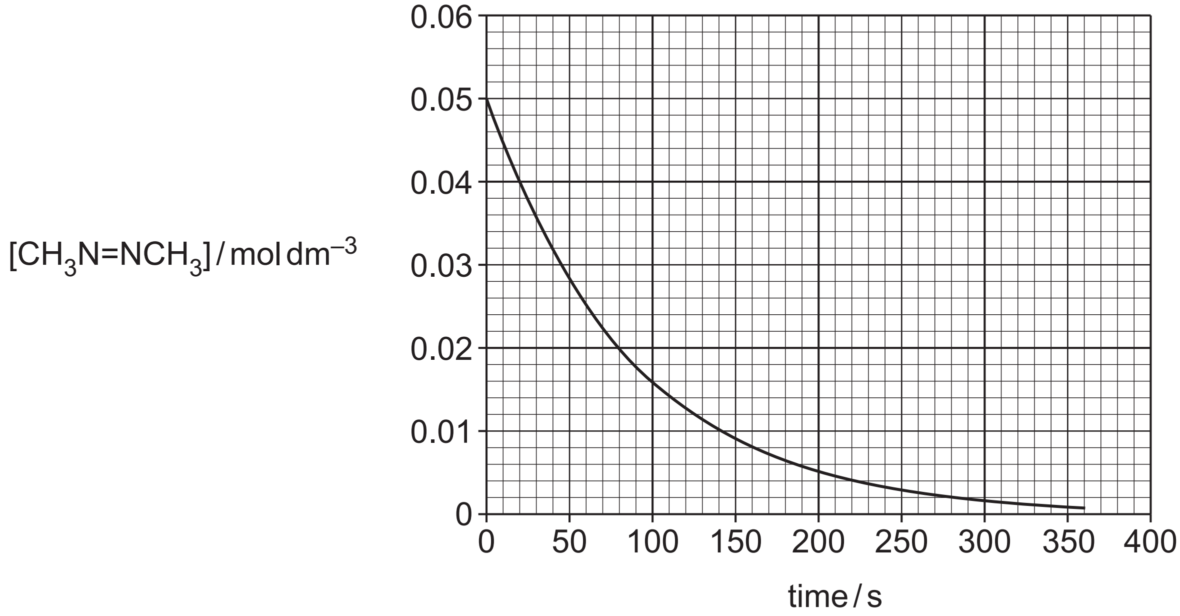

Fig. 3.1

(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]

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]