Q1.

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.

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.....[8]

Q2.

2 **(a)** What do you understand by the term *order of reaction*?

..... [1]

(b) Cyanohydrins can be made by reacting ketones with an acidified solution of sodium cyanide.

$$(CH_3)_2C{=}O + H^+ + CN^- \longrightarrow (CH_3)_2C(OH)CN$$

In a series of experiments, the reaction was carried out with different concentrations of the three reagents, and the following relative initial rates were obtained.

experiment number	$[(CH_3)_2CO]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	$[CN^-]$ / mol dm^{-3}	relative initial rate / mol dm^{-3} sec^{-1}
1	0.020	0.060	0.060	1.00
2	0.020	0.050	0.050	0.833
3	0.020	0.050	0.060	1.00
4	0.025	0.050	0.050	1.042

(i) Use the data in the table to deduce the order of the reaction with respect to

propanone .....

hydrogen ions .....

cyanide ions .....

(ii) Hence write a rate equation for this reaction.

.....

Two different mechanisms have been suggested for this reaction

Mechanism A: $(CH_3)_2C{=}O + H^+ \rightarrow (CH_3)_2COH^+$
$(CH_3)_2COH^+ + CN^- \rightarrow (CH_3)_2C(OH)CN$

Mechanism B: $(CH_3)_2C{=}O + CN^- \rightarrow (CH_3)_2C(O^-)CN$
$(CH_3)_2C(O^-)CN + H^+ \rightarrow (CH_3)_2C(OH)CN$

(iii) Which mechanism is consistent with the rate equation you deduced in **(ii)**, and which step in this mechanism is the slower (rate determining) step? Explain your answer.

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[7]

[Total: 8]

Q3.

1 The oxidation of nitrogen monoxide occurs readily according to the following equation.

$$NO(g) + \tfrac{1}{2}O_2(g) \longrightarrow NO_2(g)$$

The following table shows how the initial rate of this reaction depends on the concentrations of the two reactants.

[NO] / mol dm^{-3}	[O_2] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
0.0050	0.0050	0.02
0.0050	0.0075	0.03
0.010	0.0075	0.12

(a) (i) Use the data to determine the order of reaction with respect to each of the reagents.

order with respect to NO .....

order with respect to O_2 .....

(ii) Write the rate equation for the reaction, and use it to calculate a value for the rate constant, *k*, stating its units.

rate equation .....

numerical value of *k* = ...

units of *k* .....

(iii) Use your rate equation in **(ii)** to calculate the rate of reaction when [NO] = [O_2] = 0.0025 mol dm^{-3}.

rate of reaction =.....

[6]

(b) Nitrogen monoxide plays an important catalytic role in the oxidation of atmospheric SO_2 in the formation of acid rain.

(i) State the type of catalysis shown in this process.

.....

(ii) Explain the steps involved in this process by writing equations for the reactions that occur.

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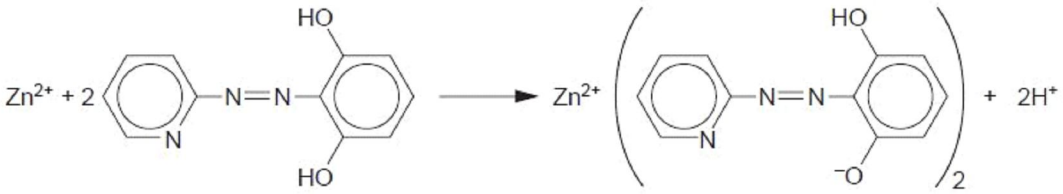
[3]

[Total: 9]

Q4.

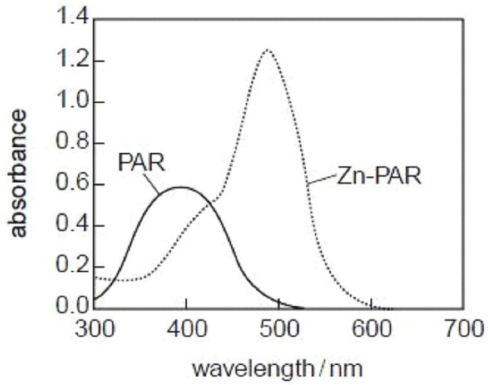
(d) Zinc is an essential element for plant and animal life. It is often administered in the form of a chelate, which is a complex between a metal ion and a polydentate ligand.

The rate of the reaction between zinc ions and the ligand 4-(2-pyridylazo)resorcinol, PAR, has been studied.



PAR Zn-PAR

Both PAR and its zinc complex absorb radiation in the UV-visible region. The figure below shows their absorption spectra.



(i) Devise a suitable experimental technique for studying how the rate of this reaction varies with $[Zn^{2+}(aq)]$.

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(ii) Describe a reaction you could carry out to show that PAR is a phenol.

.....

.....

[7]

Q5.

For Examiner's Use

4 **(a)** The reaction between iodide ions and persulfate ions, $S_2O_8^{2-}$, is slow.

$$2I^- + S_2O_8^{2-} \longrightarrow I_2 + 2SO_4^{2-} \qquad \textbf{1}$$

The reaction can be speeded up by adding a small amount of Fe^{2+} or Fe^{3+} ions. The following two reactions then take place.

$$2I^- + 2Fe^{3+} \longrightarrow I_2 + 2Fe^{2+} \qquad \textbf{2}$$

$$2Fe^{2+} + S_2O_8^{2-} \longrightarrow 2Fe^{3+} + 2SO_4^{2-} \qquad \textbf{3}$$

(i) What type of catalysis is occurring here?

.....

(ii) The rates of reactions **2** and **3** are both faster than that of reaction **1**. By considering the species involved in these reactions, suggest a reason for this.

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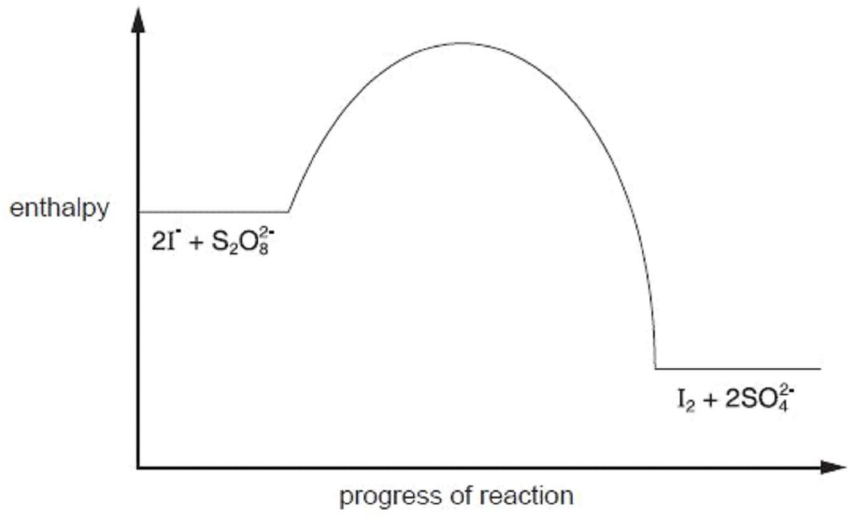
(iii) The following reaction pathway diagram shows the enthalpy profile of reaction **1**.



Use the same axes to draw the enthalpy profiles of reaction **2** followed by reaction **3**, starting reaction **2** at the same enthalpy level as reaction **1**.

[4]

(b) The oxidation of SO_2 to SO_3 in the atmosphere is speeded up by the presence of nitrogen oxides.

For Examiner's Use

(i) Describe the environmental significance of this reaction.

.....

(ii) Describe a major source of SO_2 in the atmosphere.

.....

(iii) By means of suitable equations, show how nitrogen oxides speed up this reaction.

.....

.....

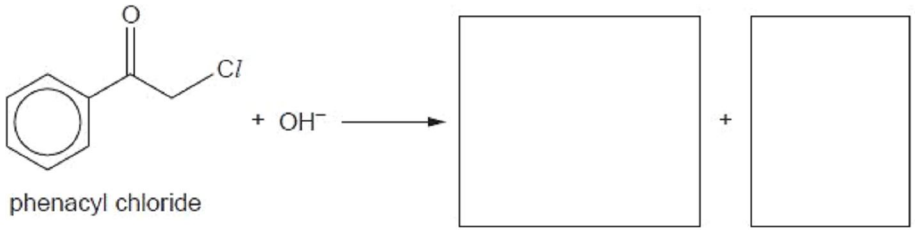
[4]

[Total: 8]

Q6.

1 Phenacyl chloride has been used as a component of some tear gases. Its lachrymatory and irritant properties are due to it reacting with water inside body tissues to produce hydrochloric acid.

It undergoes a nucleophilic substitution reaction with NaOH(aq).



phenacyl chloride

(a) Write the formulae of the products of this reaction in the two boxes above. [2]

When the rate of this reaction was measured at various concentrations of the two reagents, the following results were obtained.

experiment number	[phenacyl chloride]	[NaOH]	relative rate
1	0.020	0.10	1.0
2	0.030	0.10	1.5
3	0.025	0.20	2.5

(b) **(i)** What is meant by the term *order of reaction*?

.....

(ii) Use the above data to deduce the order with respect to each reactant. Explain your reasoning.

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(iii) Write the overall rate equation for the reaction.

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(iv) Describe the mechanism for this reaction that is consistent with your overall rate equation.
You should show all intermediates and/or transition states and partial charges, and you should represent the movements of electron pairs by curly arrows.

For Examiner's Use

[7]

(c) **(i)** Describe an experiment that would show that CH_3COCl reacts with water at a much faster rate than phenacyl chloride. Include the reagents you would use, and the observations you would make with each chloride.

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(ii) Suggest an explanation for this difference in reactivity.

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[4]

[Total: 13]

Q7.

For Examiner's Use

2 Nitrogen monoxide, NO, is formed in a reversible reaction when air is heated to the temperature of a car engine.

(a) (i) Suggest a 'dot-and-cross' electronic structure for nitrogen monoxide.

(ii) The enthalpy change of formation of nitrogen monoxide is +90 kJ mol^{-1}. What is the enthalpy change for the following reaction?

$$2NO(g) \rightarrow N_2(g) + O_2(g) \qquad \Delta H_r = \ldots\ldots\ldots\ldots \text{kJ mol}^{-1}$$

(iii) Explain why nitrogen monoxide is formed in the car engine.

.....

(iv) Using bond enthalpy values from the *Data Booklet* and your answer in **(ii)** above, calculate a value for the bond energy of nitrogen monoxide.

bond energy = ... kJ mol^{-1}
[5]

(b) At 800 K, nitrogen monoxide reacts with hydrogen according to the following equation.

equation **I** $\quad 2H_2(g) + 2NO(g) \rightarrow 2H_2O(g) + N_2(g)$

The following table shows how the initial rate of this reaction depends on the partial pressures of the reagents.

experiment	p(H_2) / atm	p(NO) / atm	initial rate / atm s^{-1}
1	0.64	1.60	1.50×10^{-7}
2	0.64	0.80	3.75×10^{-8}
3	0.32	1.60	7.50×10^{-8}

(i) Find the order of the reaction with respect to each reactant, explaining how you arrive at your answer.

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(ii) Write down the rate equation and the units of the rate constant.

For Examin Use

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The following mechanism has been put forward for this reaction.

step 1 $NO + NO \rightarrow N_2O + O$

step 2 $H_2 + O \rightarrow H_2O$

step 3 $H_2 + N_2O \rightarrow N_2 + H_2O$

(iii) Show how the overall stoichiometric equation **I** can be derived from the three equations for the individual steps given above.

(iv) Suggest which of the three reactions in the mechanism is the rate determining step. Explain your answer.

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[8]

(c) The following information on half-reactions relates to the reaction between HNO_3 and an excess of $FeSO_4$.

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad E^{\ominus} = +0.77\,V$$

$$3H^+ + NO_3^- + 2e^- \rightarrow HNO_2 + H_2O \qquad E^{\ominus} = +0.94\,V$$

$$HNO_2 + H^+ + e^- \rightarrow NO + H_2O \qquad E^{\ominus} = +0.99\,V$$

(i) Suggest the formula of the nitrogen-containing final product of this reaction.

.....

(ii) Write an equation for the formation of this nitrogen-containing product.

(iii) Nitrogen monoxide forms a dark brown complex with an excess of $FeSO_4$(aq). What kind of bonding is involved in the complex formation?

.....

(iv) Suggest a formula for this complex.

.....

[4]

[Total: 17]

Q8.

2 Carbon monoxide, CO, occurs in the exhaust gases of internal combustion engines.

(a) (i) Suggest a dot-and-cross diagram for CO.

(ii) Suggest **one** reason why CO is produced in addition to CO_2 in some internal combustion engines.

.....

.....

(iii) Carbon monoxide can be removed from the exhaust gases by a catalytic converter. Write an equation for a reaction that occurs in a catalytic converter that removes CO.

.....

[3]

(b) The standard enthalpy change of formation, $\Delta H_f^\ominus$, of CO is $-111\ kJ\ mol^{-1}$, and that of CO_2 is $-394\ kJ\ mol^{-1}$.
Calculate the standard enthalpy change of the following reaction.

$$C(s) + CO_2(g) \rightarrow 2CO(g)$$

$\Delta H^\ominus$ = ... $kJ\ mol^{-1}$

[2]

(c) Carbon monoxide reacts with a ruthenium(II) chloride complex according to the equation

$$[Ru(H_2O)_2Cl_4]^{2-} + CO \rightarrow [Ru(H_2O)(CO)Cl_4]^{2-} + H_2O.$$

(i) Describe the *type of reaction* that is occurring here.

.....

(ii) During the reaction, the colour of the solution changes from deep blue to green. Explain the origin of colour in transition element complexes, and why different complexes often have different colours.

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For Examiner's Use

The following table shows how the initial rate of this reaction varies with different concentrations of reactants.

$[[Ru(H_2O)_2Cl_4]^{2-}]$ / mol dm^{-3}	[CO] / mol dm^{-3}	rate / mol dm^{-3} s^{-1}
1.1×10^{-2}	1.7×10^{-3}	1.6×10^{-7}
1.6×10^{-2}	3.6×10^{-3}	2.3×10^{-7}
2.2×10^{-2}	2.7×10^{-3}	3.2×10^{-7}

(iii) Use these data to determine the order of reaction with respect to each reagent, and write the rate equation for the reaction.

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There are three possible mechanisms for this reaction, which are described below.

mechanism 1 $[Ru(H_2O)_2Cl_4]^{2-} + CO \xrightarrow{\text{slow}} [Ru(H_2O)(CO)Cl_4]^{2-} + H_2O$

mechanism 2 $[Ru(H_2O)_2Cl_4]^{2-} \xrightarrow{\text{slow}} [Ru(H_2O)Cl_4]^{2-} + H_2O$

$[Ru(H_2O)Cl_4]^{2-} + CO \xrightarrow{\text{fast}} [Ru(H_2O)(CO)Cl_4]^{2-}$

mechanism 3 $[Ru(H_2O)_2Cl_4]^{2-} + CO \xrightarrow{\text{slow}} [Ru(H_2O)_2(CO)Cl_4]^{2-}$

$[Ru(H_2O)_2(CO)Cl_4]^{2-} \xrightarrow{\text{fast}} [Ru(H_2O)(CO)Cl_4]^{2-} + H_2O$

(iv) Deduce which of these three mechanisms is consistent with the rate equation you suggested in part **(iii)**. Explain your answer.

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[10]

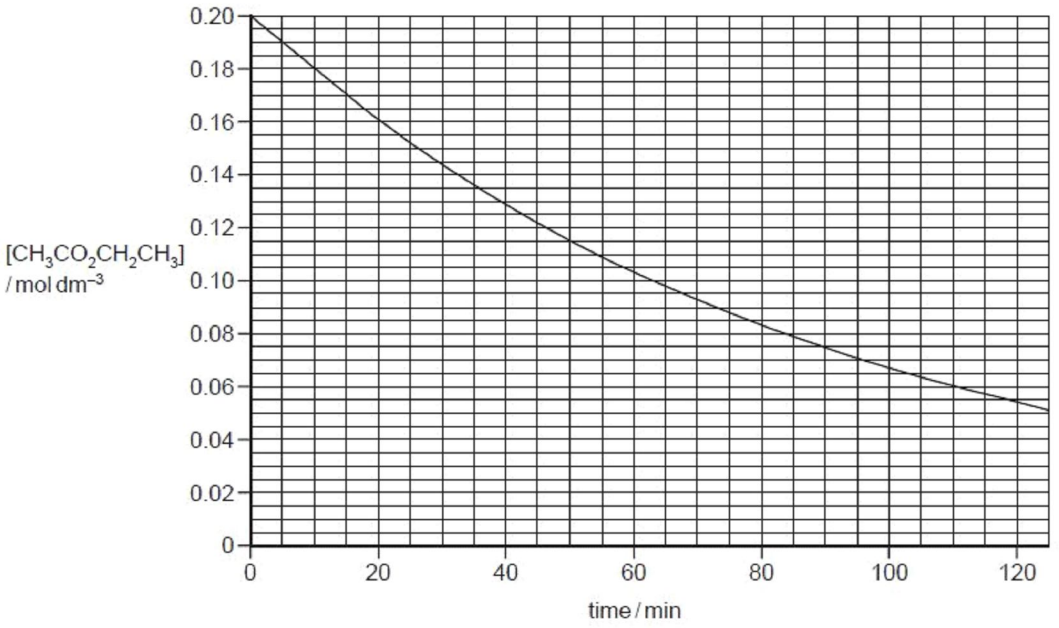
[Total: 15]

Q9.

2 Ethyl ethanoate is hydrolysed slowly by water in the following acid-catalysed reaction.

$$CH_3CO_2CH_2CH_3 + H_2O \xrightarrow{H^+} CH_3CO_2H + CH_3CH_2OH$$

The concentration of ethyl ethanoate was determined at regular time intervals as the reaction progressed.
Two separate experiments were carried out, with different HC*l* concentrations.
The following graph shows the results of an experiment using [HC*l*] = 0.1 mol dm^{-3}.



(a) When the experiment was carried out using [HC*l*] = 0.2 mol dm^{-3}, the following results were obtained.

time / min	$[CH_3CO_2CH_2CH_3]$ / mol dm^{-3}
0	0.200
10	0.160
25	0.115
50	0.067
75	0.038
100	0.022
125	0.013

(i) Plot these data on the axes above, and draw a line of best fit.

(ii) Use one of the graphs to show that the reaction is first order with respect to $CH_3CO_2CH_2CH_3$.

Show all your working, and show clearly any construction lines you draw on the graphs.

Fo Exami Us

(iii) Use the graphs to calculate the order of reaction with respect to HCl.

Show all your working, and show clearly any construction lines you draw on the graphs.

(iv) Write the rate equation for this reaction, and calculate the value of the rate constant.

rate =

[7]

(b) (i) Why is it **not** possible to determine the order of reaction with respect to water in this experiment?

.....

.....

(ii) Although $[CH_3CO_2CH_2CH_3]$ decreases during each experiment, [HCl] remains the same as its initial value.

Why is this?

.....

.....

[2]

[Total: 9]

Q10.

1 A bromoalkane, R–Br, is hydrolysed by aqueous sodium hydroxide.

(a) (i) Write a balanced equation for this reaction.

.....

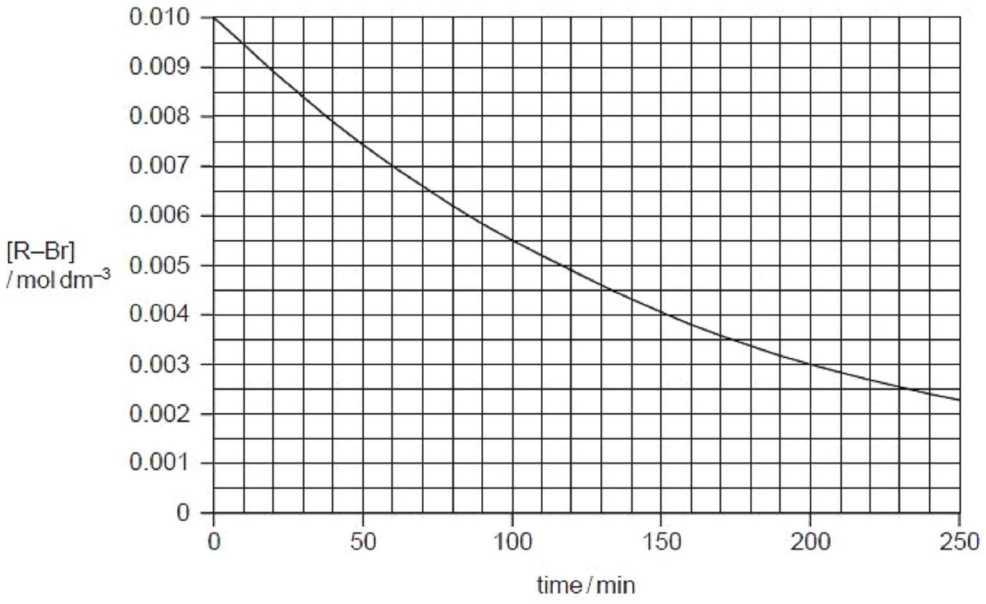
(ii) What *type of reaction* is this?

.....

[2]

(b) The concentration of bromoalkane was determined at regular time intervals as the reaction progressed.

Two separate experiments were carried out, with different NaOH concentrations.
The graph below shows the results of an experiment using [NaOH] = 0.10 mol dm^{-3}.



When the experiment was repeated using [NaOH] = 0.15 mol dm^{-3}, the following results were obtained.

time / min	[R–Br] / mol dm^{-3}
0	0.0100
40	0.0070
80	0.0049
120	0.0034
160	0.0024
200	0.0017
240	0.0012

(i) Plot these data on the axes above, and draw a line of best fit.

For Examiner's Use

(ii) Use one of the graphs to confirm that the reaction is first order with respect to R–Br. Show all your working, and show clearly any construction lines you draw.

(iii) Use the graphs to calculate the order of reaction with respect to NaOH. Show all your working, and show clearly any construction lines you draw on the graphs.

(iv) Write the rate equation for this reaction, and calculate the value of the rate constant.

rate =

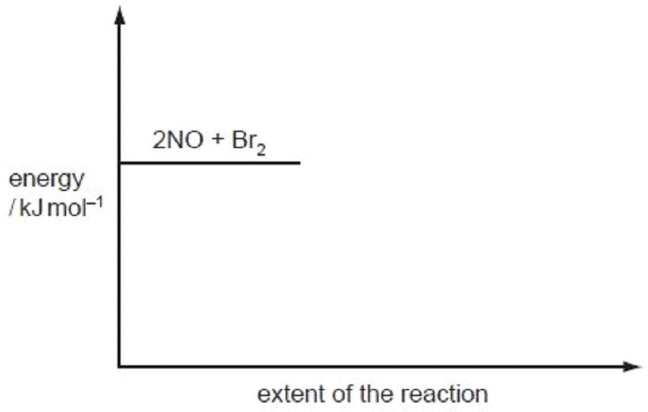
[7]

(c) Nitric oxide, NO, and bromine vapour react together according to the following equation.

$$2NO(g) + Br_2(g) \rightarrow 2NOBr(g) \qquad \Delta H = -23\,kJ\,mol^{-1}$$

The reaction has an activation energy of $+5.4\,kJ\,mol^{-1}$.

Use the following axes to sketch a fully-labelled reaction pathway diagram for this reaction.
Include all numerical data on your diagram.



[2]

[Total: 11]

Q11.

1 The reaction between iodine and propanone is catalysed by hydrogen ions.

$$CH_3COCH_3 + I_2 \xrightarrow{H^+} CH_3COCH_2I + HI$$

The reaction is found to be first order with respect to $[CH_3COCH_3]$ and with respect to $[H^+]$, and zero order with respect to $[I_2]$.

(a) What do you understand by the term *order of reaction*?

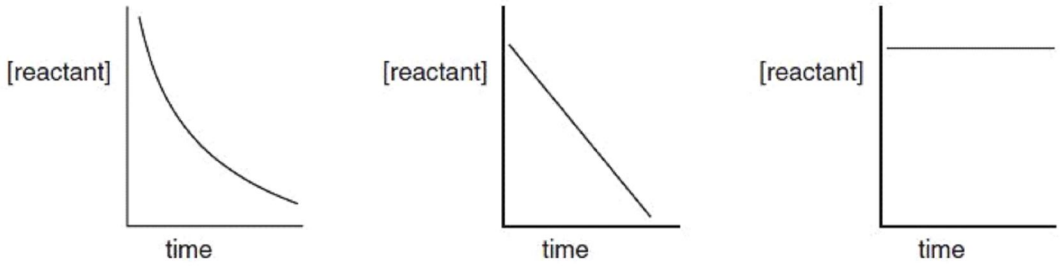
.....

.....[1]

(b) Construct a rate equation for the reaction.

.....[1]

The following sketches show three ways in which the concentration of reagents might vary during the reaction.



(c) Which of the above graphs correctly describes how the concentration of reactant changes with time for

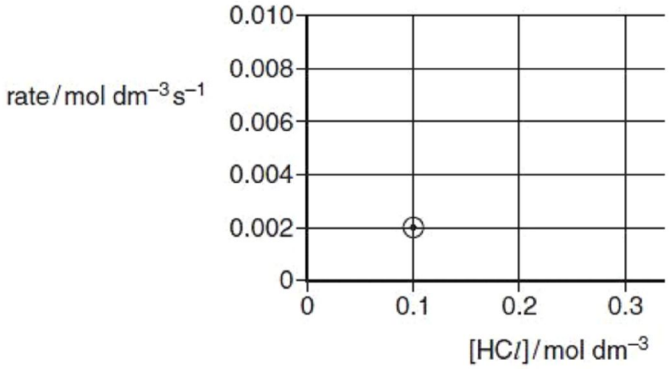
(i) the propanone concentration, _____

(ii) the iodine concentration? _____

[2]

Use

(d) When carried out in $0.1\,mol\,dm^{-3}$ HC*l* solution, the rate was found to be $0.002\,mol\,dm^{-3}\,s^{-1}$. Predict the rate of reaction in $0.2\,mol\,dm^{-3}$ HC*l* and in $0.3\,mol\,dm^{-3}$ HC*l* solution. Plot your figures on the following graph, and draw a line through the points.



[2]

(e) Only one of the following outline reaction mechanisms is consistent with the observed kinetics.

A
$I_2 + H^+ \longrightarrow$ intermediate [slow]
intermediate + $CH_3COCH_3 \longrightarrow$ products [fast]

B
$CH_3COCH_3 + H^+ \longrightarrow$ intermediate [slow]
intermediate + $I_2 \longrightarrow$ products [fast]

C
$CH_3COCH_3 + H^+ \longrightarrow$ intermediate [fast]
intermediate + $I_2 \longrightarrow$ products [slow]

D
$CH_3COCH_3 + I_2 \longrightarrow$ intermediate [slow]
intermediate + $H^+ \longrightarrow$ products [fast]

Decide which mechanism is consistent, explaining the reasons for your choice.

Mechanism letter (**A**, **B**, **C** or **D**) _____

Reasons

.....

.....

.....

.....[3]

(f) When the starting concentrations of propanone, iodine and H^+ were $0.20\,mol\,dm^{-3}$, $0.01\,mol\,dm^{-3}$ and $0.5\,mol\,dm^{-3}$ respectively, the rate of decrease of $[I_2]$ was found to be $3.3 \times 10^{-6}\,mol\,dm^{-3}\,s^{-1}$.

(i) Suggest a method you could use to measure $[I_2]$.

.....

(ii) Use these figures and your rate equation in part **(b)** to calculate a value for the rate constant *k*.

.....

(iii) What are the units of *k*?

.....

[3]

[Total : 12]

Q12.

2 In the late 19th century the two pioneers of the study of reaction kinetics, Vernon Harcourt and William Esson, studied the rate of the reaction between hydrogen peroxide and iodide ions in acidic solution.

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

This reaction is considered to go by the following steps.

step **1** $H_2O_2 + I^- \rightarrow IO^- + H_2O$

step **2** $IO^- + H^+ \rightarrow HOI$

step **3** $HOI + H^+ + I^- \rightarrow I_2 + H_2O$

The general form of the rate equation is as follows.

$$\text{rate} = k[H_2O_2]^a[I^-]^b[H^+]^c$$

(a) Suggest how the appearance of the solution might change as the reaction takes place.

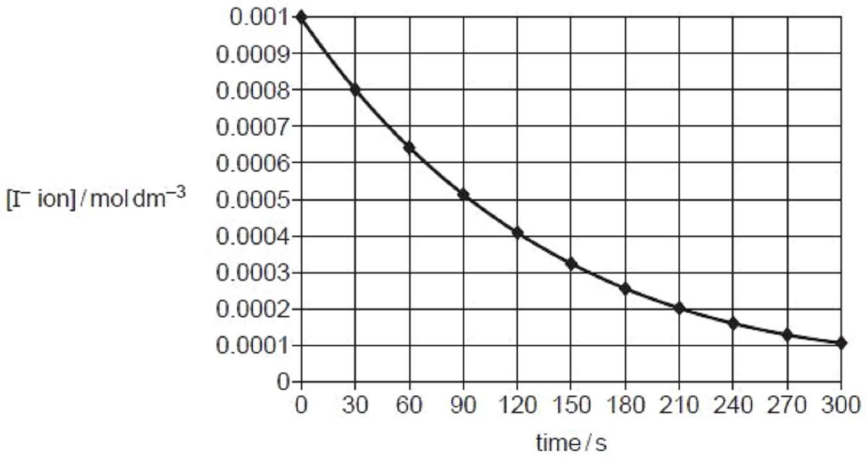
..... [1]

(b) Suggest values for the orders *a*, *b* and *c* in the rate equation for each of the following cases.

case	numerical value		
	a	*b*	*c*
step **1** is the slowest overall			
step **2** is the slowest overall			
step **3** is the slowest overall			

[3]

A study was carried out in which both $[H_2O_2]$ and $[H^+]$ were kept constant at $0.05\,mol\,dm^{-3}$, and $[I^-]$ was plotted against time. The following curve was obtained.



To gain full marks for the following answers you will need to draw relevant construction lines on the graph opposite to show your working. Draw them using a pencil and ruler.

(c) Calculate the initial rate of this reaction and state its units.

rate = ... units ..... [2]

(d) Use half-life data calculated from the graph to show that the reaction is first order with respect to $[I^-]$.

..... [2]

(e) Use the following data to deduce the orders with respect to $[H_2O_2]$ and $[H^+]$, explaining your reasoning.

$[H_2O_2]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	relative rate
0.05	0.05	1.0
0.07	0.05	1.4
0.09	0.07	1.8

.....

.....

order with respect to $[H_2O_2]$ = ...

order with respect to $[H^+]$ = ...

[2]

(f) From your results, deduce which of the three steps is the slowest (rate determining) step.

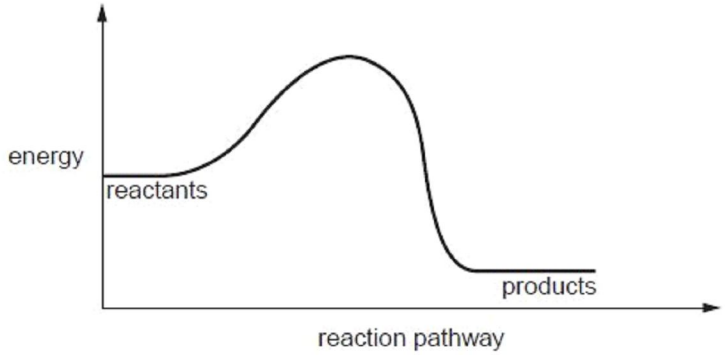
..... [1]

[Total: 11]

Q13.

8 **(a)** Enzymes play a vital role in all living organisms, helping chemical reactions to take place at body temperature.

(i) The diagram below shows the reaction pathway of an enzyme-catalysed reaction without an enzyme present. On the diagram sketch the pathway if the enzyme was present.



(ii) What type of molecule are most enzymes?

.....

(iii) Why do many enzymes lose their catalytic effectiveness above 40 °C?

.....

[3]

(b) **(i)** Explain the difference between competitive and non-competitive inhibition of an enzyme.

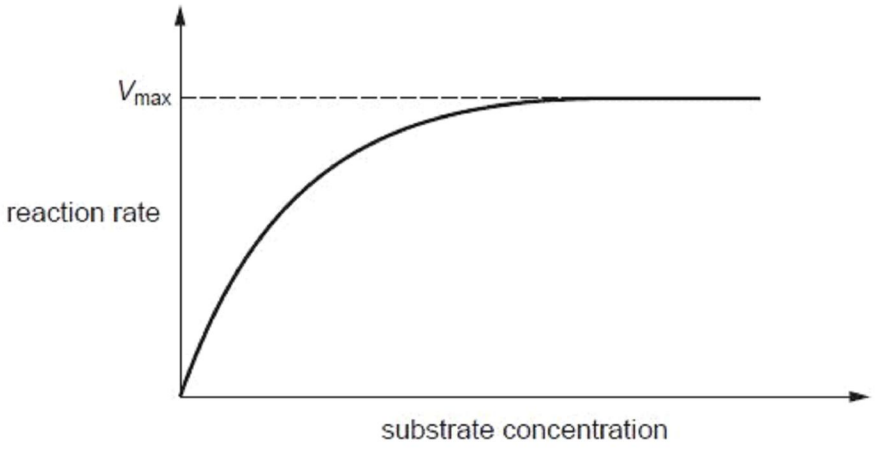
.....

.....

.....

(ii) The graph below shows how the rate of an enzyme-catalysed reaction varies with substrate concentration in the absence of an inhibitor.

For a given amount of enzyme, V_{max} represents the rate when all of the active sites on the enzyme are being used.



Sketch on the diagram curves to show the effect on the rate of reaction of:

I a competitive inhibitor;

II a non-competitive inhibitor.

Clearly label your curves.

[4]

(c) Heavy metal ions like Hg^{2+} can bind irreversibly to enzymes and this can result in poisoning.

(i) Suggest to what atom or group Hg^{2+} ions bind.

.....

(ii) Explain how this affects enzyme activity.

.....

.....

.....

[3]

[Total: 10]

Q14.

3 Iron metal and its compounds are useful catalysts in certain reactions.

(a) **Apart from its catalytic activity**, state **two** properties of iron or its compounds that show that it is a transition element.

.....

.....[2]

(b) You are provided with a solution of $KMnO_4$ of known concentration in a burette.
Outline how you could use this solution to find out the concentration of $Fe^{2+}(aq)$ in a solution. You should include relevant equations for any reactions you describe.

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.....[4]

(c) For each of the following equations, write the oxidation number of the element printed **in bold** underneath its symbol, and balance the equation by adding appropriate numbers before each species.

(i) ..... $\mathbf{Mn}O_4^-$ + ... $\mathbf{S}O_2$ + ... $H_2O \rightarrow$ ..... $\mathbf{Mn}^{2+}$ + ... $\mathbf{S}O_4^{2-}$ + ... H^+

oxidation numbers: ....

(ii) ..... $\mathbf{Cr}_2O_7^{2-}$ + ... $\mathbf{N}O_2$ + ... $H^+ \rightarrow$ ..... $\mathbf{Cr}^{3+}$ + ... $\mathbf{N}O_3^-$ + ... H_2O

oxidation numbers: ....

[6]

(d) Outline the role that Fe^{3+} ions play in catalysing the reaction between iodide ions and peroxydisulfate(VI) ions.

For Examiner's Use

$$2I^- + S_2O_8^{2-} \longrightarrow I_2 + 2SO_4^{2-}$$

.....

.....

.....[2]

[Total: 14]

Q15.

(b) Enzymes are particular types of protein molecule. Explain briefly how enzymes are able to help to break down molecules in the body.

For Examin Use

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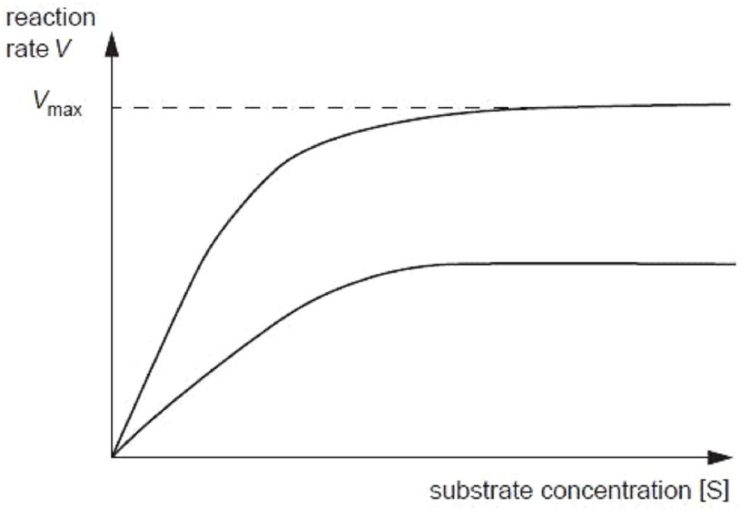
.....[2]

(c) The graph below shows the effect of inhibition on an enzyme-catalysed reaction.



State the type of inhibition shown, giving a reason to support your answer.

type of inhibition .....

reason .....

.....[2]

[Total: 10]

Q16.

1 (a) (i) Write equations to illustrate the reactions of the following oxides with water.

phosphorus(V) oxide .....

sulfur(IV) oxide .....

(ii) When NO_2 reacts with water, nitrogen undergoes a disproportionation reaction in which one nitrogen atom decreases its oxidation number by 1 and another nitrogen atom increases its oxidation number by 1. A mixture of two acids results.
Suggest an equation for the reaction between NO_2 and water.

.....

(iii) In a similar disproportionation reaction, ClO_2 reacts with aqueous NaOH to produce a solution containing two chlorine-containing sodium salts.
Suggest an equation for the reaction between ClO_2 and aqueous NaOH.

.....

[4]

(b) The major source of sulfur for the manufacture of sulfuric acid by the Contact process is the de-sulfurisation of 'sour' natural gas. Many natural gas wells produce a mixture of volatile hydrocarbons (mainly CH_4 and C_2H_6) together with up to 25% hydrogen sulfide, H_2S.

(i) Complete and balance the following equation showing the complete combustion of a gaseous mixture consisting of 2 mol of CH_4, 1 mol of C_2H_6 and 1 mol of H_2S.

$$2CH_4 + C_2H_6 + H_2S + \_\_\_\_\_ \rightarrow SO_2 + \_\_\_\_\_ + \_\_\_\_\_$$

(ii) Explain why it is important to remove the H_2S before burning the natural gas industrially.

.....

.....

The H_2S is removed by passing the 'sour' natural gas through a solvent containing ethanolamine. The following reaction takes place.

$$HOCH_2CH_2NH_2 + H_2S(g) \rightarrow HOCH_2CH_2NH_3^+ + SH^-$$

(iii) If a sample of natural gas contains 5% by volume of H_2S, calculate the mass of ethanolamine required to remove all the H_2S from a 1000 dm^3 sample of gas, measured under room conditions.

.....

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.....

The H_2S can be recovered by warming the solution to 120 °C, when the above reaction is reversed. The ethanolamine can then be recycled.

For Examiner's Use

(iv) What *type* of reaction is occurring here?

.....

The recovered H_2S is converted to sulfur by the following two reactions.

I Part of the H_2S is burned in air.

$$H_2S + 1.5O_2 \longrightarrow SO_2 + H_2O$$

II The gas stream resulting from reaction **I** is then blended with the remaining H_2S and fed into an iron oxide catalyst bed, where sulfur and water are produced according to the following equation.

$$2H_2S(g) + SO_2(g) \longrightarrow 3S(g) + 2H_2O(g)$$

(v) Use the following data to calculate $\Delta H^{\ominus}$ for the reaction between H_2S and SO_2.

compound	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
$H_2S(g)$	–21
$SO_2(g)$	–297
$H_2O(g)$	–242
S(g)	+11

$\Delta H^{\ominus}$ = ... kJ mol^{-1}

[8]

[Total: 12]

Q17.

2 Acetals are compounds formed when aldehydes are reacted with an alcohol and an acid catalyst. The reaction between ethanal and methanol was studied in the inert solvent dioxan.

For Examiner's Use

$$\underset{\text{ethanal}}{CH_3CHO} + \underset{\text{methanol}}{2CH_3OH} \overset{H^+}{\rightleftharpoons} \underset{\text{acetal } \mathbf{A}}{CH_3CH(OCH_3)_2} + H_2O$$

(a) When the initial rate of this reaction was measured at various starting concentrations of the three reactants, the following results were obtained.

experiment number	$[CH_3CHO]$ / mol dm^{-3}	$[CH_3OH]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	relative rate
1	0.20	0.10	0.05	1.00
2	0.25	0.10	0.05	1.25
3	0.25	0.16	0.05	2.00
4	0.20	0.16	0.10	3.20

(i) Use the data in the table to determine the order with respect to each reactant.

order with respect to $[CH_3CHO]$ .....

order with respect to $[CH_3OH]$ .....

order with respect to $[H^+]$ .....

(ii) Use your results from part **(i)** to write the rate equation for the reaction.

.....

(iii) State the units of the rate constant in the rate equation .....

(iv) Calculate the relative rate of reaction for a mixture in which the starting concentrations of all three reactants are 0.20 mol dm^{-3}.

relative rate = ...

[6]

(b) The concentration of the acetal product was measured when experiment number 1 was allowed to reach equilibrium. The result is included in the following table.

For Examiner's Use

	$[CH_3CHO]$ /mol dm^{-3}	$[CH_3OH]$ /mol dm^{-3}	$[H^+]$ /mol dm^{-3}	[acetal **A**] /mol dm^{-3}	$[H_2O]$ /mol dm^{-3}
at start	0.20	0.10	0.05	0.00	0.00
at equilibrium	(0.20–***x***)			***x***	
at equilibrium				0.025	

(i) Complete the second row of the table in terms of ***x***, the concentration of acetal **A** at equilibrium. You may wish to consult the chemical equation opposite.

(ii) Using the [acetal **A**] as given, 0.025 mol dm^{-3}, calculate the equilibrium concentrations of the other reactants and products and write them in the third row of the table.

(iii) Write the expression for the equilibrium constant for this reaction, K_c, stating its units.

K_c = ... units = ...

(iv) Use your values in the third row of the table to calculate the value of K_c.

K_c = ...

[9]

[Total: 15]

Q18.

2 **(a)** **(i)** What is meant by the term *ligand* as applied to the chemistry of the transition elements?

For Examiner's Use

.....

(ii) Describe the type of bonding that occurs between a ligand and a transition element.

.....

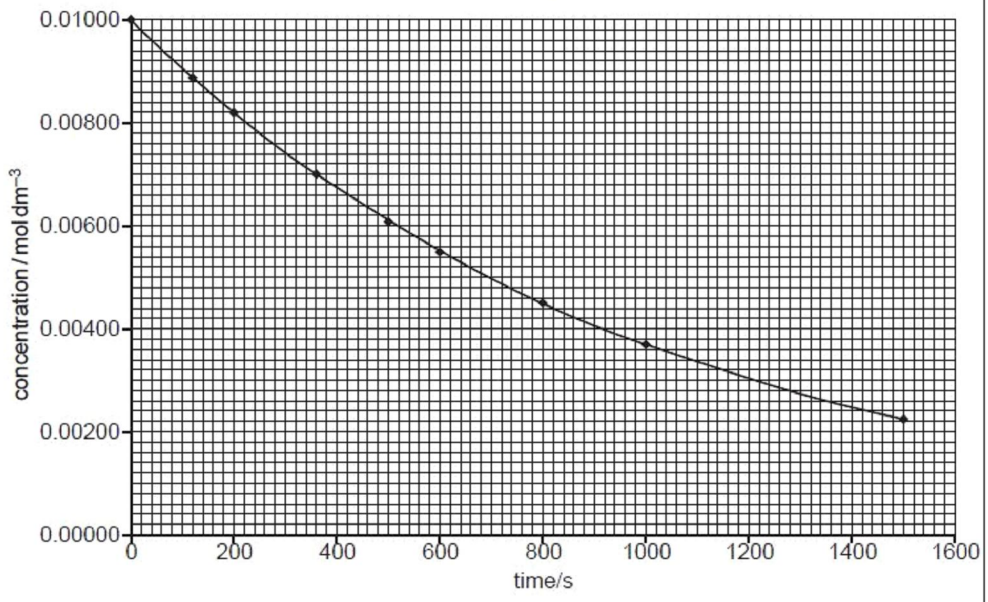
[2]

(b) Chromium hexacarbonyl undergoes the following ligand replacement reaction.

$$Cr(CO)_6 + PR_3 \longrightarrow Cr(CO)_5PR_3 + CO$$

Two separate experiments were carried out to study the rate of this reaction.
In the first experiment, the ligand PR_3 was in a large excess and $[Cr(CO)_6]$ was measured with time. The results are shown on the graph below.

In the first experiment, the ligand PR_3 was in a large excess and $[Cr(CO)_6]$ was measured with time. The results are shown on the graph below.



In the second experiment, $Cr(CO)_6$ was in a large excess, and $[PR_3]$ was measured with time. The following results were obtained.

time / s	$[PR_3]$ / mol dm^{-3}
0	0.0100
120	0.0076
200	0.0060
360	0.0028

(i) Plot the data in the table on the graph above, using the same axis scales, and draw the best-fit line through your points.

For Examiner's Use

(ii) Use the graphs to determine the order of reaction with respect to $Cr(CO)_6$ and PR_3. In each case explain how you arrived at your answer.

$Cr(CO)_6$

.....

.....

PR_3

.....

.....

(iii) Write the rate equation for the reaction, and calculate a value for the rate constant, using the method of initial rates, or any other method you prefer.

.....

.....

.....

.....

(iv) State the units of the rate constant.

.....

(v) Four possible mechanisms for this reaction are given below. Draw a **circle** around the letter next to the **one** mechanism which is consistent with the rate equation you have written in **(iii)**.

A
$Cr(CO)_6 \longrightarrow Cr(CO)_5 + CO$ fast
$Cr(CO)_5 + PR_3 \longrightarrow Cr(CO)_5PR_3$ slow

B
$Cr(CO)_6 \longrightarrow Cr(CO)_5 + CO$ slow
$Cr(CO)_5 + PR_3 \longrightarrow Cr(CO)_5PR_3$ fast

C
$Cr(CO)_6 + PR_3 \longrightarrow [OC\text{---}Cr(CO)_4\text{---}PR_3] \longrightarrow Cr(CO)_5PR_3 + CO$
(transition state)

D
$Cr(CO)_6 + PR_3 \longrightarrow Cr(CO)_6PR_3$ slow
$Cr(CO)_6PR_3 \longrightarrow Cr(CO)_5PR_3 + CO$ fast

Explain your answer.

.....

.....

[9]

[Total: 11]

Q19.

For Examiner's Use

3 **(a)** Catalysts can be described as homogeneous or heterogeneous.

(i) What is meant by the terms *homogeneous* and *heterogeneous*?

.....

.....

(ii) By using iron and its compounds as examples, outline the different modes of action of homogeneous and heterogeneous catalysis.
Choose **one** example of each type, 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,
- outline how the catalyst you have chosen works to decrease the activation energy.

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[8]

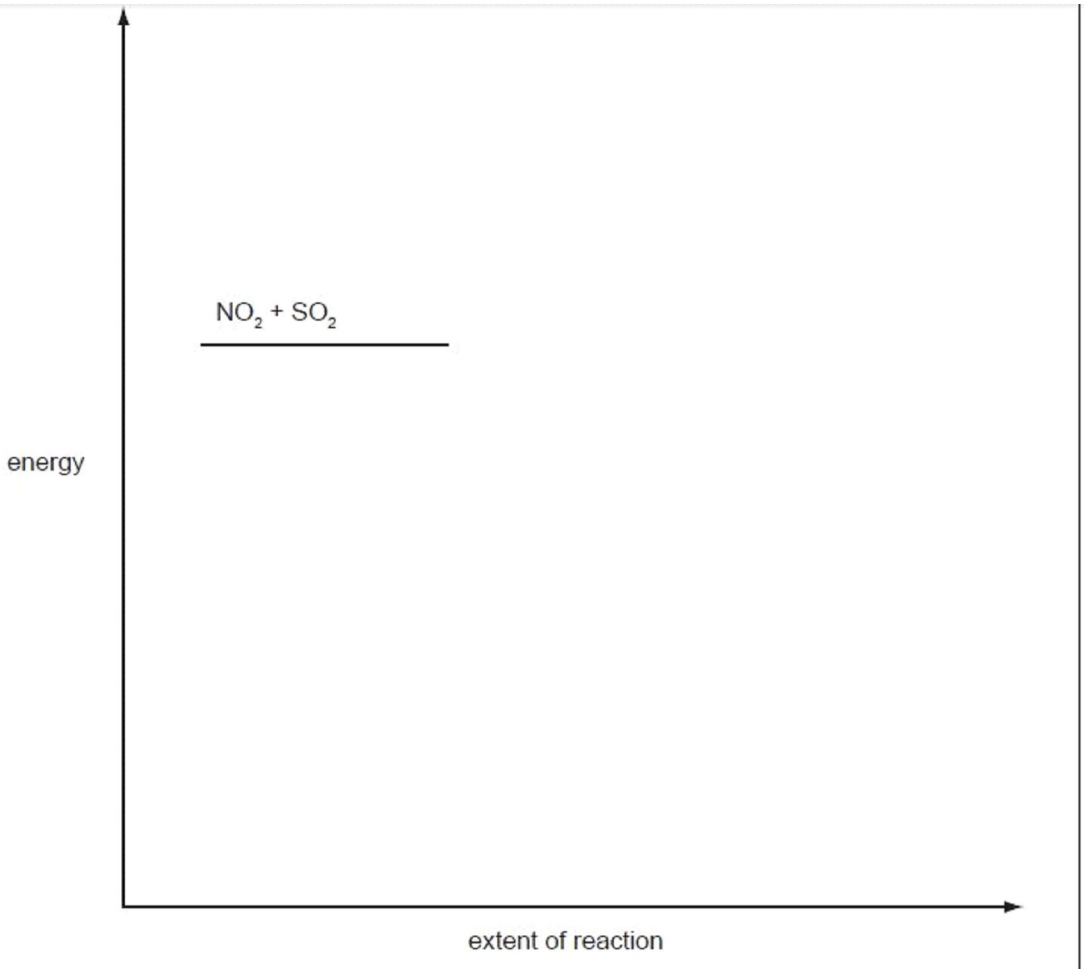
(b) The reaction between SO_2, NO_2 and O_2 occurs in two steps.

$$NO_2 + SO_2 \rightarrow NO + SO_3 \qquad \Delta H_1^{\ominus} = -88\ \text{kJ mol}^{-1}$$

$$NO + \tfrac{1}{2}O_2 \rightarrow NO_2 \qquad \Delta H_2^{\ominus} = -57\ \text{kJ mol}^{-1}$$

The activation energy of the first reaction, E_{a_1}, is higher than that of the second reaction, E_{a_2}.

Use the axes below to construct a fully-labelled reaction pathway diagram for this reaction, labelling E_{a_1}, E_{a_2}, $\Delta H_1^{\ominus}$ and $\Delta H_2^{\ominus}$.



[2]

[Total: 10]

Q20.

2 Nitrogen oxides in the atmosphere are homogeneous catalysts in the formation of acid rain.

For Examin Use

(a) What is meant by the following terms?

catalyst

.....

.....

homogeneous

.....

.....

[2]

(b) **(i)** State a major source of nitrogen oxides in the atmosphere, explaining how they are formed.

.....

.....

.....

(ii) Use equations to describe the chemical role played by nitrogen oxides in the formation of acid rain.

.....

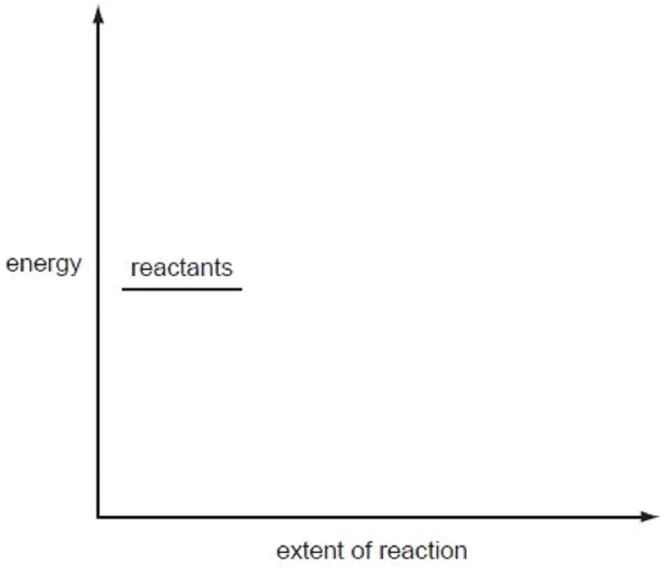
.....

.....

.....

[5]

(c) Use the following axes to draw a fully labelled reaction pathway diagram showing the effect of a catalyst on an exothermic reaction. Label the ΔH and E_a values.



[3]

[Total: 10]

Q21.

4 **(a)** Explain what is meant by the term *bond energy*.

.....

.....

[2]

(b) **(i)** Describe and explain the trend in bond energies of the C–X bond in halogenoalkanes, where X = F, Cl, Br or I.

.....

.....

(ii) Describe the relationship between the reactivity of halogenoalkanes, RX, and the bond energies of the C–X bond.

.....

.....

[3]

(c) Use the *Data Booklet* to suggest an explanation as to why CFCs such as CF_2Cl_2 are much more harmful to the ozone layer than fluorocarbons such as CF_4 or hydrocarbons such as butane, C_4H_{10}.

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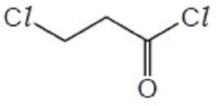
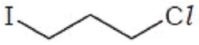
[3]

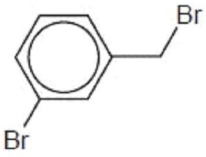
(d) Predict the products of the following reactions and draw their structures in the boxes below. The molecular formula of each product is given, where X = Cl, Br or I.

H_2O + 

→ $C_3H_5O_2X$

H_2O + 

→ C_3H_7OX

H_2O + 

→ C_7H_7OX

[3]

(e) Ethane reacts with chlorine according to the following equation.

$$C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$$

(i) State the conditions needed for this reaction.

.....

(ii) State the *type of reaction* occurring here.

.....

One of the steps during this reaction is the following process.

$$Cl^{\bullet} + CH_3CH_3 \rightarrow HCl + CH_3CH_2^{\bullet}$$

(iii) Use the *Data Booklet* to calculate the enthalpy change, ΔH, of this step.

ΔH = ... kJ mol^{-1}

(iv) Use the *Data Booklet* to calculate the enthalpy change, ΔH, of the similar reaction:

$$I^{\bullet} + CH_3CH_3 \rightarrow HI + CH_3CH_2^{\bullet}$$

ΔH = ... kJ mol^{-1}

(v) Hence suggest why it is **not** possible to make iodoethane by reacting together iodine and ethane.

.....

(vi) Complete the following equations of some possible steps in the formation of chloroethane.

$Cl_2 \rightarrow$ .....

$Cl^{\bullet} + CH_3CH_3 \rightarrow HCl + CH_3CH_2^{\bullet}$

$CH_3CH_2^{\bullet}$ + ... → ..... + ...

..... + ... → CH_3CH_2Cl

[8]

[Total: 19]

Q22.

3 **(a)** Write equations, with state symbols, to define the following.

(i) the C–Br bond energy in CH_3Br

.....

(ii) the A*l*–C*l* bond energy in A*l*C*l*$_3$

.....

[3]

(b) **(i)** Describe and explain the trend in bond energies of the bonds in C*l*$_2$, Br_2 and I_2.

.....

.....

.....

(ii) Fluorine, F_2, does **not** follow this trend.
Suggest a possible reason why.

.....

.....

[3]

(c) **(i)** Use data from the *Data Booklet* to calculate the enthalpy change of the following reaction.

$$H_2(g) + X_2(g) \rightarrow 2HX(g)$$

when X = C*l*

ΔH = ... kJ mol^{-1}

when X = I

ΔH = ... kJ mol^{-1}

(ii) Use these results to describe and explain the trend in the thermal stabilities of the hydrides of Group VII.

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.....

.....

[5]

(d) Bromine reacts with hot NaOH(aq) to give a solution which on cooling produces white crystals of compound **A**.
A has the following percentage composition by mass: Na, 15.2; O, 31.8; Br, 53.0.

The remaining solution contains mostly NaBr, with a little of compound **A**.

(i) Calculate the empirical formula of **A**.

(ii) Construct an equation for the reaction between Br_2 and hot NaOH(aq).

.....

[4]

[Total: 15]