RAFFLES INSTITUTION
2017 YEAR 5 PROMOTION EXAMINATION

Higher 2

CHEMISTRY

27 September 2017
2 h 30 min

Additional Materials: Multiple Choice Answer Sheet
Data Booklet
Writing Paper
Graph Paper

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number in the spaces provided on the OMR Answer Sheet, the cover sheet on **page 11** and the writing paper used for Section **C**.

Do not use staples, paper clips, highlighters, glue or correction fluid.

This paper consists of three sections, **A**, **B** and **C**. Answer **all** questions.

Section A (16 marks)
You must answer this section first. The OMR Answer Sheet will be collected **35 minutes** after the commencement of the examination.

There are **sixteen** questions in this section. For each question, there are four possible answers **A**, **B**, **C** and **D**.

Choose the one you consider correct and record your choice in **soft pencil** on the OMR Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in the question booklet.

Section B (34 marks)
Answers to this section are to be written on the question paper in the spaces provided.

Section C (40 marks)
Answers to this section are to be written on the writing paper provided.

Write in dark blue or black pen. You may use a soft pencil for any diagrams, graphs or rough working.

You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten your answers to Section **C** securely together. Answers to Sections **A**, **B** and **C** are to be handed in separately.

This document consists of **22** printed pages.

Section A

For each question, there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

1 Which statement about relative molecular mass is correct?

A It is the sum of the relative isotopic masses of the most abundant isotope of each atom within the molecule.

B It is the ratio of the weighted average mass of a molecule to $\frac{1}{12}$ the mass of 1 mole of ^{12}C atoms.

C It is the ratio of the weighted average mass of 6.02×10^{23} molecules to the mass of a ^{12}C atom.

D It is the sum of the relative atomic masses of all the atoms within the molecule.

2 A cation $\mathbf{G}^{2+}$ is isoelectronic to PH_3.

What is the ground state electronic configuration of **G**?

A $1s^2\,2s^2\,2p^6\,3s^2\,3p^4$

B $1s^2\,2s^2\,2p^6\,3s^2\,3p^6$

C $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^2$

D $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2$

3 Which particles have one unpaired d electron?

1 copper ion in Cu_2O

2 zinc ion in $Zn(NO_3)_2$

3 titanium ion in $Ti_2(SO_4)_3$

A 3 only

B 1 and 2

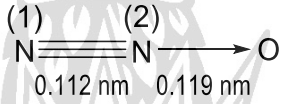
C 1 and 3

D 2 and 3

4 The table below shows some typical bond lengths.

bond	bond length / nm
N=N	0.120
N≡N	0.110
N–O	0.147
N=O	0.115

The bond lengths in nitrous oxide, N_2O, are not what might be expected. The nitrogen–nitrogen bond length in N_2O is 0.112 nm and the nitrogen–oxygen bond length is 0.119 nm.



Which statement explains why the N≡N bond length in N_2O is longer than 0.110 nm?

A The π bonds between N(1) and N(2) are weakened by the dative covalent bond between N(2) and O.

B The electrons in the O atom are attracted towards the π bonds between N(1) and N(2).

C The electrons in the unhybridised 2p orbitals on N(1) and N(2) repel one another.

D The π electrons between N(1) and N(2) are delocalised over N(2) and O.

5 A frictionless gas syringe contains gas **J** and 0.058 g of a volatile liquid **L** (M_r = 46.0). Upon heating to 100 °C, liquid **L** is completely vaporised. The gases occupy a total volume of 80 cm^3.

Atmospheric pressure is 101 kPa.

Assuming that the gases behave ideally and do not react with each other, what is the mole fraction of **J** in the gaseous mixture?

A 0.999

B 0.870

C 0.516

D 0.484

6 The lattice energies (LE) of two compounds are given below.

compound	experimental LE / kJ mol^{-1}
NaF	–915
MgO	–3933

Which statement best explains the difference between the two values?

A The radius of the oxide ion is greater than that of the fluoride ion.

B The charge on the magnesium ion is greater than that on the sodium ion.

C The radius of the magnesium atom is smaller than that of the sodium atom.

D The difference in electronegativity between sodium and fluorine is greater than that between magnesium and oxygen.

7 Propanone reacts with iodine in the presence of sulfuric acid as the catalyst.

$$\underset{\text{propanone}}{CH_3COCH_3(aq)} + I_2(aq) \xrightarrow{H_2SO_4} CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

Which is the most suitable method to determine the order of this reaction with respect to sulfuric acid?

A Measure the rate of change of $[H^+]$ several times by sampling and titrating against a standard solution of NaOH, but with a different initial $[CH_3COCH_3]$ each time.

B Measure the rate of change of $[I_2]$ several times by sampling and titrating against a standard solution of $Na_2S_2O_3$, but with a different initial $[I_2]$ each time.

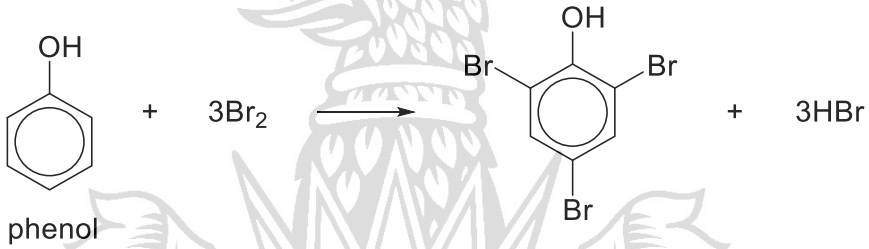
C Measure the rate of change of electrical conductivity several times, but at a different temperature each time.

D Measure the rate of decolourisation of I_2 several times, but with a different initial $[H_2SO_4]$ each time.

8 Bromide ions can be oxidised by bromate(V) ions under acidic conditions.

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$$

The progress of the reaction may be followed by adding a small amount of phenol together with three drops of methyl red indicator. The bromine produced during the above reaction reacts quickly with phenol as shown below.



phenol

Once all the phenol is consumed, any additional bromine that is produced will bleach the indicator completely. The time taken, t, for the complete disappearance of the red colour of the indicator is measured.

experiment number	volume of $KBrO_3$ / cm^3	volume of KBr / cm^3	volume of H_2SO_4 / cm^3	volume of phenol / cm^3	volume of water / cm^3	time, t / s
1	5	25	30	2	40	104
2	5	25	60	2	10	26
3	10	25	60	2	5	13
4	5	50	15	2	30	208
5	10	100	30	4	60	**x**

Which of the following statements is correct?

A The value of **x** is 416.

B The overall order of the reaction is 4.

C The units of the rate constant are $mol^{-2}\ dm^6\ s^{-1}$.

D Increasing the concentration of phenol added will result in a smaller value of t.

9 The Harcourt and Esson reaction is shown below.

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

The rate equation of the reaction is rate = $k[H_2O_2][I^-]$.

The following two reaction mixtures are prepared to study the change in concentration of H_2O_2 during the reaction.

reaction mixture	initial $[H_2O_2]$ / mol dm^{-3}	initial $[I^-]$ / mol dm^{-3}	initial $[H^+]$ / mol dm^{-3}
I	0.0200	0.400	0.400
II	0.0200	0.200	0.200

The half-life of H_2O_2 in reaction mixture **I** is 80 s.

How long will it take for the mole ratio of H_2O_2 to I_2 to reach 1:7 in reaction mixture **II**?

A 480 s
B 240 s
C 160 s
D 80 s

10 Equal volumes of SO_2 and O_2 gases are mixed in a container and left to react. After equilibrium has been reached, the partial pressure of SO_3 is found to be 50% of the total pressure.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

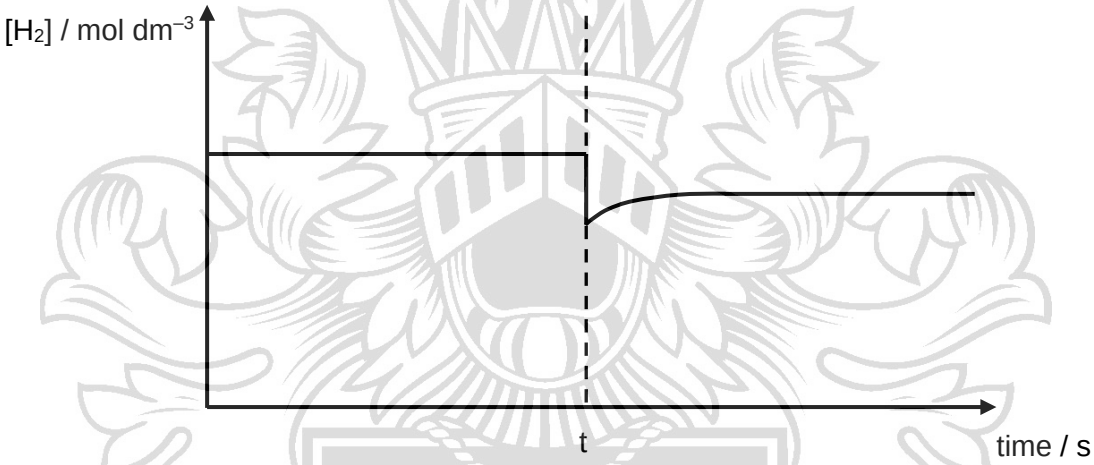
What is the mole fraction of SO_2 in the equilibrium mixture?

A $\frac{1}{8}$ **B** $\frac{1}{4}$ **C** $\frac{1}{3}$ **D** $\frac{1}{2}$

11 At 60 °C, a gas syringe contains a mixture of $CS_2(g)$, $H_2(g)$, $CH_4(g)$ and $H_2S(g)$, in equilibrium.

$$CS_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2S(g) \quad \Delta H^{\ominus} > 0$$

The graph below shows the concentration of H_2 gas against time. The reaction mixture in the syringe is subjected to a change at time t.

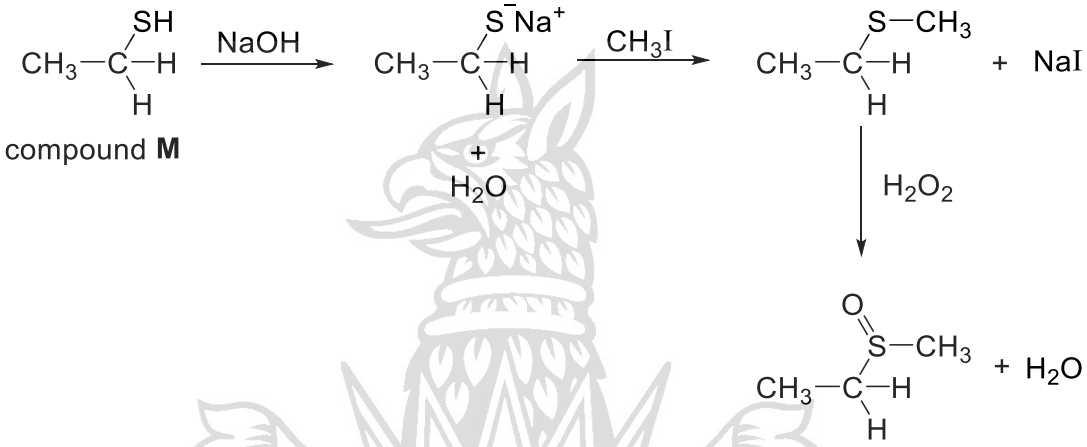


Which of the following changes, when carried out separately, could have given the graph above?

1 increasing the volume of the mixture by pulling the plunger
2 lowering the temperature in the syringe from 60 °C to 50 °C
3 adding a small amount of Ar(g), while keeping the pressure and temperature in the syringe constant

A 1 only
B 2 only
C 1 and 3
D 1, 2 and 3

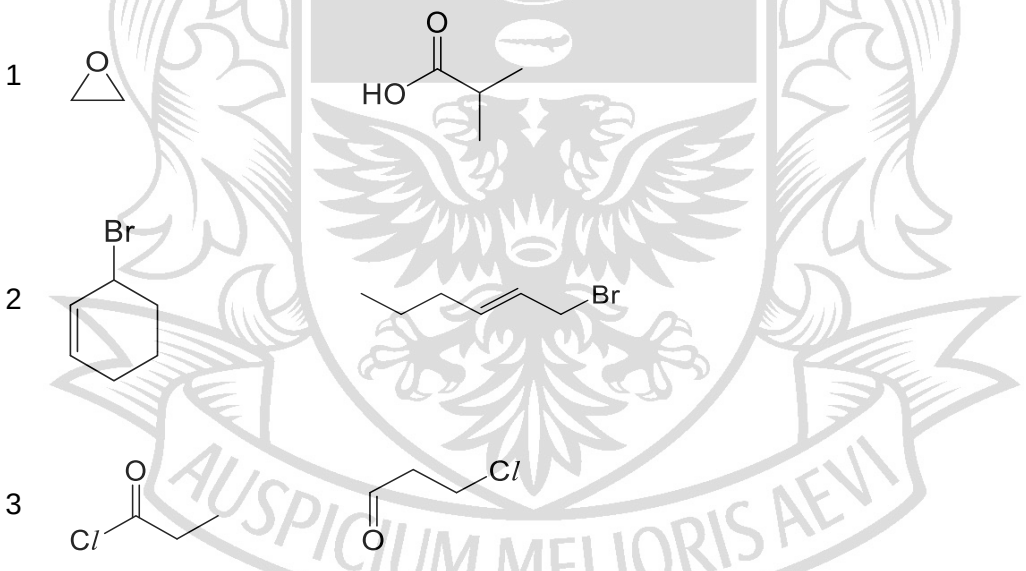
12 Compound **M** undergoes a sequence of reactions.



Which of the following reactions did **not** occur?

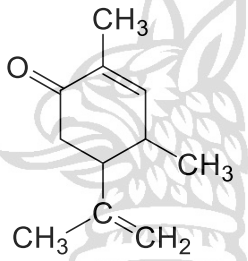
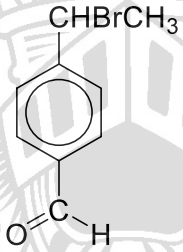
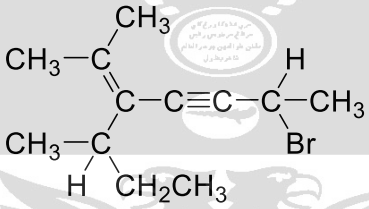
A substitution
B oxidation
C addition
D acid-base

13 In which pairs do both compounds have the same empirical formula?



A 1 only
B 1 and 3
C 2 and 3
D 1, 2 and 3

14 Three molecules **P**, **Q** and **R** have the following structures:

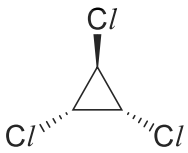
P	
Q	
R	

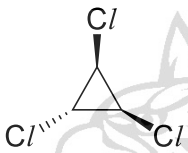
Which molecules have two chiral carbons and six π electrons?

A **P** only
B **P** and **R**
C **Q** and **R**
D **P**, **Q** and **R**

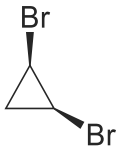
15 Which of the following pairs are cis-trans isomers?

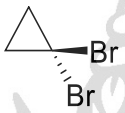
A



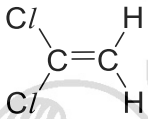


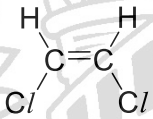
B



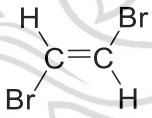


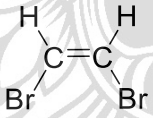
C





D





16 Which of the following reagents and conditions are the most favourable for forming hexabromoethane from ethane?

A excess Br_2, in the dark

B limited Br_2, in the dark

C excess Br_2, in the presence of ultraviolet light

D limited Br_2, in the presence of ultraviolet light

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Higher 2

CANDIDATE NAME			
CLASS		INDEX NUMBER	

CHEMISTRY 9729

27 September 2017

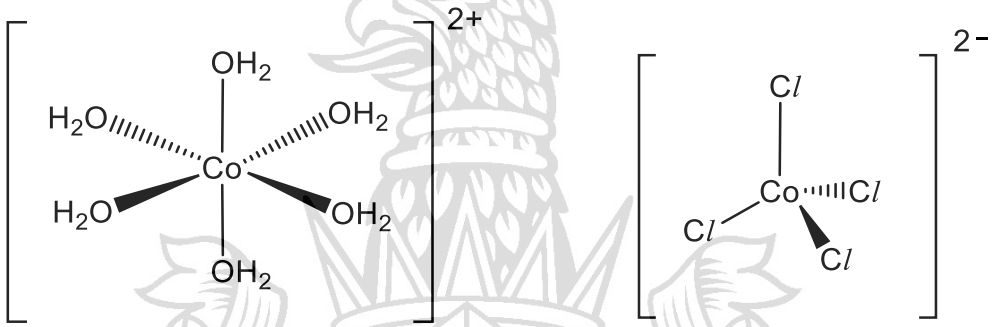
Section		Marks		
A				/ 16
B	B1			/ 14
	B2			/ 20
C	C1			/ 20
	C2			/ 20
Total				/ 90
Percentage				/ 100
Penalty (–1%)		sig. fig.	units	others:
Final Score				/ 100
Grade				

For examiner's use

Section B (34 marks)

This section consists of **2** questions.
Answer **all** the questions in this section in the spaces provided.

1 Cobalt(II) ions form various coloured complexes such as $Co(H_2O)_6^{2+}$ and $CoCl_4^{2-}$.



$Co(H_2O)_6^{2+}$ $CoCl_4^{2-}$

In aqueous solution, cobalt(II) ions exist as faint pink $Co(H_2O)_6^{2+}$ complex. In the presence of chloride ions, *reaction 1* occurs, with the formation of blue $CoCl_4^{2-}$ complex. This reaction involves the breaking of Co–O bonds and forming of Co–Cl bonds.

reaction 1: $Co(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6H_2O(l)$ $\Delta H > 0$
faint pink blue

(a) (i) Suggest a reason why *reaction 1* is endothermic.

……

……[1]

(ii) Predict, with a reason, the sign of the entropy change (ΔS) of *reaction 1*.

sign of ΔS: ……

reason: ……

……[1]

For examiner's use

(b) Equal volumes of 12 mol dm^{-3} HC*l* solution and 0.8 mol dm^{-3} of $Co(H_2O)_6^{2+}$ are mixed at a temperature of 298 K. The equilibrium concentration of $CoCl_4^{2-}$ is 3.3×10^{-3} mol dm^{-3}.

(i) Write an expression for K_c and state its units.

.....[2]

(ii) Calculate the value of K_c at 298 K.

[3]

(iii) State a method by which the concentration of $CoCl_4^{2-}$ in a sample can be determined.

.....

.....[1]

For examiner's use

(c) Deduce how K_c might alter when

(i) temperature is increased,

……

……

……

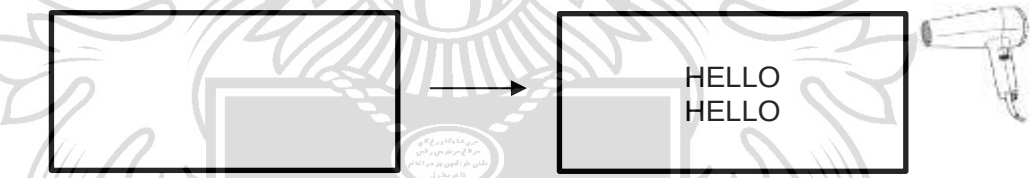
……[2]

(ii) NaC*l*(s) is added.

……

……[1]

(d) A solution of $Co(H_2O)_6^{2+}$ and Cl^- ions can be used as an invisible ink. Words written with this ink on white paper are invisible initially as the pink colour of the $Co(H_2O)_6^{2+}$ complex is very faint. However, the words will appear upon heating with a hair dryer.



words written are invisible initially words appear upon heating

(i) With reference to *reaction 1* on page **12**, explain why the words appear upon heating.

……

……

……

……[2]

(ii) The paper with the words is heated until it is completely dry.

Suggest and explain whether the words could be made "invisible" again by decreasing the temperature.

……

……[1]

[Total: 14]

For examiner's use

2 The table below lists the data of some physical and thermodynamic properties of alkanes.

alkane	boiling point / K	$\Delta H_c^{\ominus}$ / kJ mol^{-1}	CO_2 emissions per unit of energy released / 10^{-3} mol kJ^{-1}
methane	109.1	–890.3	1.123
ethane	184.5	–1559.7	1.282
propane	231.0	–2219.2	1.352
cyclopropane	240.0	–2019.4	1.486
2-methylpropane	261.4	–2868.5	1.394
butane	272.6	–2876.5	1.391
cyclobutane	285.5	–2720.9	1.470
2,2-dimethylpropane	282.6	–3492.5	1.432
2-methylbutane	301.0	–3503.4	1.427
pentane	309.2	–3509.1	1.425
cyclopentane	322.0	–3289.4	1.520
2-methylpentane	333.4	–4157.0	1.443
hexane	342.1	–4163.0	1.441
cyclohexane	353.9	–3919.5	1.531

(a) Alkanes are very unreactive. Suggest **two** reasons why this is the case.

……

……

……

……[2]

(b) Explain why the boiling point of propane is higher than that of ethane.

……

……

……

……[2]

(c) Alkanes, on complete combustion, give carbon dioxide and water.

(i) State the change in oxidation number of carbon when ethane is converted to carbon dioxide.

oxidation number of C changes from: ……. to ……. [1]

For examiner's use

(ii) The magnitudes of $\Delta H_c^{\ominus}$ increases by approximately 660 kJ mol^{-1} from ethane to propane and from propane to butane.

Suggest what this regular increase of approximately 660 kJ mol^{-1} in the magnitude of $\Delta H_c^{\ominus}$ represents.

……

……[1]

(iii) As the combustion of alkanes is highly exothermic, alkanes can be used as fuels. Petroleum consists of large saturated hydrocarbons, while natural gas is a mixture of hydrocarbons comprising mainly methane. However, combustion of alkanes produces carbon dioxide, which traps heat in Earth's atmosphere and worsens the global warming crisis.

Based on data given in the table, suggest why natural gas is a more environmentally friendly option compared to petroleum.

……

……[1]

(d) **(i)** Given that the $\Delta S^{\ominus}$ for the complete combustion of methane is –7.10 J mol^{-1} K^{-1}, calculate $\Delta G^{\ominus}$ for this reaction.

[1]

(ii) Although the $\Delta G^{\ominus}$ for the combustion of methane is exergonic, methane will not spontaneously combust when it comes into contact with oxygen gas. Methane combusts only if it is ignited with a spark. Suggest why this is so.

……

……[1]

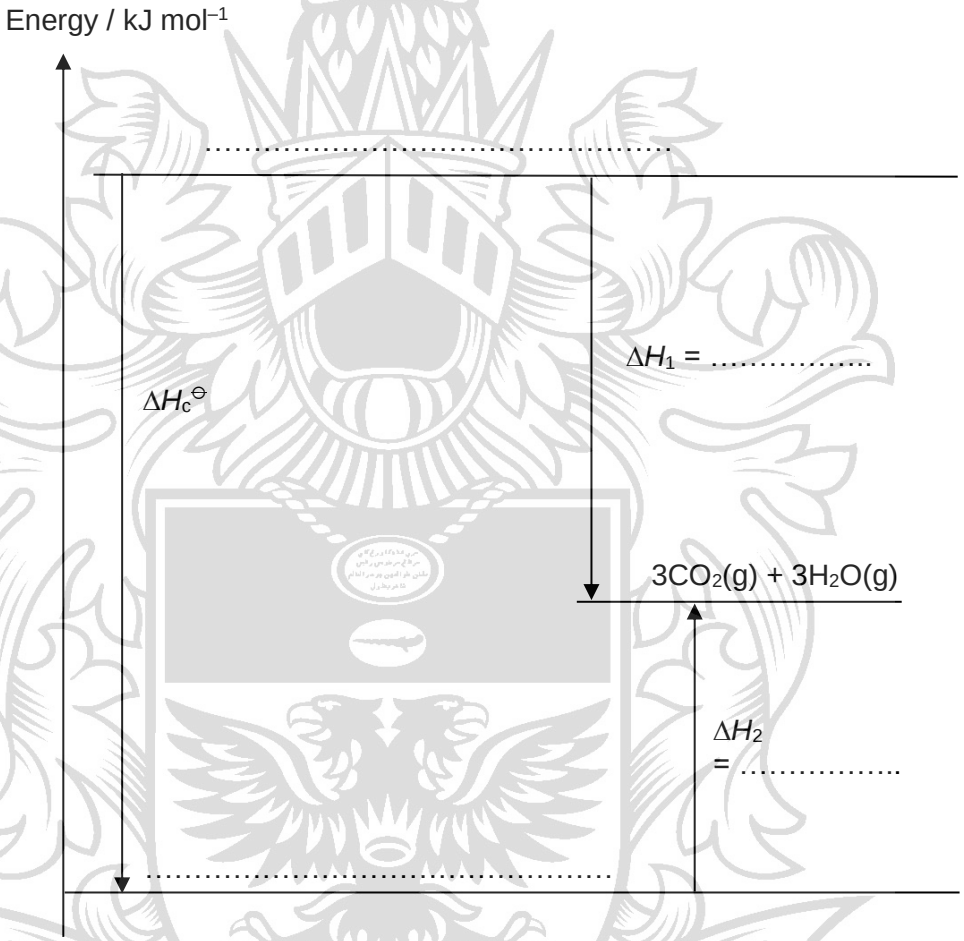
For examiner's use

(e) (i) The $\Delta H_c^{\ominus}$ for cyclopropane, C_3H_6, can be calculated by using the energy level diagram given below.

Given that the standard enthalpy change of vaporisation of water is +40.7 kJ mol^{-1} and using appropriate data from the *Data Booklet*,

- label each level in the energy level diagram with the appropriate molecular formulae and state symbols;
- calculate ΔH_1 and ΔH_2 and write their values in the spaces given below.

Hence, calculate the $\Delta H_c^{\ominus}$ for cyclopropane.



$\Delta H_c^{\ominus}$: ……

[4]

For examiner's use

(ii) State the C–C–C bond angle and the hybridisation of each C atom in cyclopropane. Hence, explain why the $\Delta H_c^{\ominus}$ value given in the table on page **15** is much more exothermic than the calculated value in **(e)(i)**.

……

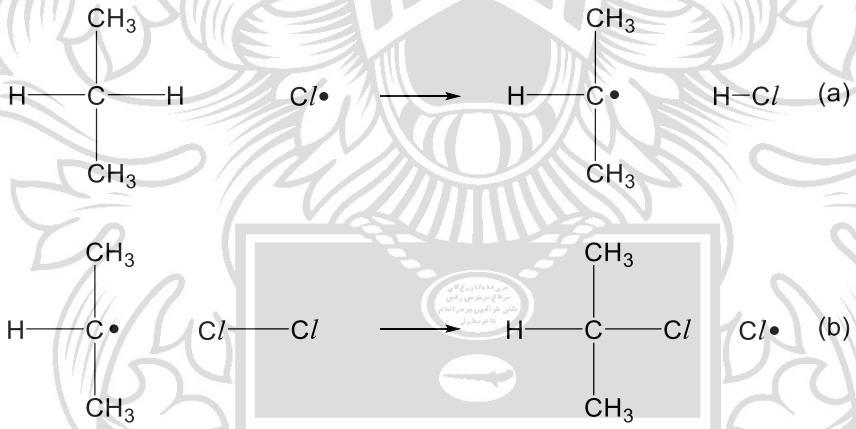
……

……[2]

(f) The mono-chlorination of propane to form 2-chloropropane proceeds via a free radical substitution mechanism. This mechanism consists of three steps: initiation, propagation and termination.

Initiation

Propagation



Then (a), (b), (a), (b)….

Termination

Answer **(f)(i)** and **(f)(ii)** in the mechanism above.

(i) Draw curly arrows to show the movement of electrons in the propagation steps.

[1]

(ii) A hydrocarbon by-product is formed in trace quantities in the termination step. Write an equation to show the formation of this hydrocarbon by-product. (No curly arrows are required.) [1]

For examiner's use

(g) If all the hydrogen atoms were equally reactive, the mono-chlorination of propane should give a 3:1 ratio of 1-chloropropane to 2-chloropropane. However, an experiment carried out at 25 ºC gave 45% 1-chloropropane and 55% 2-chloropropane, via the formation of primary and secondary free radical intermediates respectively.

(i) Based on the information given above, comment on the relative stability of the primary and secondary free radical intermediates.

……..…..

……[1]

(ii) Given that alkyl groups are electron donating groups, explain your answer to **(g)(i)**.

……..…..

……[1]

(iii) Hence, justify why the bond dissociation energy of the $(CH_3)_2CH–H$ bond is less endothermic than that of the $CH_3CH_2CH_2–H$ bond.

C–H bond	bond dissociation energy / kJ mol^{-1}
$CH_3CH_2CH_2–H$	422.2
$(CH_3)_2CH–H$	410.5

……..…..

……[1]

[Total: 20]

Section C (40 marks)

Answer **all** questions in this section.
Write your answers on the writing paper provided.
Begin **each** question on a **fresh sheet** of paper.

1 Nitrogen monoxide, NO, is a by-product of the combustion of hydrocarbon fuels in internal combustion engines and is readily converted into nitrogen dioxide, NO_2.

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

(a) In order to determine the rate equation for the reaction, an investigation was carried out at a constant temperature and with the same initial partial pressure of oxygen, ρ_{O_2}, for each experiment.

The following results were obtained.

initial rate / N m^{-2} s^{-1}	16.2	47.2	82.2	126	169
ρ_{NO} / N m^{-2}	0.30	0.50	0.66	0.82	0.95
$(\rho_{NO})^2$ / N^2 m^{-4}	0.09	0.25	0.44	0.67	0.90

(i) To determine the order of reaction with respect to ρ_{NO}, use these data to plot a suitable graph on the graph paper provided. [3]

(ii) State the order of reaction with respect to ρ_{NO}. Explain your answer. [2]

(b) To find the order of reaction with respect to ρ_{O_2}, the investigation in **(a)** was repeated at the same temperature with the initial ρ_{O_2} halved. A similar graph was plotted and the gradient at each point was half that obtained from the graph in **(a)(i)**.

Determine the order of reaction with respect to ρ_{O_2}. Explain your answer. [2]

(c) Construct the rate equation for the reaction between NO and O_2, and state the units for the rate constant. [2]

(d) NO_2 acts as a homogeneous catalyst in the atmospheric oxidation of SO_2 to SO_3 via a two-step process.

Write balanced equations to show the catalysis by NO_2. [2]

To remove pollutants (such as oxides of nitrogen) from the internal combustion engines, the exhaust gases are passed through a catalytic converter substrate, which is coated with platinum (Pt), palladium (Pd), or rhodium (Rh).

(e) The metal in a catalytic converter functions as a *heterogeneous* catalyst.
Explain what the term in *italics* means. [1]

(f) **(i)** With the aid of the Maxwell-Boltzmann distribution curve, explain how a catalyst increases the rate of a reaction. [3]

(ii) What effect will the presence of a catalyst have on the rate constant for a reaction? Explain your answer. [1]

The operating temperature of the catalytic converter may reach 700 ^{o}C and the transition metals, e.g. platinum, are suitable for use due to their high melting points.

(g) With the aid of a suitable diagram, explain why platinum has a high melting point. [2]

(h) Nickel is not used in the catalytic converter as a heterogeneous catalyst because it is prone to "poisoning" by molecules and ions with lone pairs of electrons. Explain what is "poisoning" and how it affects the catalytic property of nickel. [2]

[Total: 20]

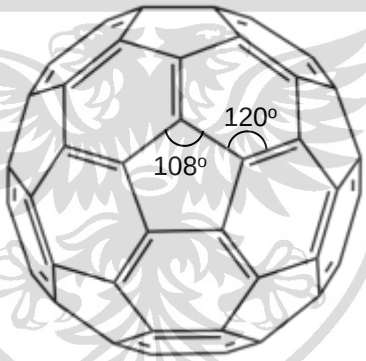
2 The two most common allotropes of carbon are diamond and graphite.

(a) Sketch the shape of the hybrid orbitals around a carbon atom in

(i) diamond [1]

(ii) graphite [1]

Besides diamond and graphite, carbon also exists as fullerenes, which is a series of hollow carbon molecules. Buckminsterfullerene, C_{60}, is a molecule with 60 carbon atoms arranged in pentagons and hexagons that are similar to those in a football:



Buckminsterfullerene, C_{60}

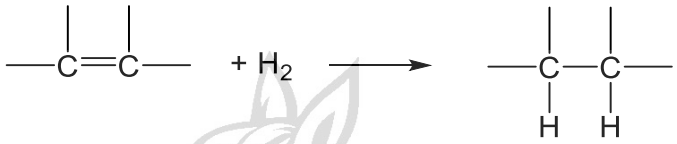
The C–C–C bond angle in a carbon pentagon is 108^{o}, while the C–C–C bond angle in a carbon hexagon is 120^{o} as shown above.

(b) Explain the following statements in terms of structure and bonding.

(i) Diamond and graphite are insoluble in all solvents, but C_{60} dissolves readily in non-polar solvents such as benzene. [2]

(ii) Graphite is an electrical conductor, while diamond and C_{60} are insulators. [4]

(c) Substances with carbon–carbon double bonds react with H_2 as shown by the equation below:



C_{60} reacts with hydrogen to form hydrofullerenes with the molecular formula $C_{60}H_n$.

(i) When 60 g of C_{60} is reacted with hydrogen gas at 673 K and 1.20×10^5 kPa, the volume of hydrogen gas is decreased by 69.9 cm^3. Show that the formula of the hydrofullerene formed is $C_{60}H_{36}$. [2]

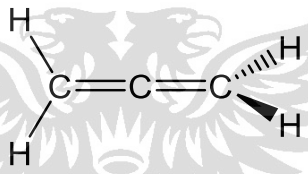
(ii) When C_{60} is reacted with excess hydrogen at high pressure and temperature, instead of forming the completely hydrogenated $C_{60}H_{60}$, it is found that the spherical C_{60} breaks apart and a mixture of hydrocarbons is formed.

With reference to the structure of the C_{60} molecule shown on page **21**, suggest why $C_{60}H_{60}$ is unstable and cannot be formed. [2]

(iii) A potential application of $C_{60}H_{36}$ is in hydrogen gas storage devices for electric vehicles powered by fuel cells. When heated, $C_{60}H_{36}$ decomposes to C_{60} and hydrogen gas which can be used as fuel to power an electric vehicle.

13.5 g of H_2 is needed for every 1 km travelled by an electric vehicle. Calculate the mass of $C_{60}H_{36}$ that is needed if the vehicle travels 100 km. [2]

A molecule of allene contains a carbon atom which forms double bonds with each of its two adjacent carbon atoms. The simplest allene, compound **X**, has a molecular formula of C_3H_4 and the following structure.



compound **X**

(d) Besides compound **X**, there are two other constitutional isomers that have the molecular formula C_3H_4. Draw the structures of these two isomers of **X**. [2]

(e) Another allene, compound **Y**, has the structure $CH_3CH=C=CHCH_3$ and is able to exhibit stereoisomerism.

(i) Name the type of stereoisomerism exhibited by compound **Y**. Draw two structures to illustrate this stereoisomerism. [3]

(ii) Which physical property is different for the two stereoisomers you have drawn in **(e)(i)**? [1]

[Total: 20]