SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 1

Candidate Name

Class

CHEMISTRY **8872/01**

JC2 Preliminary Examination 22 Sept 2017 (AM)
Paper 1 Multiple Choice 50 min

Additional Materials: Data Booklet
Optical Mark Sheet (OMS)

READ THESE INSTRUCTIONS FIRST

On the separate multiple choice OMS given, write your name, subject title and class in the spaces provided.
Shade correctly your FIN/NRIC number.

There are **30** questions in this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the one you consider correct and record your choice using a **soft pencil** on the separate OMS.

You are advised to fill in the OMS as you go along; no additional time will be given for the transfer of answers once the examination has ended.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer. Any rough working should be done in this question paper.
The use of an approved scientific calculator is expected, where appropriate.

Section A

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

1 In a titration, a 30.0 cm^3 sample of 0.05 mol dm^{-3} of the phosphoric acid, H_3PO_4, was found to require 15.00 cm^3 of 11.22 g dm^{-3} solution of potassium hydroxide to reach the endpoint. Which of the following is the salt formed from the reaction?

A KH_2PO_4

B K_2HPO_4

C K_3PO_4

D KPO_3

2 Which species are oxidised and reduced in the following reaction?

$$IO_3^- + 2I^- + 6H^+ + 6Cl^- \rightarrow 3ICl_2^- + 3H_2O$$

	species oxidised	species reduced
A	IO_3^-	I^-
B	I^-, IO_3^-	Cl^-
C	I^-	IO_3^-
D	H^+, Cl^-	IO_3^-

3 How many unpaired electrons are present in S and S^{2-} respectively?

	S	S^{2-}
A	1	0
B	1	2
C	2	0
D	2	2

4 Which statement about $(CH_3)_3NAlH_3$ is correct?

A It exist as a dimer.

B It contains hydrogen bonding.

C The A*l* atom is electron deficient.

D The bonds around the A*l* atom are in a tetrahedral arrangement.

5 In which substance must covalent bonds break on melting?

A Phosphorus(V) chloride

B Beryllium chloride

C Silicon carbide

D Iron(II) hydroxide

6 Which of the following elements has an oxide with a giant structure and a chloride which is readily hydrolysed?

A Silicon

B Sodium

C Carbon

D Phosphorus

7 Archaeologists used $_{14}C$, a radioactive isotope, in carbon dating. An artefact is analysed and its $_{14}C$ content is measured to be 20% of the typical initial amount of $_{14}C$ in trees. Given that the radioactive decay of $_{14}C$ has a half–life of 5500 years, what is the approximate age of this artefact?

A 1.10×10^4 years

B 1.28×10^4 years

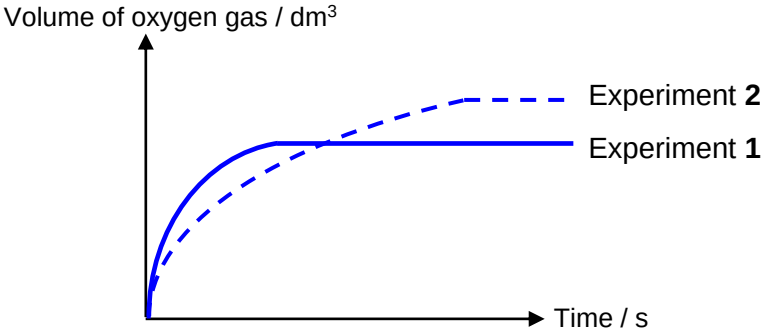
C 1.38×10^4 years

D 1.65×10^4 years

8 Experiments were carried out to investigate the rates of decomposition of 100 cm^3 of 1.0 mol dm^{-3} hydrogen peroxide, catalysed by manganese (IV) oxide.

$$H_2O_2\ (aq) \longrightarrow H_2O\ (l) + \tfrac{1}{2}\ O_2\ (g)$$

The volume of oxygen gas collected using a gas syringe was monitored. The results are shown in the diagram below.



Which of the following alteration to the experimental conditions in Experiment **1** would produce the curve observed in Experiment **2**?

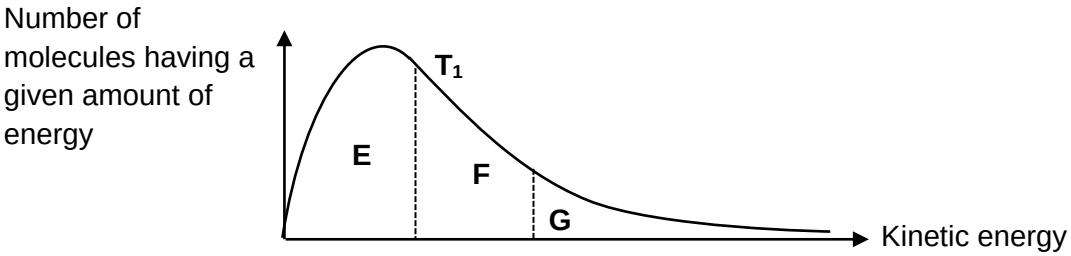
A Lowering the temperature.

B Decreasing the amount of MnO_2 used.

C Diluting the hydrogen peroxide solution with water.

D Adding 100 cm^3 of 0.1 mol dm^{-3} hydrogen peroxide.

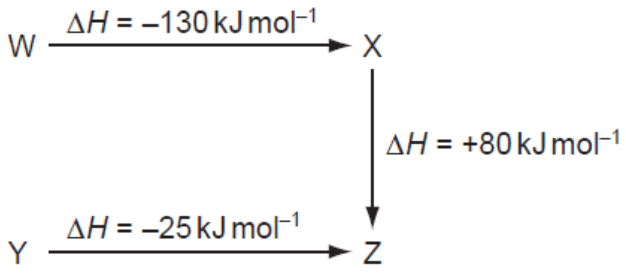
9 The Maxwell Boltzman distribution curve shows the number of molecules having a given amount of kinetic energy at constant temperature, $\mathbf{T_1}$.



How would the size of the areas labelled **E**, **F** and **G** change if a lower temperature, $\mathbf{T_2}$ was used?

	E	**F**	**G**
A	Increase	Increase	Decrease
B	Increase	Decrease	Decrease
C	Decrease	Increase	Increase
D	Decrease	Decrease	Increase

10 The diagram represents the energy changes for some reactions.



What are the natures of the conversions **W → Y**, **Y → X** and **Z→W**?

	W → Y	**Y → X**	**Z → W**
A	Exothermic	Endothermic	Endothermic
B	Exothermic	Exothermic	Endothermic
C	Endothermic	Exothermic	Exothermic
D	Endothermic	Endothermic	Exothermic

11 Consider the following equilibrium system:

$$2AlCl_3(g) \rightleftharpoons Al_2Cl_6(g)$$

Which of the following statements will cause the position of the equilibrium to shift to the left?

A Increasing the temperature.

B Pumping $AlCl_3$ gas into the vessel.

C Decreasing the volume of the vessel.

D Adding a solid catalyst into the vessel.

12 Cyanidin (Cy) is a water-soluble plant pigment which can be found in blackberries. Blackberry juice is usually preserved by the addition of a small amount of $SO_2(g)$ and the following equilibrium is set up:

$$CyH^+(aq) + SO_2(aq) + H_2O(l) \rightleftharpoons CySO_3H_2(aq) + H^+(aq)$$

What are the units for K_c?

A mol dm^{-3}

B mol dm^{-3} s^{-1}

C mol^{-1} dm^3

D no units

13 A solution of an acid **H** has the same pH as a solution of acid **J.** Equal dilution increases the pH of acid **H** more than that of acid **J**. Which of the following pairs of acids would show this behaviour?

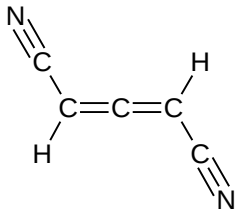
	H	**J**
A	H_3PO_4	HC*l*
B	HC*l*	CH_3CO_2H
C	HC*l*	H_2SO_4
D	CH_3CO_2H	H_2SO_4

14 What is the total number of isomers possible for the molecular formula of $C_2H_2Br_2$?

A 1 **C** 3

B 2 **D** 4

15 Which statement is **incorrect** for the compound shown below?



A There are 6 π bonds.

B There are 8 σ bonds.

C There are two different bond angles.

D There are three sp^2 hybridised carbons.

16 Samples of $C_6H_5CHCH_2$ and Br_2 were mixed under different conditions. Which pair of conditions and products are correctly paired together?

	Conditions	Product
A	Br_2 (aq)	$C_6H_4BrCH(OH)CH_2Br$
B	Br_2 (g), uv light	$C_6H_4BrCHCH_2$
C	Br_2 (g)	$C_6H_4BrCH(Br)CH_2Br$
D	Br_2 (g), Fe (s)	$C_6H_4BrCH(Br)CH_2Br$

17 Which of these statements is true for the reaction of 2,3,4−trimethylpenta−2,3,4−triol with concentrated sulfuric acid at 443 K.

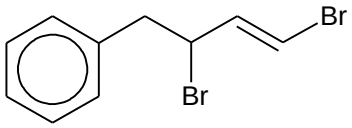
A Oxidation reaction taken place.

B Carbon dioxide gas is a by-product.

C There are a total of 8 possible geometrical isomers.

D Organic product with three carbon-carbon double bonds is formed.

18 Which of the following reagents and conditions will not yield any reaction with the compound shown below.



A Cold aqueous hydrogen cyanide with trace amounts of sodium hydroxide.

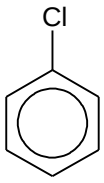
B Hot potassium dichromate in aqueous potassium hydroxide.

C Cold potassium manganate(VII) in aqueous sulfuric acid.

D Aqueous sodium hydroxide and heat.

19 Which of the following compounds would be the most inert towards a nucleophilic attack?

A



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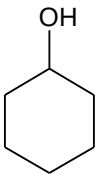
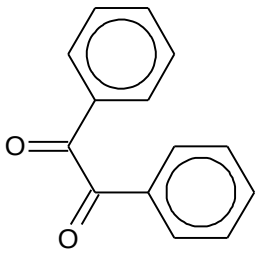
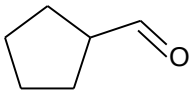


C



D



20 Penta−1,3−diene was heated with acidified potassium manganate(VII) to form compound **L** and **M**.

Compound **L** was then added to lithium aluminium hydride in dry ether to form compound **N**. Compound **N** was then bubbled with hydrogen bromide gas to form compound **O**.

Which of these statements can be correctly deduced from the information above?

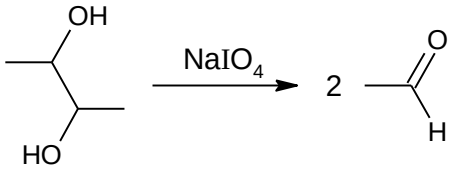
A Compound **O** cannot undergo further nucleophilic substitution with ethanolic potassium cyanide.

B 1 mol of compound **N** forms 1 mol of hydrogen gas when reacted with sodium metal.

C Compound **L** is a gas which forms white precipitate with calcium hydroxide.

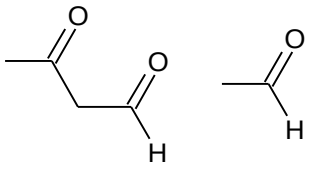
D Compound **M** is a non-polar acidic gas.

21 Buta-2,3-diol can be oxidized by $NaIO_4$ as shown below,

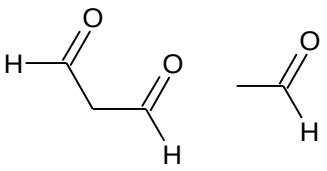


Deduce the products when $CH_3CH=C(CH_3)–CH_2–CH=CH(CH_3)$ is first treated with cold alkaline aqueous $KMnO_4$ followed by $NaIO_4$.

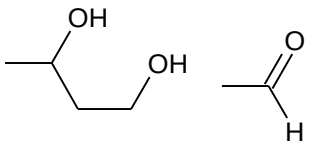
A



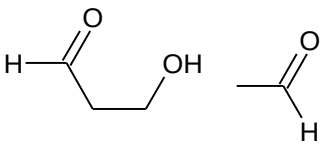
B



C



D



22 Which reagent could be used to distinguish between pentan-2-ol and pentan-2-one?

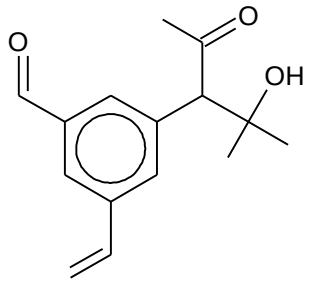
A Acidified potassium manganate(VII)

B Alkaline aqueous iodine

C Sodium carbonate

D Aqueous bromine

23 Which of the following chemical tests will yield a **positive** observation with the compound shown below?



A Fehling's solution

B Hot ethanolic silver nitrate

C Sodium carbonate

D Alkaline aqueous iodine

24 Which compound can undergo a reaction when treated with hot ethanolic potassium hydroxide?

A CH_2Br_2

B CBr_3CBr_3

C $(CH_3)_2CCBr_2$

D $CH_3CBr_2CH_3$

25 Which of these would have the lowest pH value in solution?

A $CH_2(Cl)CH_2CO_2H$

B $CH_2CH(Cl)CO_2H$

C $CH_3CO_2CH_2CH_3$

D $CH_3CH_2NH_2$

For **questions 26 – 30**, one or more of the numbered statements **1** to **3** may be correct. Decide whether each of the statements is or is not correct. The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is to be used as correct response.

26 Which of the following contain hydrogen bonding?

1 NH_4Cl (s)

2 $NH_3(l)$

3 $CH_3CH_2CH_2OH$ (l)

27 Which reaction represents standard enthalpy change at 298 K?

1 HBr (aq) + NaOH (aq) → NaBr (aq) + H_2O (l)

2 P_4 (s) → 4P (g)

3 H_2 (g) + Br_2 (g) → 2HBr (g)

28 At 50 °C, pure water is found to have a pH value of 6.6. Which of the following statements are true?

1 Concentration of hydrogen ion in water is higher at 50 °C compared to at 25°C.

2 The K_w value is smaller at 50 °C compared to at 25°C.

3 Water is acidic at 50 °C.

29 Which of these compounds are planar?

1 Ethene

2 Benzene

3 Propanone

30 Glucose is a simple molecular solid.

$HOCH_2CH(OH)CH(OH)CH(OH)CH(OH)CHO$

Which of the following statements are correct?

1 The hydrogen atom in the hydroxyl groups can form hydrogen bonds with water.

2 The hydrogen atom in the aldehyde group form hydrogen bonds with ethanol.

3 All the oxygen atoms in glucose can form hydrogen bonds with propanone.

END OF PAPER

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This document consists of __ 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 In a titration, a 30.0 cm^3 sample of 0.05 mol dm^{-3} of the phosphoric acid, H_3PO_4, was found to require 15.00 cm^3 of 11.22 g dm^{-3} solution of potassium hydroxide to reach the endpoint. Which of the following is the salt formed from the reaction?

A	KH_2PO_4
B	K_2HPO_4
C	K_3PO_4
D	KPO_3

Answer: B

$$n H_3PO_4 = \frac{30}{100} \times 0.05 = 0.0015 mol$$

$$n KOH = \frac{11.22}{56.1} \times \frac{15}{1000} = 0.003 mol$$

$0.0015\ H_3PO_4 \equiv 0.003\ KOH$

$H_3PO_4 \equiv 2\ KOH$

$\therefore$ K_2HPO_4 is formed.

2 Which species are oxidised and reduced in the following reaction?

$$IO_3^- + 2I^- + 6H^+ + 6Cl^- \rightarrow 3ICl_2^- + 3H_2O$$

	species oxidised	species reduced	
A	IO_3^-	I^-	
B	I^-, IO_3^-	Cl^-	
C	I^-	IO_3^-	
D	H^+, Cl^-	IO_3^-	

Answer: C

$$\underset{\textbf{+5}}{IO_3^-} + \underset{\textbf{-1}}{2I^-} + \underset{\textbf{+1}}{6H^+} + \underset{\textbf{-1}}{6Cl^-} \rightarrow \underset{\textbf{+1 -1}}{3ICl_2^-} + \underset{\textbf{+1}}{3H_2O}$$

3 How many unpaired electrons are present in S and S^{2-} respectively?

	S	S^{2-}
A	1	0
B	1	2
C	2	0
D	2	2

Answer: C

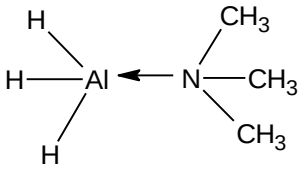
$_{16}S$: $1s^2 2s^2 2p^6 3s^2 3p^4$ (2 unpaired electron)

$_{16}S^{2-}$: $1s^2 2s^2 2p^6 3s^2 3p^6$ (0 unpaired electrons)

4 Which statement about $(CH_3)_3NAlH_3$ is correct?

A	It exist as a dimer.
B	It contains hydrogen bonding.
C	The Al atom is electron deficient.
D	The bonds around the Al atom are tetrahedrally arranged.

Answer: D



Al has energetically accessible orbitals to accept the lone pair of electrons form N. There are four bond pairs about Al. The shape about Al is tetrahedral.

5 In which substance must covalent bonds break on melting?

A	Phosphorus(V) chloride
B	Beryllium chloride
C	Silicon carbide
D	Iron(II) hydroxide

Answer: C

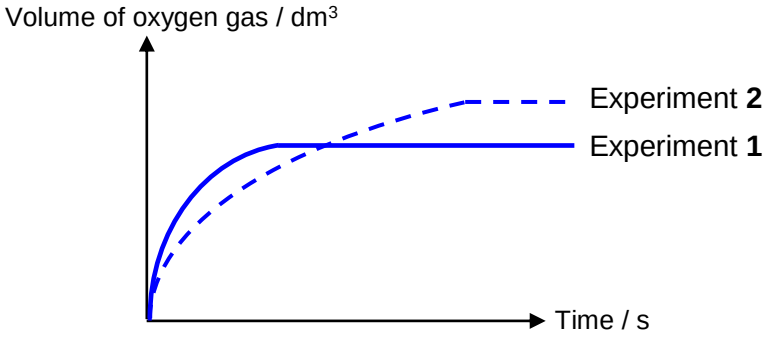
A and B are simple molecular compounds. C has a giant molecular structure and thus

	covalent bonds are broken during boiling. D has a giant ionic lattice structure.			
6	Which of the following elements has an oxide with a giant structure and a chloride which is readily hydrolysed?			
	A	Silicon		
	B	Sodium		
	C	Carbon		
	D	Phosphorus		
	Answer: A SiO_2 is a giant molecular compound. $SiCl_4$ is readily hydrolysed in water to form HCl. $SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl\ (aq)$			
7	Archaeologists used $_{14}C$, a radioactive isotope, in carbon dating. An artefact is analysed and its $_{14}C$ content is measured to be 20% of the typical initial amount of $_{14}C$ in trees. Given that the radioactive decay of $_{14}C$ has a half–life of 5500 years, what is the approximate age of this artefact?			
	A	1.10×10^4 years	**C**	1.38×10^4 years
	B	1.28×10^4 years	**D**	1.65×10^4 years
	Answer: B $\frac{C}{C_o} = \left(\frac{1}{2}\right)^n$ $\frac{20}{100} = \left(\frac{1}{2}\right)^n$ n = 2.32 $t_{1/2} = 2.32 \times 5500 = 1.28 \times 10^4$ years			

8 Experiments were carried out to investigate the rates of decomposition of 100 cm^3 of 1.0 mol dm^{-3} hydrogen peroxide, catalysed by manganese (IV) oxide.

$$H_2O_2\ (aq) \longrightarrow H_2O\ (l) + \tfrac{1}{2}\ O_2\ (g)$$

The volume of oxygen gas collected using a gas syringe was monitored. The results are shown in the diagram below.



Which of the following alteration to the experimental conditions in Experiment **1** would produce the curve observed in Experiment **2**?

	A	Lowering the temperature.
	B	Decreasing the amount of MnO_2 used.
	C	Diluting the hydrogen peroxide solution with water.
	D	Adding 100 cm^3 of 0.1 mol dm^{-3} hydrogen peroxide.

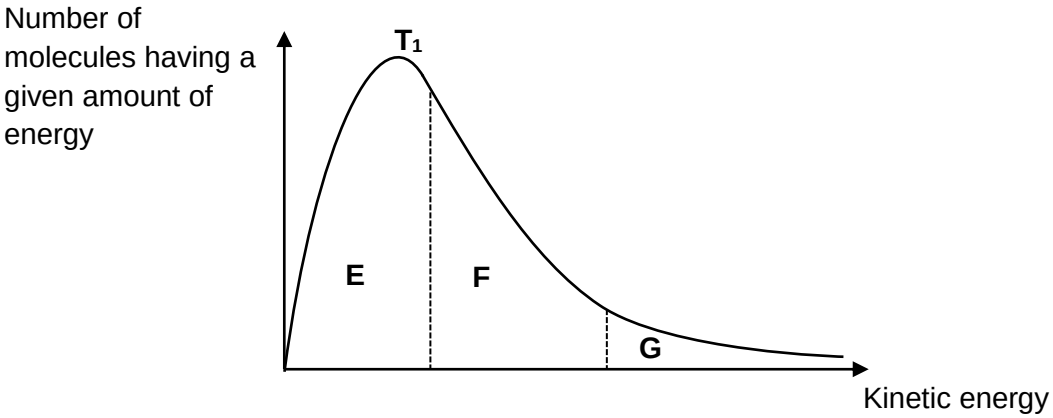
Answer: D

Lowering the temperature and decreasing the amount of MnO_2 will slow down the rate of reaction (less steep curve) but will not change the volume of oxygen produced.

Diluting hydrogen peroxide solution with water will slow down the rate of reaction (less steep curve) and decrease the volume of oxygen produced.

Adding some 0.1 mol dm^{-3} hydrogen peroxide will lower the concentration of hydrogen peroxide which leads to slower rate of reaction (less steep curve). As there are moles of hydrogen peroxide in the vessel, it will lead to more oxygen gas being produced.

9 The Maxwell Boltzman distribution curve shows the number of molecules having a given amount of kinetic energy at constant temperature, T_1.



How would the size of the areas labelled **E**, **F** and **G** change if a lower temperature, T_2 was used?

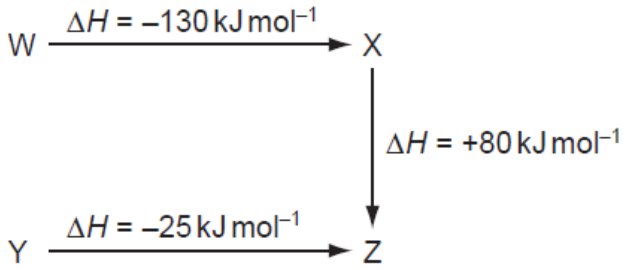
	E	F	G
A	Increase	Increase	Decrease
B	Increase	Decrease	Decrease
C	Decrease	Increase	Increase
D	Decrease	Decrease	Increase

Answer: B

At a lower temperature T_2, the graph will shift to the left hand side and the peak of the graph will be higher than the original. Since there is no change to the number of molecules, the area under both graphs (T_1 and T_2) should be the same.

At a lower temperature, the number of molecules of lower kinetics energy will increase thus the area of E will increase. Also, there will be less molecules of higher kinetics energy thus area F and G will decrease.

10 The diagram represents the energy changes for some reactions.



What are the natures of the conversions **W → Y**, **Y → X** and **Z→W**?

	W → Y	**Y → X**	**Z → W**
A	Exothermic	Endothermic	Endothermic
B	Exothermic	Exothermic	Endothermic
C	Endothermic	Exothermic	Exothermic
D	Endothermic	Endothermic	Exothermic

Answer: B

W → Y : ΔH = -130 +80 – (-25) = - 25 kJ mol^{-1}

Y → X : ΔH = -25 -80 = -105 kJ mol^{-1}

Z → W: -80 + 130 = + 50 kJ mol^{-1}

11 Consider the following equilibrium system:

$$2AlCl_3(g) \rightleftharpoons Al_2Cl_6(g)$$

Which of the following statements will cause the position of the equilibrium to shift to the left?

A	Increasing the temperature
B	Pumping $AlCl_3$ gas into the vessel
C	Decreasing the volume of the vessel
D	Adding a solid catalyst into the vessel

Answer: A

This reaction involves bond formation between 2 monomers of $AlCl_3$ to form the dimer

Al_2Cl_6 hence forward reaction is exothermic. By Le Chatelier's Principle, increasing the temperature will shift position of equilibrium to the left to favour endothermic reaction to absorb the excess heat.
Adding $AlCl_3$ gas into the vessel will shift position of equilibrium to the right to use up the excess $AlCl_3$ gas.
Decreasing the volume of the vessel will increase the partial pressure of both gases. By LCP, the position of equilibrium will shift to the right to produce lesser moles of gas.
Adding a catalyst has no effect on the position of equilibrium. It will just lower the E_a and speed up both forward and backward reaction equally.

12 Cyanidin (Cy) is a water-soluble plant pigment which can be found in blackberries. Blackberry juice is usually preserved by the addition of a small amount of $SO_2(g)$ and the following equilibrium is set up:

$$CyH^+(aq) + SO_2(aq) + H_2O(l) \rightleftharpoons CySO_3H_2(aq) + H^+(aq)$$

What are the units for K_c?

	A	mol dm^{-3}	**C**	mol^{-1} dm^3
	B	mol dm^{-3} s^{-1}	**D**	no units

Answer: D

$$K_c = \frac{[CySO_3H_2][H^+]}{[CyH^+][SO_2]}$$ no units

13 A solution of an acid **H** has the same pH as a solution of acid **J.** Equal dilution increases the pH of acid **H** more than that of acid **J**. Which of the following pairs of acids would show this behaviour?

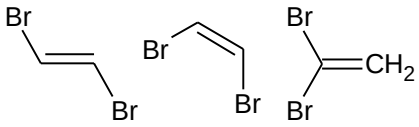
		H	**J**	
	A	H_3PO_4	HCl	
	B	HCl	CH_3CO_2H	
	C	HCl	H_2SO_4	
	D	CH_3CO_2H	H_2SO_4	

Answer: B
H is a strong acid and **J** is a weak acid.
Strong acid: pH = – lg [strong acid]
Weak acid: pH = – lg $\sqrt{(}$Ka ×[Weak acid])
As shown from the equations, the pH of the strong acid will increase more than that of the weak acid when both are diluted to the same extent.

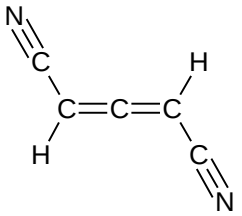
14 What is the total number of isomers possible for the molecular formula of $C_2H_2Br_2$?

A	1	**C**	3
B	2	**D**	4

Answer: C

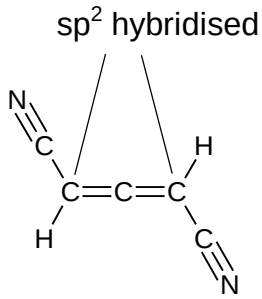


15 Which statement is **incorrect** for the compound shown below?



A	There are 6 π bonds.
B	There are 8 σ bonds.
C	There are two different bond angles.
D	There are three sp^2 hybridised carbons.

Answer: D



16 Samples of $C_6H_5CHCH_2$ and Br_2 were mixed under different conditions. Which pair of conditions and products are correctly paired together?

	Conditions	Product	

	A	Br_2 (aq)	$C_6H_4BrCH(OH)CH_2Br$	
	B	Br_2 (g), uv light	$C_6H_4BrCHCH_2$	
	C	Br_2 (g)	$C_6H_4BrCH(Br)CH_2Br$	
	D	Br_2 (g), Fe (s)	$C_6H_4BrCH(Br)CH_2Br$	

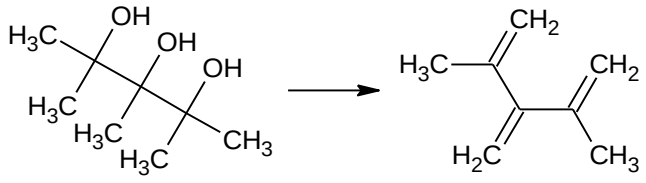
Answer: D

Both electrophilic substitution and electrophilic addition took place when exposed to Br_2 (g), Fe (s).

17 Which of these statements is true for the reaction of 2,3,4−trimethylpenta−2,3,4−triol with concentrated sulfuric acid at 443 K.

	A	Oxidation reaction taken place.
	B	Carbon dioxide gas is a by-product.
	C	There are a total of 8 possible geometrical isomers.
	D	Organic product with three carbon-carbon double bonds is formed.

Answer: D



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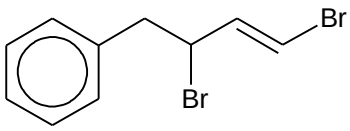
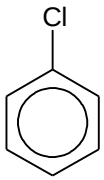
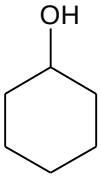
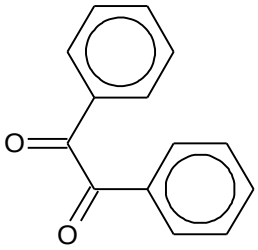
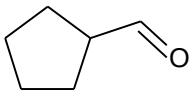
18 Which of the following reagents and conditions will not yield any reaction with the compound shown below.



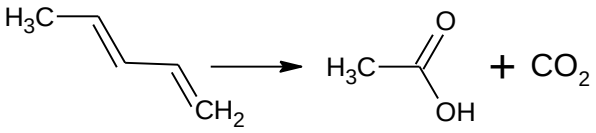
	A	Cold aqueous hydrogen cyanide with trace amounts of sodium hydroxide.
	B	Hot potassium dichromate in aqueous potassium hydroxide.
	C	Cold potassium manganate(VII) in aqueous sulfuric acid.
	D	Aqueous sodium hydroxide and heat.

Answer: A

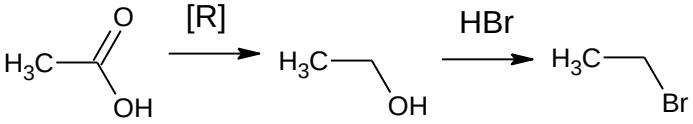
	Cold aqueous hydrogen cyanide with trace amounts of sodium hydroxide is the reagent and conditions for nucleophilic addition of carbonyls	
19	Which of the following compounds would be the most inert towards a nucleophilic attack?	
	A	
	B	
	C	
	D	
	Answer: A C−C*l* bond in chlorobenzene is very strong and cannot be broken easily.	
20	Penta−1,3−diene was heated with acidified potassium manganate(VII) to form compound **L** and **M**. Compound **L** was then added to lithium aluminium hydride in dry ether to form compound **N**. Compound **N** was then bubbled with hydrogen bromide gas to form compound **O**. Which of these statements can be correctly deduced from the information above?	
	A	Compound **O** cannot undergo further nucleophilic substitution with ethanolic potassium cyanide.
	B	1 mol of compound **N** forms 1 mol of hydrogen gas when reacted with sodium metal.

	C	Compound **L** is a gas which forms white precipitate with calcium hydroxide.
	D	Compound **M** is a non-polar acidic gas.

Answer: D



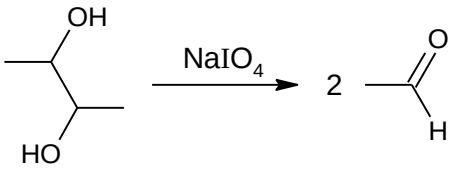
L M



N O

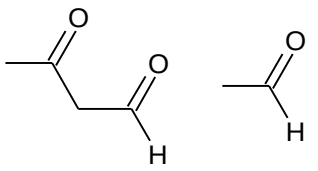
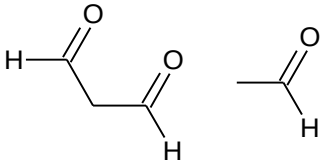
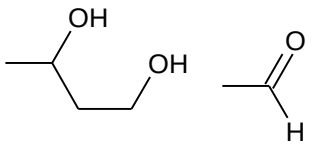
Compound M is carbon dioxide which is a non-polar acidic gas.

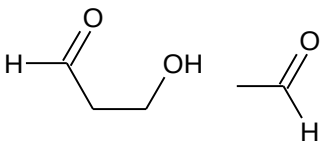
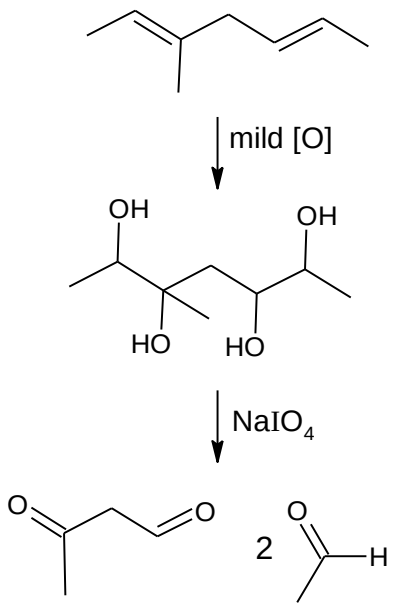
21 Buta-2,3-diol can be oxidized by $NaIO_4$ as shown below,

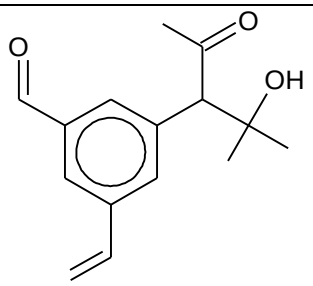


What would be the final organic products obtained when compound **P** is first treated with cold alkaline aqueous $KMnO_4$ followed by $NaIO_4$?

Compound **P** is $CH_3CH=C(CH_3)–CH_2–CH=CH(CH_3)$

	A	
	B	
	C	

	D	
	Answer: A	
22	Which reagent could be used to distinguish between pentan-2-ol and pentan-2-one?	
	A	Acidified potassium manganate(VII)
	B	Alkaline aqueous iodine
	C	Sodium carbonate
	D	Aqueous bromine
	Answer: A A: Pentan-2-ol, a 2^{o} alcohol can be oxidised by acidified potassium maganate(VII) to form a ketone. Purple solution decolourise B: Both react with aq I_2. C: Both do not react with Na_2CO_3. D: Both do not react with aqueous bromine.	
23	Which of the following chemical tests will yield a **positive** observation with the compound shown below?	



	A	Fehling's solution
	B	Hot ethanolic silver nitrate
	C	Sodium carbonate
	D	Alkaline aqueous iodine
	Answer: D Brown iodine solution will decolourise due to the alkene functional group and methyl ketone present in the side chains.	
24	Which compound can undergo a reaction when treated with hot ethanolic potassium hydroxide?	
	A	CH_2Br_2
	B	CBr_3CBr_3
	C	$(CH_3)_2CCBr_2$
	D	$CH_3CBr_2CH_3$
	Answer: D Only compound D has a bromine atom on a carbon with an adjacent carbon atom that has a H atom for it to undergo elimination.	
25	Which of these would have the lowest pH value in solution?	
	A	$CH_2(Cl)CH_2CO_2H$
	B	$CH_2CH(Cl)CO_2H$
	C	$CH_3CO_2CH_2CH_3$
	D	$CH_3CH_2NH_2$
	Answer: B The electron withdrawing chlorine atom is nearer to COO^- and the negative charge is more dispersed, hence stabilising the anion.	

For **questions 26 – 30**, one or more of the numbered statements **1** to **3** may be correct. Decide whether each of the statements is or is not correct. The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is to be used as correct response.

26	Which of the following contain hydrogen bonding?	
	1	NH_4Cl (s)
	2	$NH_3(l)$
	3	$CH_3CH_2CH_2OH$ (l)
	Answer: C (2 & 3 are correct only) 1: Ionic salt. No hydrogen bonding 2 and 3: Both NH_3 and $CH_3CH_2CH_2OH$: Both can form intermolecular hydrogen bonding as they have lone pairs on N and O, with H attached to N and O respectively.	
27	Which reaction represents standard enthalpy change at 298 K?	
	1	HBr (aq) + NaOH (aq) → NaBr (aq) + H_2O (l)
	2	P_4 (s) → 4P (g)
	3	H_2 (g) + Br_2 (g) → 2HBr (g)
	Answer: B (1 & 2 are correct only) Bromine is a liquid and not a gas at 298 k.	
28	At 50 °C, pure water is found to have a pH value of 6.6. Which of the following statements are true?	
	1	Concentration of hydrogen ion in water is higher at 50 °C compared to at 25°C.
	2	The K_w value is smaller at 50 °C compared to at 25°C
	3	Water is acidic at 50 °C
	Answer: D (only 1 is correct)	

	1: Since pH = – lg $[H^+]$, $[H^+]$ is higher at pH 6.6 at 50 °C compared to pH 7 at 25°C. 2: Kw is temperature dependent and is larger at higher temperatures, as H_2O dissociation is endothermic 3: $[OH^-] = [H^+]$, water is still neutral at 50 °C.	
29	Which of these compounds are planar?	
	1	Ethene
	2	Benzene
	3	Propanone
	Answer: **B (1 & 2 only)** Propanone is not planar due to the two CH_3 groups being tetrahedral in shape	
30	Glucose is a simple molecular solid. $HOCH_2CH(OH)CH(OH)CH(OH)CH(OH)CHO$ Which of the following statements are correct?	
	1	The hydrogen atom in the hydroxyl groups can form hydrogen bonds with water.
	2	The hydrogen atom in the aldehyde group form hydrogen bonds with ethanol.
	3	All the oxygen atoms in glucose can form hydrogen bonds with propanone.
	Answer: D 1 Hydrogen is directly bonded to oxygen in the hydroxyl group, hence it can form hydrogen bonds with water. 2: Hydrogen in aldehyde is not bonded to oxygen, hence no hydrogen bonds can be formed 3: There are no hydrogen atoms bonded directly to oxygen in propanone, hence no hydrogen bonds can be formed.	

END OF PAPER

P1 SOLUTIONS

1	B	**11**	A	**21**	A
2	C	**12**	D	**22**	A
3	C	**13**	B	**23**	D
4	D	**14**	C	**24**	D
5	C	**15**	D	**25**	B
6	A	**16**	D	**26**	C
7	B	**17**	D	**27**	B
8	D	**18**	A	**28**	D
9	B	**19**	A	**29**	B
10	B	**20**	D	**30**	D

SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 1

Candidate Name
Class

CHEMISTRY **8872/02**
JC2 Preliminary Examination **13th Sep 2017 (AM)**
Paper 2 **2 hours**

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark or blue pen.
You may use an HB pencil for any diagrams or graphs.

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

The use of an approved scientific calculator is expected, where appropriate.

Section A
Answer **all** the questions

Section B
Answer **two** questions on a separate answer paper.

At the end of the examination, fasten all your work securely together. The number of marks is given in brackets [ ] at the end of each question of part question.

FOR EXAMINER'S USE		
P1 (MCQ)		/30
P2	Section A	
	1	/15
	2	/15
	3	/10
	Section B	
		/20
		/20
Total		/110

This document consists of **15** printed pages and **1** blank page.

For Examiner's Use

Section A

Answer **all** the questions in the spaces provided.

1 **(a)** An excess of water was added to 3.9 g of unknown phosphorus chloride, PCl_x, and the resulting solution was made up to 250 cm^3 in a standard flask. 25.0 cm^3 of this solution was titrated with 0.40 $moldm^{-3}$ NaOH and required 37.40 cm^3 for neutralisation.

(i) Write equations, for the reactions of PCl_5 and PCl_3 with water. [1]

……

……

(ii) Calculate the total amount, in moles, of H^+ ions present in the 250 cm^3 standard flask. [2]

(iii) Hence, calculate the numerical value of x. [2]

(iv) Draw out the Lewis structure of H_3PO_4. State the bond angles and shape about any central atoms. [3]

(v) Explain why PCl_5 exist but not NCl_5. [1]

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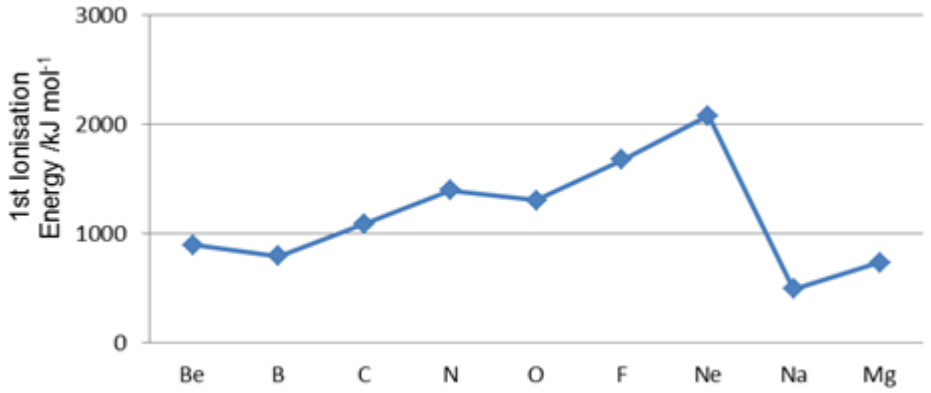
For Examiner's Use

(b) The graph below shows the first ionisation energy of the elements beryllium to magnesium.



(i) Define the term *first ionisation energy*. [1]

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(ii) Account for the increasing ionisation energy from beryllium to neon. [2]

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(iii) Explain why the first ionisation energy decreases from beryllium to boron and nitrogen to oxygen. [2]

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For Examiner's Use

(iv) Explain why the first ionisation energy decreases sharply from neon to sodium. [1]

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[Total: 15]

For Examiner's Use

2 Ethyl propanoate can be hydrolysed according to the following equation.

$$C_2H_5OCOCH_2CH_3 + H_2O \rightarrow C_2H_5OH + CH_3CH_2CO_2H$$

The kinetics of the above hydrolysis may be investigated by measuring the concentration of propanoic acid produced. In this investigation, 0.240 moles of the ester was mixed with a suitable catalyst in 1 dm^3 of water and the mixture was kept at a constant temperature of 35 °C.

10 cm^3 samples were withdrawn periodically at hourly intervals and rapidly cooled by the addition of cold water. The resulting solution was then titrated against a solution of standard sodium hydroxide every hour over a period of four hours. The following results were obtained.

Time / h	Concentration of propanoic acid / mol dm^{-3}
0	0.000
1	0.084
2	0.140
3	0.178
4	0.195

(a) (i) Identify the role of the cold water used prior to the titration and explain why it is necessary. [2]

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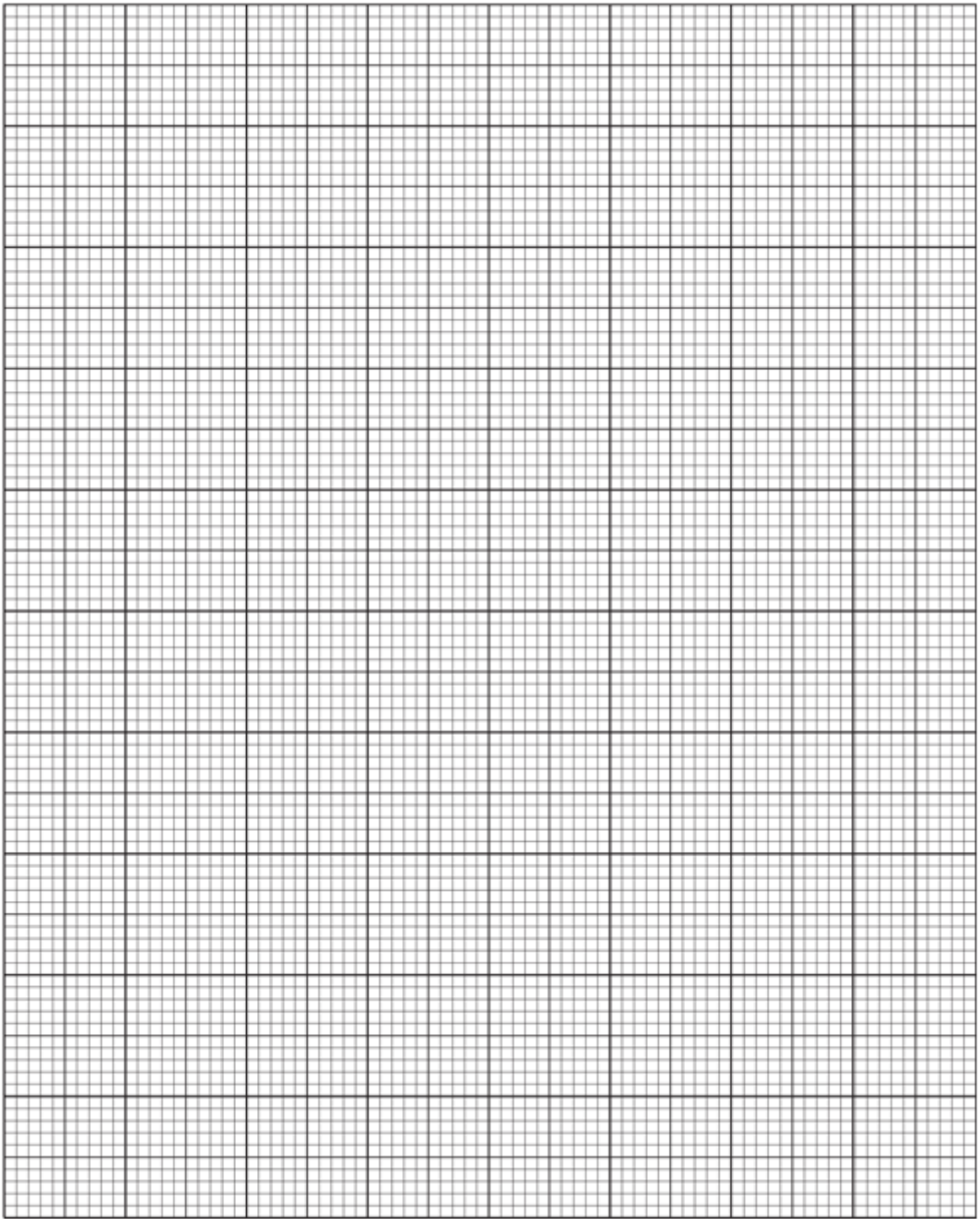
For Examiner's Use

(ii) By using a suitable graphical method, determine the half-life of the reaction and hence show that the hydrolysis reaction is first order with respect to the ester. [4]



For Examiner's Use

(b) The ester, ethyl propanoate, can also undergo base hydrolysis and the reaction is monitored using the initial rates method. The initial rate of the hydrolysis reaction between the ester and NaOH(aq) was measured in three separate experiments at a constant temperature.

The results are obtained below:

Experiment	Temperature / ^{o}C	Initial [NaOH] / mol dm^{-3}	Initial [ester] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	T_1	0.020	0.015	2.70×10^{-3}
2	T_1	0.030	0.015	4.05×10^{-3}
3	T_1	0.060	0.020	r_1
4	T_2	0.120	0.020	4.32×10^{-2}

(i) Deduce the order of reaction with respect to NaOH. [2]

……

……

……

(ii) Given that the reaction is first order with respect to the ester, calculate the initial rate of reaction, r_1, for Experiment 3. [1]

(iii) Calculate the value of the rate constant in experiment 1 and experiment 4, specifying the correct unit. Hence, deduce whether T_1 or T_2 is higher. [3]

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For Examiner's Use

(iv) Draw the Maxwell-Boltzmann distribution curve, explain how the increase in temperature increases the rate of reaction. [3]

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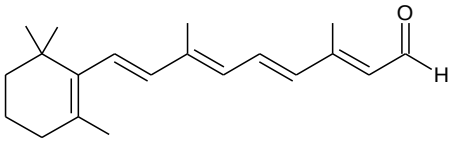
[Total: 15]

For Examiner's Use

3 This question revolves around carbonyl compounds involved in biological applications in living things.

(a) Retinal is one of the many forms of vitamin A, bound to proteins called opsins. It is the chemical basis of vision in animals and humans as well as allowing certain microorganisms to convert light into metabolic energy.



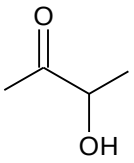
Retinal

(i) State the number of geometrical isomers for retinal. [1]

……

(ii) Draw all the organic products formed when retinal is reacted with cold acidified potassium manganate(VII). [1]

(b) Acetoin is a colorless or pale yellow liquid with a pleasant buttery odour. It is a neutral, four-carbon molecule used as an external energy store by a number of fermentive bacteria.



Acetoin

(i) Suggest a chemical test to **positively** distinguish acetoin from retinal, including relevant chemical equations. [3]

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For Examiner's Use

(ii) Compound **F** is an isomer of acetoin and contains an aldehyde and a tertiary alcohol. **F** was reacted in a sequential procedure as shown below.

Step 1:
It is reacted with aqueous hydrogen cyanide at low temperatures.

Step 2:
Hot acidified potassium dichromate(VI) added to product formed earlier

Step 3:
2,4-dinitrophenylhydrazine added to product formed in step 2 to form compound **G**.

Draw the structures of compounds **F** and **G** and state the types of reactions taken place. [5]

Step 1: ……..……

Step 2: ……..……

Step 3: ……..……

F	**G**

[Total: 10]

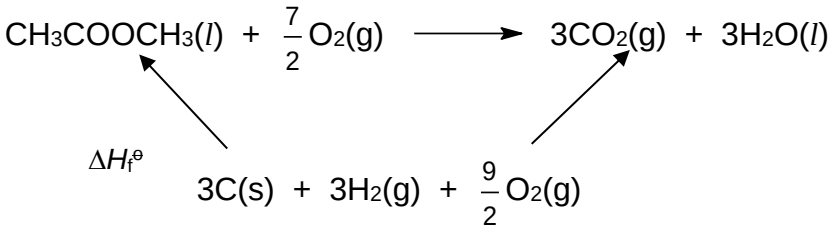
Section B

Answer **two** questions from this section on separate answer paper.

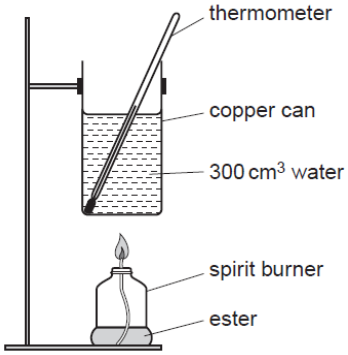
1 (a) (i) Define standard enthalpy change of formation. [1]

(ii) Use the energy cycle below and the standard enthalpy changes of combustion, $\Delta H_c^{\ominus}$, in the table to calculate the standard enthalpy change of formation, $\Delta H_f^{\ominus}$, of methyl ethanoate, CH_3COOCH_3. [2]

	$\Delta H_c^{\ominus}$ / kJ mol^{-1}
carbon	–393.5
hydrogen	–285.8
methyl ethanoate	–1592.1



(b) A student used the apparatus shown to carry out experiments to determine the standard enthalpy change of combustion of methyl ethanoate, CH_3COOCH_3.



Mass of copper can = 250 g

An initial experiment was carried out using methyl ethanoate. This ester was burnt in a spirit burner underneath a copper can so that the flame from the burner heated 300 cm^3 of water in the can. It was found that 0.980 g of ester was required to raise the temperature of the water in the can by 10.0 ^{o}C

(i) Calculate the heat gain by the water given that the specific heat capacity of water is 4.18 J g^{-1} K^{-1}. Take the density of water to be 1.00 g cm^{-3}. [1]

(ii) Given that the **total** heat energy gain is 13.5 kJ, calculate the specific heat capacity of the copper can used in this experiment. [2]

(iii) Using the $\Delta H_c^{\ominus}$ of methyl ethanoate given in the table of part **(a)**, calculate the total theoretical heat energy **in kJ** released by the mass of methyl ethanoate burnt in this experiment. [2]

(iv) Calculate the percentage efficiency of heat transfer in this experiment and suggest a reason for this value. [2]

(c) Methane is used to produce synthesis gas (syngas), a mixture that includes carbon monoxide and hydrogen, by reacting with steam on a nickel catalyst in a 2 dm^3 vessel. Syngas is then used to produce liquid hydrocarbons and methanol.

$$CH_4\,(g) + H_2O\,(g) \rightleftharpoons CO\,(g) + 3H_2\,(g) \qquad \Delta H > 0$$

The equilibrium mixture was found to contain 1 mole of methane, 1 mole of steam, 1.5 moles of carbon monoxide and 4.5 moles of hydrogen gas.

(i) State Le Chatelier's Principle. [1]

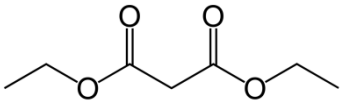
(ii) Write an expression for the equilibrium constant, K_c and determine its value, including units. [2]

(iii) Define the term *endothermic reaction*. [1]

(iv) With reference to the above equilibrium, predict and explain the effect of **separately** increasing pressure and decreasing temperature on the position of equilibrium, yield and K_c. [6]

[Total : 20]

2 Diethyl malonate, also known as DEM exist as a colourless liquid, commonly used in the manufacture of perfumes, artificial flavourings and vitamins. The structure of diethyl malonate is shown below.

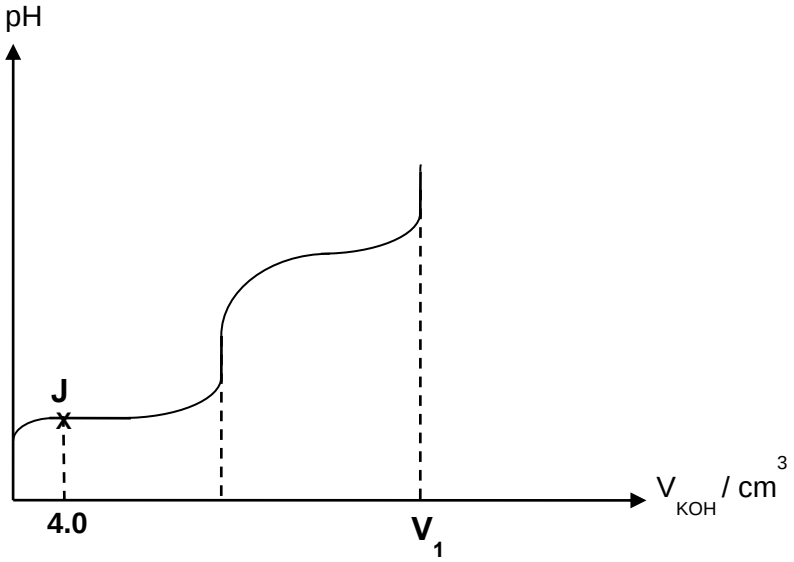


diethyl malonate

(a) **(i)** Diethyl malonate is synthesised from the esterification of malonic acid and an alcohol. Draw the structure of malonic acid and state the reagents and conditions required for this process. Write a balanced chemical equation for this synthesis. [3]

(ii) State the number of moles of H_2 gas produced per mole of malonic acid with Mg. [1]

(b) 7.0 grams of malonic acid was dissolved in 250 cm^3 of distilled water. The following titration curve was obtained when 25 cm^3 of this solution was titrated against 0.40 mol dm^{-3} potassium hydroxide.



The dissociation of malonic acid (H_2A) can be regarded as follows.

$H_2A \rightleftharpoons HA^- + H^+$ $\quad K_{a1} = 1.479 \times 10^{-3}$

$HA^- \rightleftharpoons A^{2-} + H^+$ $\quad K_{a2} = 2.042 \times 10^{-6}$

(i) Suggest why K_{a2} is much smaller than K_{a1}. [1]

(ii) Write an expression for K_{a1} stating its units. [2]

(iii) Ignoring the effects of K_{a2}, hence, or otherwise, calculate the initial pH of the solution. [2]

(iv) Calculate the volume of KOH, $\mathbf{V_1}$, required to completely neutralise malonic acid in 25 cm^3 of solution. [1]

(v) Explain what it means to be a buffer solution. [1]

(vi) The pH of a buffer solution can be determined by the following equation.

$$pH = -\lg K_a + \lg \frac{[\text{conjugate base}]}{[\text{acid}]}$$

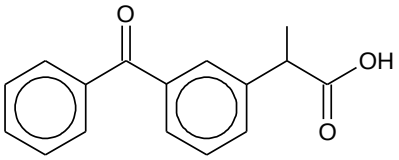
Identify the species present at point **J**. Calculate the amount of malonic acid remaining, and use the above equation to calculate the pH. [3]

(vii) The pH at the second end point is more than 7. Explain this observation with the aid of relevant equations. [2]

(c) Account for the relative acidities of ethanoic acid, ethanol and fluoroethanoic acid. [4]

[Total: 20]

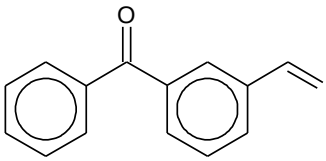
3 Ketoprofen, is one of the propionic acid class of nonsteroidal anti-inflammatory drugs (NSAID) with analgesic and antipyretic effects. It is generally prescribed for arthritis-related inflammatory pains or severe toothaches that result in the inflammation of the gums.



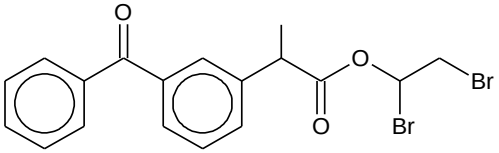
Ketoprofen

(a) Describe the bonding in benzene in terms of orbital overlap, illustrating your answer with a suitable diagram. [3]

(b) Propose a synthetic pathway for the formation of ketoprofen from the structure below. [3]



(c) Ketoprofen is reacted with an alcohol and forms an ester as shown.

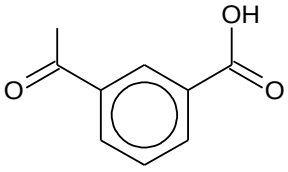


(i) Name the alcohol used in forming the ester. [1]

(ii) The alcohol was heated in the presence of aluminum oxide. Draw the structures of the two isomeric products formed and name them accordingly. [2]

(iii) Predict the relative boiling points of the products formed, giving reasons for your answer. [1]

(d) Compound **K**, a sweet smelling liquid, is an isomer of ketoprofen. Upon heating **K** with dilute sulfuric acid, compound **L** and benzoic acid are produced. Compound **L** is an alcohol which also produces a silver mirror with Tollens' reagent and a blue solution with Fehling's solution. It also reacts with hot acidified potassium dichromate(VI) to form compound **M** as shown below.



Compound **M**

Compound **L** reacts with hot acidified potassium manganate(VII) to form carbon dioxide and compound **N** which will subsequently react with liquid bromine and anhydrous aluminium bromide solid to form compound **O**.
Deduce, with reasoning, the structures for compounds **K**, **L**, **N** and **O.** [10]

[Total: 20]

END OF PAPER

SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 1

Candidate Name
Class

CHEMISTRY **8872/02**
JC2 Preliminary Examination **14th Sep 2017 (AM)**
Paper 2 **2 hours**

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark or blue pen.
You may use an HB pencil for any diagrams or graphs.

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

The use of an approved scientific calculator is expected, where appropriate.

Section A
Answer **all** the questions

Section B
Answer **two** questions on a separate answer paper.

At the end of the examination, fasten all your work securely together. The number of marks is given in brackets [ ] at the end of each question of part question.

FOR EXAMINER'S USE		
P1 (MCQ)		/30
P2	Section A	
	1	/15
	2	/15
	3	/10
	Section B	
		/20
		/20
Total		/110

This document consists of **15** printed pages and **1** blank page.

Section A

Answer **all** the questions in the spaces provided.

1 **(a)** An excess of water was added to 3.9 g of unknown phosphorus chloride, PCl_x, and the resulting solution was made up to 250 cm^3 in a standard flask. 25.0 cm^3 of this solution was titrated with 0.40 $moldm^{-3}$ NaOH and required 37.40 cm^3 for neutralisation.

(i) Write equations, for the reactions of PCl_5 and PCl_3 with water. [1]

$PCl_5 + 4H_2O \rightarrow 5HCl + H_3PO_4$
$PCl_3 + 3H_2O \rightarrow 3HCl + H_3PO_3$ **[1] for both equations**

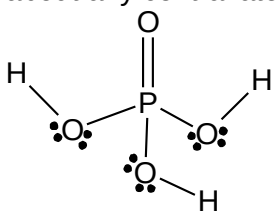
(ii) Calculate the total amount, in moles, of H^+ ions present in the 250 cm^3 standard flask. [2]
$n(H^+)$ in 25.0 cm^3 = n(NaOH) = 0.40 x 37.40/1000 = 0.01496 mol **[1]**
$n(H^+)$ in 250 cm^3 = 0.01496 x 250/25 = 0.1496 mol **[1]**

(iii) Hence, calculate the numerical value of x. [2]
Assuming it is PCl_5:

8 x $n(PCl_5) = n(H^+)$ **[1]**
$n(PCl_5)$ $^{0.1496}/_{8}$ = = 1.87 x 10^{-2} mol
$n(PCl_5)$ = $^{3.9}/_{208.2}$ = 1.87 x 10^{-2} mol
x = **5** **[1]**
Identify of phosphorus chloride = PCl_5

The amounts would not match if you assumed it to be PCl_3

(iv) Draw out the Lewis structure of H_3PO_4. State the bond angles and shape about any central atoms. [3]

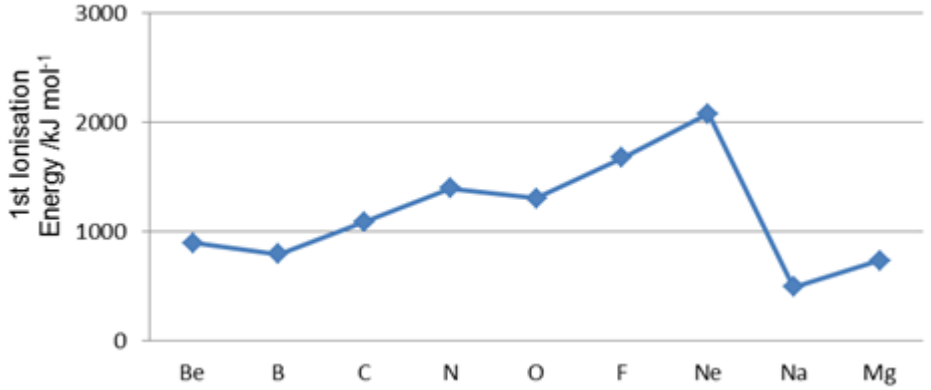


[1] show all bond angles and lp.
P: tetrahedral, 109.5º**[1]**
O: Bent, 104.5º**[1]**

(v) Explain why PCl_5 exist but not NCl_5. [1]

PCl_5 belongs to **period 3** and is able to **expand octet configuration** **[1]** due to energetically accessible 3d orbitals.

(b) The graph below shows the first ionisation energy of the elements beryllium to magnesium.



(i) Define the term *first ionisation energy*. [1]

First ionisation energy is the **energy required to remove one mole of electrons from one mole of gaseous atoms to form one mole of singly positively-charged gaseous ions.** **[1]**

(ii) Account for the increasing ionisation energy from beryllium to neon. [2]

Across the period,
Nuclear charge increases.
Shielding effect is similar **[1]** since successive elements in the period have an additional electron in the same valence shell.
Effective nuclear charge increases. **More energy is required to overcome the stronger electrostatic forces of attraction between the nucleus and the valence electron** to be removed. **[1]**

(iii) Explain why the first ionisation energy decreases from beryllium to boron and nitrogen to oxygen. [2]

Be : $1s^2\ 2s^2$ B : $1s^2\ 2s^2\ 2p^1$
The **2p electron** to be removed from B is at a **higher energy level** compared to the **2s electron** to be removed from Be. **Less energy** is required to overcome the **weaker electrostatic forces of attraction between the nucleus and the valence 2p electron in B**. **[1]**

N**:** $1s^2\ 2s^2\ 2p^3$ O: $1s^2\ 2s^2\ 2p^4$
There is **interelectronic repulsion between the pair of electrons in the doubly-filled 2*p* orbital of O**.
Less energy is required to overcome the **weaker electrostatic forces of attraction between the nucleus and the paired valence 2*p* electron in O compared to the unpaired valence 2*p* electron in N.** **[1]**

(iv) Explain why the first ionisation energy decreases sharply from neon to sodium. [1]

Sodium (Na) is in period 3 while neon (Ne) is in period 2.
Na: $1s^2\ 2s^2\ 2p^6\ 3s^1$ Ne: $1s^2\ 2s^2\ 2p^6$
The number of filled **principal quantum shells increases**. The **valence electrons in Na** are **further** from the nucleus. **Less energy** is required to overcome the **weaker electrostatic forces of attraction between the nucleus and the valence electron** to be removed. **[1]**

[Total: 15]

2 Ethyl propanoate can be hydrolysed according to the following equation.

$$C_2H_5OCOCH_2CH_3 + H_2O \rightarrow C_2H_5OH + CH_3CH_2CO_2H$$

The kinetics of the above hydrolysis may be investigated by measuring the concentration of propanoic acid produced. In this investigation, 0.240 moles of the ester was mixed with a suitable catalyst in 1 dm^3 of water and the mixture was kept at a constant temperature of 35 °C.

10 cm^3 samples were withdrawn periodically at hourly intervals and rapidly cooled by the addition of cold water. The resulting solution was then titrated against a solution of standard sodium hydroxide every hour over a period of four hours. The following results were obtained.

Time / h	Concentration of propanoic acid / mol dm^{-3}
0	0.000
1	0.084
2	0.140
3	0.178
4	0.195

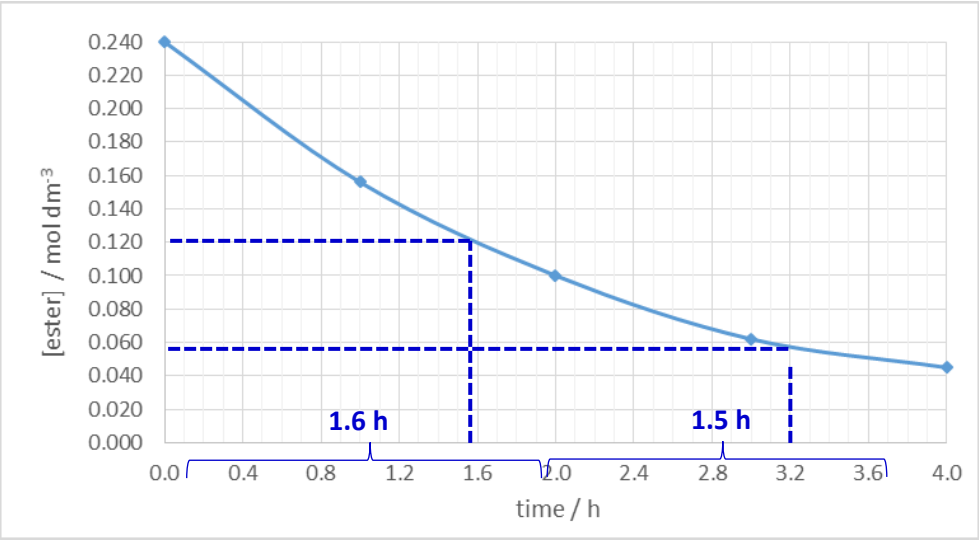
(a) (i) Identify the role of the cold water used prior to the titration and explain why it is necessary. [2]

The cold water is a **quenching agent** **[1]**.
It is necessary to **slow down the reaction significantly** (by lowering concentration and temperature of the reaction) so that the reaction is **considered to have stopped at that instant**. **[1]**

(ii) By using a suitable graphical method, determine the half-life of the reaction and hence show that the hydrolysis reaction is first order with respect to the ester. [4]

Time / h	Concentration of propanoic acid / mol dm^{-3}	**Concentration of ester / mol dm^{-3}**
0	0.000	**0.240**
1	0.084	**0.156**
2	0.140	**0.100**
3	0.178	**0.062**
4	0.195	**0.045**

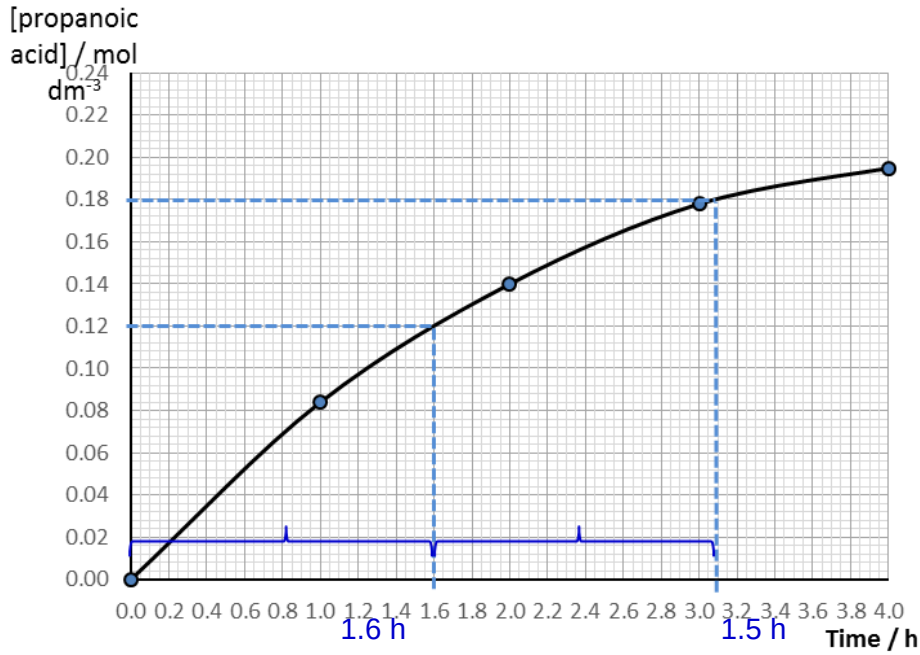
[Reactant]-time graph
Correct labelled axis and plotted points: 1m; Show at least 2 $t_{1/2}$: 1m; Smooth curve: 1m



The **half life is constant** **[1]** hence it is first order with respect to the ester. **Accept : 1.45 h < $t_{1/2}$ < 1.75 h**

OR

[Product]-time graph



Assuming the reaction goes into completion, the 0.24 mol dm^{-3} of the ester would form 0.24 mol dm^{-3} of propanoic acid.
The first half-life of a product-time graph would be the time taken to form half the total amount of propanic acid (0.12 mol dm^{-3}) and the time subsequently taken to form 3/4 of the total amount of propanoic acid (0.18 mol dm^{-3}).

(b) The ester, ethyl propanoate, can also undergo base hydrolysis and the reaction is monitored using the initial rates method. The initial rate of the hydrolysis reaction between the ester and NaOH(aq) was measured in three separate experiments at a constant temperature.

The results are obtained below:

Experiment	Temperature / ^oC	Initial [NaOH] / mol dm^{-3}	Initial [ester] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	T_1	0.020	0.015	2.70×10^{-3}
2	T_1	0.030	0.015	4.05×10^{-3}
3	T_1	0.060	0.020	r_1
4	T_2	0.120	0.020	4.32×10^{-2}

(i) Deduce the order of reaction with respect to NaOH. [2]

Comparing expt 1 and 2, when **[OH^-]** increased **1.5 times** while keeping **[ester] constant**, **initial rate increased 1.5 times**. **[1]**

Hence, **order of reaction wrt [OH^-]** is **1**. **[1]**

(ii) Given that the reaction is first order with respect to the ester, calculate the initial rate of reaction, r_1, for Experiment 3. [1]

rate = k [NaOH] [ester]

Comparing expts 2 and 3,

$$\frac{r_1}{4.05\times10^{-3}} = \frac{k(0.06)(0.02)}{k(0.03)(0.015)}$$

r_1 = **0.0108** mol dm^{-3} s^{-1} **[1] allow ecf**

(iii) Calculate the value of the rate constant in experiment 1 and experiment 4, specifying the correct unit. Hence, deduce whether T_1 or T_2 is higher. [3]

For experiment 1: $2.70 \times 10^{-3} = k\ (0.020)\ (0.015)$

k = 9 $mol^{-1}dm^3\ s^{-1}$ **[1] allow ecf**

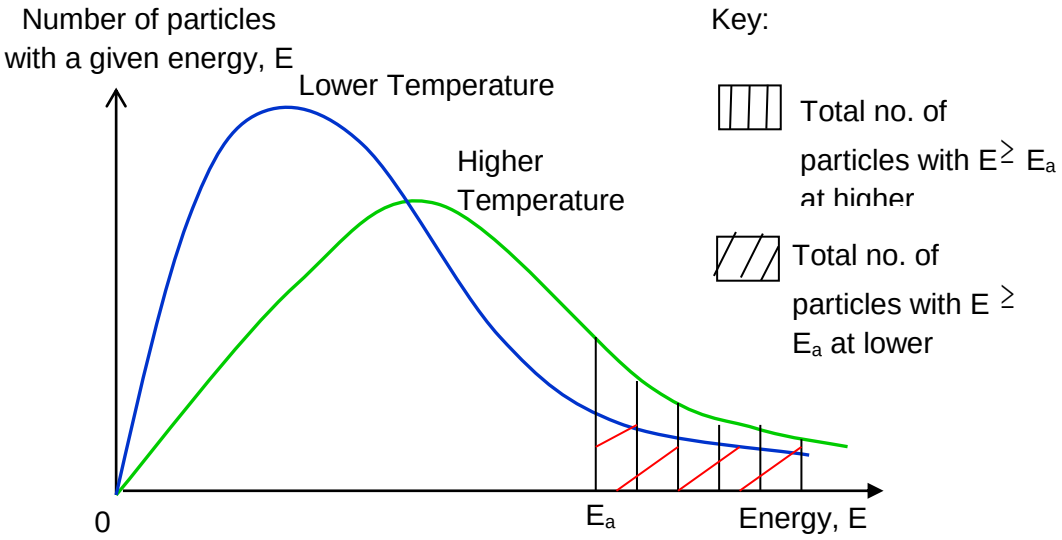
For experiment 2: $4.32 \times 10^{-2} = k\ (0.120)\ (0.020)$

k = 18 $mol^{-1}dm^3\ s^{-1}$ **[1] allow ecf**

T_2 is higher **[1]** as the rate constant for Experiment **4** is **larger** than that of Experiment **1**. **Increasing the temperature increases the value of the rate constant.**

(iv) Draw the Maxwell-Boltzmann distribution curve, explain how the increase in temperature increases the rate of reaction. [3]

Marking point: [Any 2 mistakes minus 1m]



-Correctly labelled axis & orgin
-Correctly labelled curve & E_a
-Correct legend & shading

When temperature of the reaction increases,

- **average kinetic energy** of the reactant particles **increases**
- **more reactant particles with energy ≥ E_a**

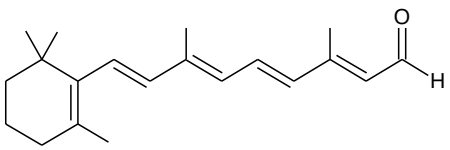
} **[1]**

- **more effective collisions**
- Since **rate of reaction** is proportional to the **frequency of effective collisions**, **rate** of reaction **increases** **[1]**

[Total: 15]

3 This question revolves around carbonyl compounds involved in biological applications in living things.

(a) Retinal is one of the many forms of vitamin A, bound to proteins called opsins. It is the chemical basis of vision in animals and humans as well as allowing certain microorganisms to convert light into metabolic energy.

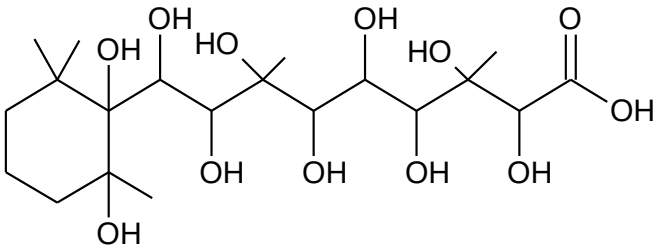


Retinal

(i) State the number of geometrical isomers for retinal. [1]

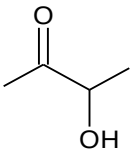
2^4 = **16 isomers** **[1]**

(ii) Draw all the organic products formed when retinal is reacted with cold acidified potassium manganate(VII). [1]



[1]

(b) Acetoin is a colorless or pale yellow liquid with a pleasant buttery odour. It is a neutral, four-carbon molecule used as an external energy store by a number of fermentive bacteria.

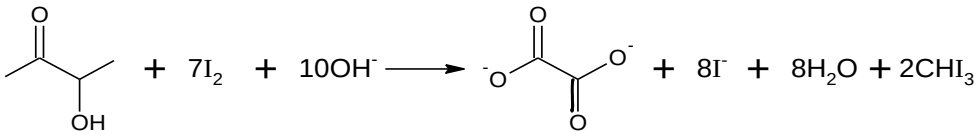


Acetoin

(i) Suggest a chemical test to **positively** distinguish acetoin from retinal, including relevant chemical equations. [3]

Test:
Add **aqueous iodine and sodium hydroxide to both samples and heat**. **[1]**

Observation:
Acetoin would **decolourise the brown iodine solution** and **yellow precipitate** of tri-iodomethane would be formed, but retinal **no decolourisation and no yellow ppt**. **[1]**



[1]

(ii) Compound **F** is an isomer of acetoin and contains an aldehyde and a tertiary alcohol. **F** was reacted in a sequential procedure as shown below.

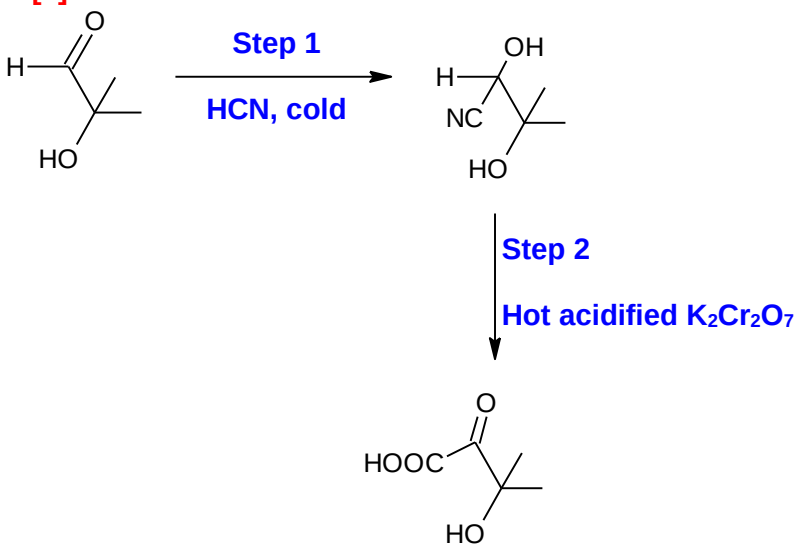
Step 1:
It is reacted with aqueous hydrogen cyanide at low temperatures.

Step 2:
Hot acidified potassium dichromate(VI) added to product formed earlier

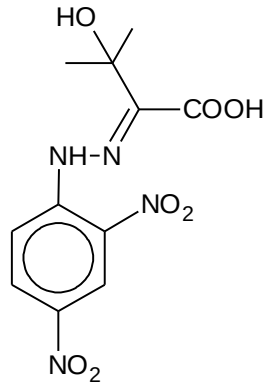
Step 3:
2,4-dinitrophenylhydrazine added to product formed in step 2 to form compound **G**.

Draw the structures of compounds **F** and **G** and state the types of reactions taken place. [5]

F [1]



G:



[1]

Step 1: Nucleophilic Addition
Step 2: Oxidation and acidic hydrolysis
Step 3: Condensation **[1 each]**

[Total: 10]

Section B

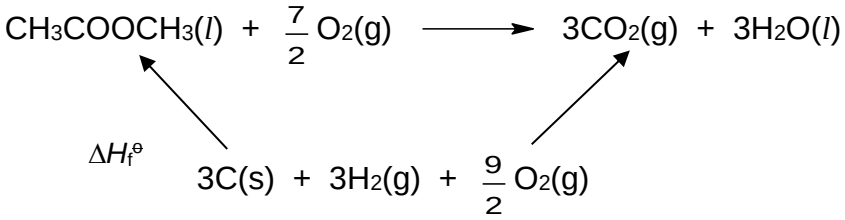
Answer **two** questions from this section on separate answer paper.

1 (a) (i) Define standard enthalpy change of formation. [1]

Standard enthalpy change of formation ($\Delta H_f^{\ominus}$) of a substance is the **energy change** when ***one mole*** of the **substance** is formed from its **elements** under **standard conditions**. **[1]**

(ii) Use the energy cycle below and the standard enthalpy changes of combustion, $\Delta H_c^{\ominus}$, in the table to calculate the standard enthalpy change of formation, $\Delta H_f^{\ominus}$, of methyl ethanoate, CH_3COOCH_3. [2]

	$\Delta H_c^{\ominus}$ / kJ mol^{-1}
carbon	–393.5
hydrogen	–285.8
methyl ethanoate	–1592.1



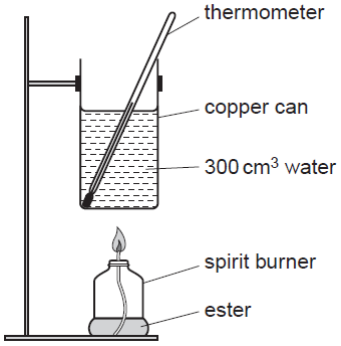
By Hess's law,

$\Delta H_f^{\ominus}(CH_3COOCH_3) = \mathbf{3}\Delta H_f^{\ominus}(CO_2) + \mathbf{3}\Delta H_f^{\ominus}(H_2O) - \Delta H_c^{\ominus}(CH_3COOCH_3)$

$= 3(-393.5) + 3(-285.8) - (-1592.1)$ **[M1]**

$= -445.8 \approx$ **-446 kJ mol^{-1}** **[1]**

(b) A student used the apparatus shown to carry out experiments to determine the standard enthalpy change of combustion of methyl ethanoate, CH_3COOCH_3.



Mass of copper can = 250 g

An initial experiment was carried out using methyl ethanoate. This ester was burnt in a spirit burner underneath a copper can so that the flame from the burner heated 300 cm^3 of water in the can. It was found that 0.980 g of ester was required to raise the temperature of the water in the can by 10.0 ^{o}C.

(i) Calculate the heat gain by the water given that the specific heat capacity of water is 4.18 J g^{-1} K^{-1}. Take the density of water to be 1.00 g cm^{-3}. [1]

Heat energy gained by water = (300)(4.18)(10)
= **12540 J [1]**

(ii) Given that the **total** heat energy gain is 13.5 kJ, calculate the specific heat capacity of the copper can used in this experiment. [2]

Heat energy gained by copper can = 13500- 12540
= **960 J [1]**

Specific heat capacity of copper can= $\frac{960}{(250)(10)}$ = **0.384 J g^{-1} K^{-1} [1]**

(iii) Using the $\Delta H_c^{\ominus}$ of methyl ethanoate given in the table of part **(a)**, calculate the total theoretical heat energy **in kJ** released by the mass of methyl ethanoate burnt in this experiment. [2]

n(methyl ethanoate) = $\frac{0.98}{74.0}$ = **0.01324 mol [1]**

Heat energy released = 0.01324 x 1592.1 = **21.1 kJ [1]**

(iv) Calculate the percentage efficiency of heat transfer in this experiment and suggest a reason for this value. [2]

Percentage efficiency of heat transfer = $\frac{13500}{21100}$ x 100 % = **64.0 % [1]**

Heat loss to surroundings/ Room temperature was not constant. **[1]**

(c) Methane is used to produce synthesis gas (syngas), a mixture that includes carbon monoxide and hydrogen, by reacting with steam on a nickel catalyst in a 2 dm^3 vessel. Syngas is then used to produce liquid hydrocarbons and methanol.

$$CH_4\,(g) + H_2O\,(g) \rightleftharpoons CO\,(g) + 3H_2\,(g) \qquad \Delta H > 0$$

The equilibrium mixture was found to contain 1 mole of methane, 1 mole of steam, 1.5 moles of carbon monoxide and 4.5 moles of hydrogen gas.

(i) State Le Chatelier's Principle. [1]

Le Chatelier's Principle states that when a system in equilibrium is disturbed, the **system will react to counteract the change imposed** so as to **re-establish the equilibrium**. **[1]**

(ii) Write an expression for the equilibrium constant, K_c and determine its value, including units. [2]

$$K_c = \frac{[CO][H_2]^3}{[CH_4][H_2O]} = \frac{(\frac{1.5}{2})(\frac{4.5}{2})^3}{\frac{1}{2}(\frac{1}{2})} = \textbf{34.2 [1] mol}^2\textbf{ dm}^{-6}\textbf{[1]}$$

(iii) Define the term *endothermic reaction*. [1]

Endothermic means that ***heat/energy*** **is absorbed/[1]** from the surrounding / **required** to take place.

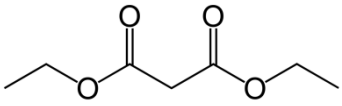
(iv) With reference to the above equilibrium, predict and explain the effect of **separately** increasing pressure and decreasing temperature on the position of equilibrium, yield and K_c. [6]

On increasing the pressure, by Le Chatelier's Principle, the **position of equilibrium will shift to the left to reduce the total number of moles of gas.** [1] **Yield decreases**. [1] **K_c remained unchanged** as it is **temperature dependent**. [1]

On decreasing the temperature, by Le Chatelier's Principle, the **position of equilibrium will shift to the left towards the exothermic reaction to release heat.** [1] **Yield decreased**. [1] **K_c decreased.** [1]

[Total : 20]

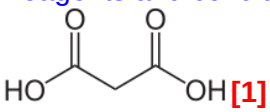
2 Diethyl malonate, also known as DEM exist as a colourless liquid, commonly used in the manufacture of perfumes, artificial flavourings and vitamins. The structure of diethyl malonate is shown below.



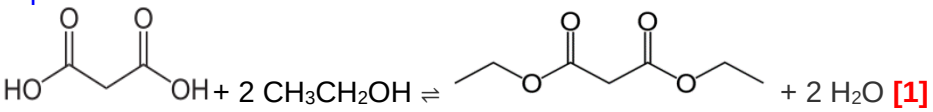
diethyl malonate

(a) **(i)** Diethyl malonate is synthesised from the esterification of malonic acid and an alcohol. Draw the structure of malonic acid and state the reagents and conditions required for this process. Write a balanced chemical equation for this synthesis. [3]

Reagents and conditions: **conc H_2SO_4, heat**. [1]


[1]

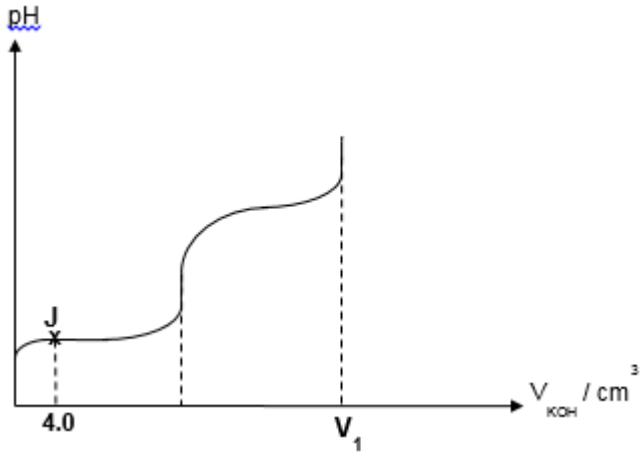
Equation:


[1]

(ii) State the number of moles of H_2 gas produced per mole of malonic acid with Mg. [1]

1 [1]

(b) 7.0 grams of malonic acid was dissolved in 250 cm^3 of distilled water. The following titration curve was obtained when 25 cm^3 of this solution was titrated against 0.40 mol dm^{-3} potassium hydroxide.



The dissociation of malonic acid (H_2A) can be regarded as follows.

$H_2A \rightleftharpoons HA^- + H^+$ $\quad K_{a1} = 1.479 \times 10^{-3}$
$HA^- \rightleftharpoons A^{2-} + H^+$ $\quad K_{a2} = 2.042 \times 10^{-6}$

(i) Suggest why K_{a2} is much smaller than K_{a1}. [1]

It is **more difficult to remove** a second positively charged **proton** from a **negatively charged anion** in the second dissociation as compared to the first dissociation from a **neutral molecule**. **[1]**

OR

The **'second' acidic proton** in the COOH group is **held more tightly** by the monoanion via **intramolecular hydrogen bonding**, resulting in a /**very stable monoanion**. This stabilisation effect also explains why the second K_a of these 2 acids is significantly smaller as the second acid proton will not be dissociated easily.

(ii) Write an expression for K_{a1} stating its units. [2]

$K_{a1} = \dfrac{[HA^-][H^+]}{[H_2A]}$ **[1]**

$moldm^{-3}$ **[1]**

(iii) Ignoring the effects of K_{a2}, hence, or otherwise, calculate the initial pH of the solution. [2]

n_{H_2A} in 250 $cm^3 = \dfrac{7.0}{104} = 0.06731$ mol

$[H_2A] = \dfrac{0.06731}{\frac{250}{1000}} =$ **$0.2692\ moldm^{-3}$ [1]**

$[H^+] = \sqrt{K_a \times [H2A]} = \sqrt{1.479 \times 10^{-3} \times 0.2692} = 0.01996\ mol\ dm^{-3}$

$pH = -\lg [H^+] =$ **1.70** **[A1]**

(iv) Calculate the volume of KOH, $\mathbf{V_1}$, required to completely neutralise malonic acid in 25 cm^3 of solution. [1]

$n_{malonic\ acid}$ in 25 $cm^3 = \dfrac{0.06731}{\mathbf{10}} = 0.006731$ mol

V_{KOH} required for **complete neutralisation, V_1**

$= \dfrac{0.006731}{\mathbf{0.40}} \times 2 = 0.033653\ dm^3 =$ **33.7 cm^3 [1] with ecf**

(v) Explain what it means to be a buffer solution. [1]

It is the **buffer** which is able to **resist pH change/maintain a fairly constant pH** when a **small amount** of acid or base is added to. **[1]**

(vi) The pH of a buffer solution can be determined by the following equation.

$$pH = -\lg K_a + \lg \frac{[\text{conjugate base}]}{[\text{acid}]}$$

Identify the species present at point **J**. Calculate the amount of malonic acid remaining, and use the above equation to calculate the pH. [3]

Species present: **H_2A and HA^- [1] ignore H_2O**
$n_{NaOH} = 4.0/1000 \times 0.4 = 1.60 \times 10^{-3}$
$nH_2A = (0.006731 - 1.60 \times 10^{-3}) =$ **0.005131 mol [1]**

$nHA^- = (1.60 \times 10^{-3})$
$pH = -\lg 1.479 \times 10-3 + \lg \frac{\frac{[0.00160]}{V}}{\frac{[0.005131]}{V}} =$ **2.32 [1] ecf**

(vii) The pH at the second end point is more than 7. Explain this observation with the aid of relevant equations. [2]
Only A^{2-} and water is present at the second end-point.
$A^{2-} + H_2O \rightleftharpoons HA^- + OH^-$ [1]
A^{2-} undergoes **salt hydrolysis to produce OH^-[1]** ions. Hence pH > 7.

(c) Account for the relative acidities of ethanoic acid, ethanol and fluoroethanoic acid. [4]

Acid strength: **ethanol < ethanoic acid < fluoroethanoic acid [1]**

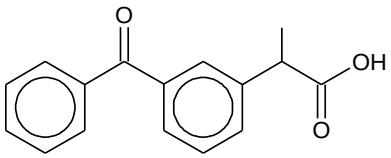
The **electron-donating R group** on ethanol **intensifies the negative charge on the carboxylate anion** hence **destabilising the ethoxide anion relative to the acid.** Hence, ethanol is the weakest acid. **[1]**

The carboxylate anion ($RCOO^-$) is **resonance stabilised** by the **delocalisation of the negative charge over the C atom and both oxygen atoms** in **ethanoic and fluoroethanoic** anion, hence stabilising the carboxylate anion relative to acid. Hence, both carboxylic acids are stronger acids then ethanol. **[1]**

The electron-withdrawing fluoro group disperses the negative charge on the fluoroethanoic anion hence **stabilises the carboxylate anion relative to the acid. Fluoroethanoic acid is a stronger acid then ethanoic acid. [1]**

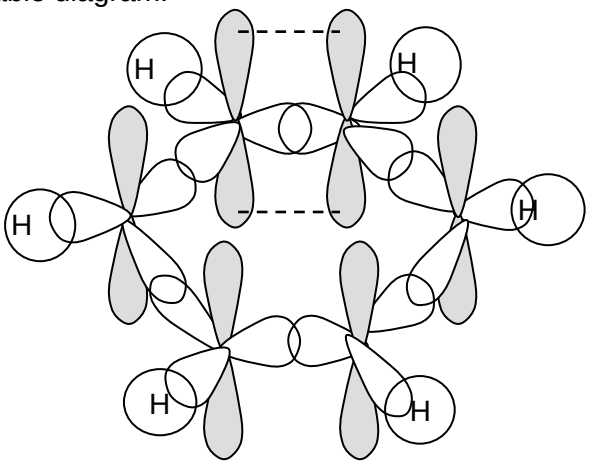
[Total: 20]

3 Ketoprofen, is one of the propionic acid class of nonsteroidal anti-inflammatory drugs (NSAID) with analgesic and antipyretic effects. It is generally prescribed for arthritis-related inflammatory pains or severe toothaches that result in the inflammation of the gums.



Ketoprofen

(a) Describe the bonding in benzene in terms of orbital overlap, illustrating your answer with a suitable diagram. [3]

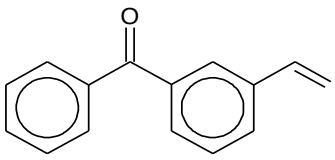


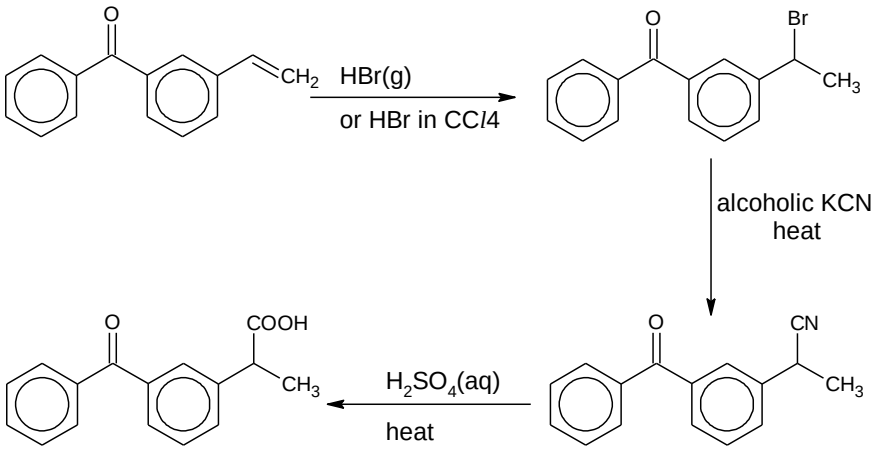
[1] for correct diagram

The carbon atoms in benzene are **sp² hybridised** forms **3 σ bonds with 2 adjacent C and 1 H via head on overlap.** making the molecule **planar** in shape**.** **[1]**

The **p-orbitals** overlaps with its **adjacent p-orbitals** via **side on overlap**, forming **π bonds.** **[1]**

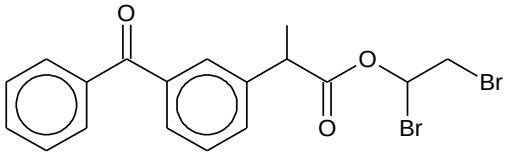
(b) Propose a synthetic pathway for the formation of ketoprofen from the structure below. [3]





[1] for logical sequence of steps
[1] for all reagents and conditions correct
[1] for all correct intermediates drawn

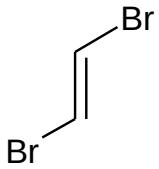
(c) Ketoprofen is reacted with an alcohol and forms an ester as shown.



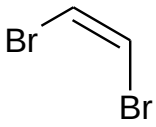
(i) Name the alcohol used in forming the ester. [1]

1,2−dibromoethanol **[1]**

(ii) The alcohol was heated in the presence of aluminum oxide. Draw the structures of the two isomeric products formed and name them accordingly. [2]



trans−1,2−dibromoethene



cis−1,2−dibromoethene

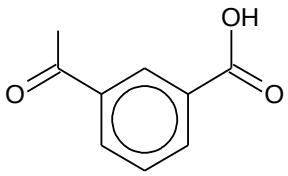
[1] for each correct structure + name

(iii) Predict the relative boiling points of the products formed, giving reasons for your answer. [1]

Both are simple molecular structures, but **cis−1,2−dibromoethene is polar with stronger intermolecular permanent dipole permanent dipole interactions which requires more energy to overcome than the weaker intermolecular instantaneous dipole induced dipole interactions in the non polar trans−1,2−dibromoethene**.

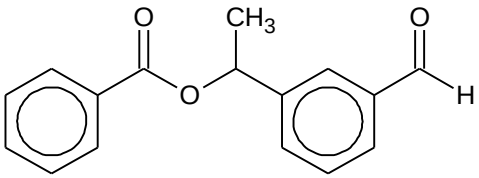
Hence trans−1,2−dibromoethene has a **lower boiling point** than cis−1,2−dibromoethene. **[1]**

(d) Compound **K**, a sweet smelling liquid, is an isomer of ketoprofen. Upon heating **K** with dilute sulfuric acid, compound **L** and benzoic acid are produced. Compound **L** is an alcohol which also produces a silver mirror with Tollens' reagent and a blue solution with Fehling's solution. It also reacts with hot acidified potassium dichromate(VI) to form compound **M** as shown below.

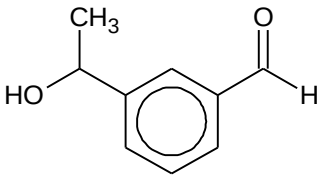


Compound **M**

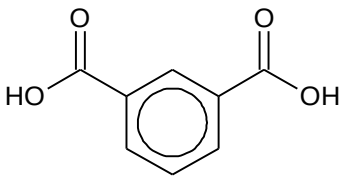
Compound **L** reacts with hot acidified potassium manganate(VII) to form carbon dioxide and compound **N** which will subsequently react with liquid bromine and anhydrous aluminium bromide solid to form compound **O**.
Deduce, with reasoning, the structures for compounds **K**, **L**, **N** and **O.** [10]



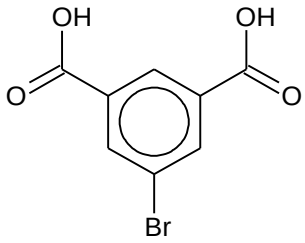
K



L



N



O

[1] each for each structure

Compound **K** undergoes **acidic hydrolysis** to form **L** and benzoic acid
⇒ **K** is an **ester** **[1]**

Compound **L** is **oxidised** by Tollens' reagent but not Fehling's solution
⇒ **L** contains **aromatic aldehyde** **[1]**

Compound **L** reacted with $K_2Cr_2O_7$ to form **M**
⇒ **aldehyde oxidised** to **carboxylic acid** **[1]**
⇒ **secondary alcohol oxidised** to **ketone** **[1]**

Compound **L** reacted with $KMnO_4$ to form **N**
⇒ **aldehyde oxidised** to **carboxylic acid** **[1]**
⇒ **sidechain oxidised** to **carboxylic acid** **[1]**

Compound **N** undergoes **electrophilic substitution** with Br_2 to form **O**
⇒ **O** is a **bromoarene** **[1]**

Statements max 6 out of 7 marks

[Total: 20]

END OF PAPER