H

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 1

CANDIDATE NAME **ANSWERS**

CT GROUP **1 5** INDEX NUMBER

CHEMISTRY 8872/02

13 September 2016

2 hours

Additional Materials: Data Booklet
Writing Paper
Cover Page for Section B

READ THESE INSTRUCTIONS FIRST

Write your name, CT group and index number in the spaces provided.
Write in dark blue or black pen.
You may use a soft 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 in the spaces provided.

Section B
Answer **two** questions on separate writing papers. If there is no answer to the question, a *blank sheet* of paper must still be submitted.

You are advised to show all working in calculations.
You may use a calculator.
The number of marks is given in brackets [ ] at the end of each question or part question.

At the end of the examination, fasten all your work securely together.

FOR EXAMINER'S USE			
Paper 1		**Paper 2 Section B**	
Total	/ 30	Total	/ 40
Paper 2 Section A			
1	/ 16	Penalty	s.f. / units
2	/ 11	**TOTAL**	**/ 110**
3	/ 13	**GRADE**	
Total	/ 40		

Section A (40 marks)

Answer **all** questions. Write your answers in the spaces provided.

1 This question is about Period 3 elements and their compounds.

(a) **(i)** Write the full electronic configuration of magnesium.

Mg: $1s^2\ 2s^2\ 2p^6\ 3s^2$

[1]

(ii) Account for the high melting point of magnesium in terms of its structure and bonding.

Magnesium has a giant lattice of Mg^{2+} ions in a sea of delocalised, mobile electrons. As strong electrostatic forces of attraction (metallic bonds) exist between the electrons and Mg^{2+} ions, large amount of energy is required to overcome them, accounting for its high melting point.

[2]

(iii) When a beam of Mg^{2+} particles travels through a uniform electric field which is at right angle to its direction of travel, it is deflected at an angle of +5.0°.

Determine the angle of deflection of a beam of Al^{3+} particles if it travels at the same speed through the same electric field.

Particle	z/m ratio	angle of deflection
Mg^{2+}	$\frac{+2}{24.3}$	+5.0°
Al^{3+}	$\frac{+3}{27.0}$	$[\frac{+3}{27.0} \div \frac{+2}{24.3}]$ x (+5.0°) = +6.75°

[2]

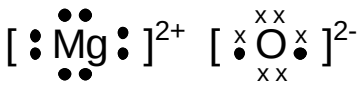
(iv) Suggest the property of magnesium for its use in flares and fireworks.

Magnesium burns with a bright white light.

[1]

(b) Both magnesium and sulfur form oxides.

(i) Construct the dot-and-cross diagram for magnesium oxide.



[1]

(ii) When sulfur dioxide is dissolved in water, an acidic solution is formed.

Write a balanced equation to show the reaction between sulfur dioxide and water.

$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$

[1]

(c) Chlorine is a yellow-green diatomic gas which is highly reactive.

(i) In an acidic medium, chlorine reacts with thiosulfate ions, $S_2O_3^{2-}$, to form sulfate ions, SO_4^{2-}.

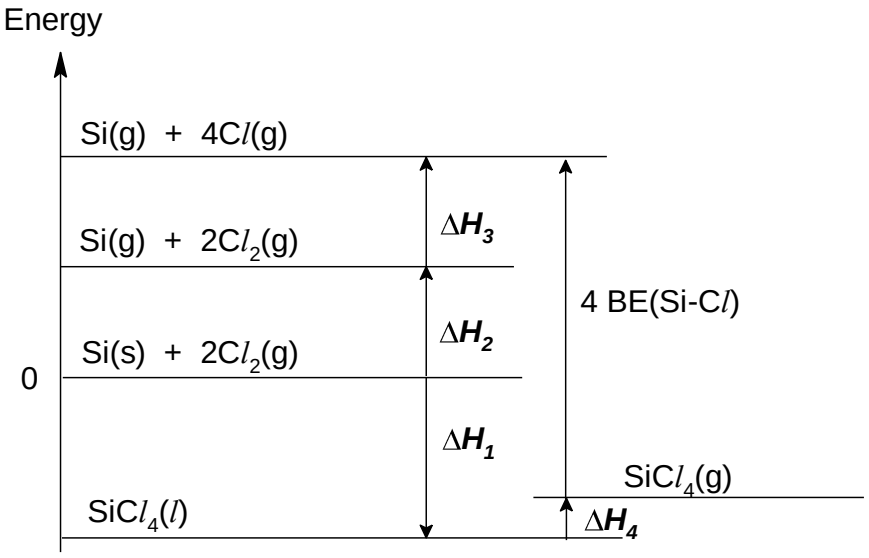
By means of two half-equations, construct a balanced equation for the reaction.

[O]: $S_2O_3^{2-} + 5H_2O \rightarrow SO_4^{2-} + 10H^+ + 8e^-$
[R]: $Cl_2 + 2e^- \rightarrow Cl^-$
Overall eqn: $4Cl_2 + S_2O_3^{2-} + 5H_2O \rightarrow 8Cl^- + 2SO_4^{2-} + 10H^+$

[2]

(ii) When chlorine is passed over silicon powder heated in a tube, silicon tetrachloride is produced.

The Si-C*l* bond energy may be calculated using the energy cycle shown below.



(I) Name the enthalpy change represented as ΔH_1.

ΔH_1: enthalpy change of formation of $SiCl_4$

[1]

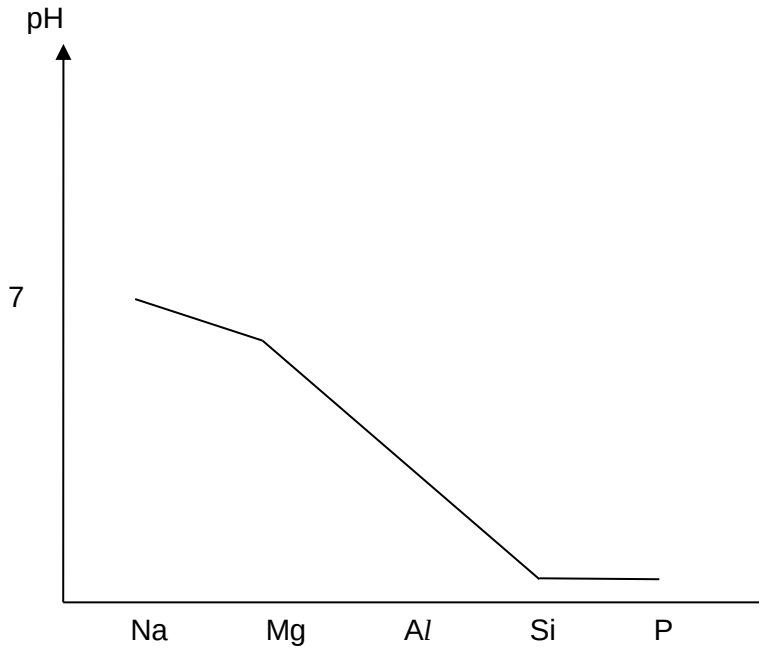
(II) Using relevant information from the *Data Booklet* and the following information, calculate the Si-C*l* bond energy.

$Si(s) + 2Cl_2(g) \rightarrow SiCl_4(s)$	$\Delta H_1 = -692$ kJmol^{-1}
$Si(s) \rightarrow Si(g)$	$\Delta H_2 = +450$ kJmol^{-1}
$SiCl_4(l) \rightarrow SiCl_4(g)$	$\Delta H_4 = +28.7$ kJmol^{-1}

4 BE(Si-C*l*) = – (+28.7) – (–692) + (+450) + 2(+244)
BE(Si-C*l*) = +400 kJ mol^{-1}

[3]

(d) On the grid below, sketch the graph of the variation in pH of the solutions produced when the chlorides of Period 3 elements are added to water.



[2]

[Total: 16]

2 Benzoic acid is a weak acid which has antifungal abilities and had been used for a long time in preservation of berries in the 19th century.

(a) **(i)** Explain what is meant by a *weak acid*?

A weak acid is a proton donor that dissociates partially.

[1]

(ii) Given that a 0.150 mol dm^{-3} of benzoic acid have a pH of 3.1. Calculate the acid dissociation constant, K_a of benzoic acid.

pH = - lg √ (K_a x [benzoic acid])
3.1 = - lg √(K_a x 0.150)
K_a = 4.21 x 10^{-6} mol dm^{-3}

OR
pH = -lg $[H_3O^+]$
$[H_3O^+]$ = 0.000794 mol dm^{-3}

Equation	$C_6H_5COOH(aq)$ +	H_2O ⇌	$C_6H_5COO^-$ +	H_3O^+
Initial [ ] / mol dm^{-3}	0.150	-	0	0
Change in [ ] / mol dm^{-3}	-0.000794	-	+0.000794	+0.000794
Equilibrium [ ] / mol dm^{-3}	0.1492	-	0.000794	0.000794

$K_a = \frac{(0.000794)(0.000794)}{(0.1492)}$ = 4.23 × 10^{-6} mol dm^{-3}

[2]

(b) In an experiment, 20 cm^3 of 0.01 mol dm^{-3} aqueous benzoic acid is added to 10 cm^3 of 0.01 mol dm^{-3} sodium hydroxide.

Explain, with the aid of **two** equations, how the resultant mixture can act as a buffer upon addition of small amounts of H_3O^+ and OH^-.

The solution is an acidic buffer which is made up of CH_3COOH and $CH_3COO^-Na^+$.

$C_6H_5COO^- + H_3O^+ \rightarrow C_6H_5COOH$
When a small amount of H_3O^+ is added, $C_6H_5CO_2^-$ mainly from the salt neutralises the H_3O^+ added and there is negligible change in pH.

$C_6H_5COOH + OH^- \rightarrow C_6H_5COO^- + H_2O$
When a small amount of OH^- is added, $C_6H_5CO_2H$ neutralises the OH^- added and there is negligible change in pH.

[3]

(c) Benzoic acid reacts with an unknown alcohol, **L**, to give an ester with molecular formula $C_{11}H_{14}O_2$.

$$C_6H_5CO_2H(l) + \mathbf{L}(l) \rightleftharpoons C_{11}H_{14}O_2(l) + H_2O(l)$$

(i) **L** produces a yellow precipitate when warmed with alkaline aqueous iodine.

Suggest a possible structure for **L**. Explain your answer.

Molecular formula of **L** = $C_{11}H_{14}O_2 + H_2O - C_6H_5COOH$
= $C_4H_{10}O$

L contains $CH_3CH(OH)$- group which undergoes oxidation when warmed with alkaline aqueous iodine.

L is $CH_3CH_2CH(OH)CH_3$.

[2]

(ii) 0.05 mol of benzoic acid and 0.075 mol of **L** are mixed and shaken for a long time to reach equilibrium. The mixture is titrated quickly with 1.00 mol dm^{-3} of aqueous sodium hydroxide and 24.80 cm^3 of alkali is required.

Calculate a value for the equilibrium constant for this reaction.

Amount of NaOH required = 24.80/1000 x 1.00
= 0.0248 mol
= amount of benzoic acid present at eqm

Equation	$C_6H_5COOH(l) + \mathbf{L}(l) \rightleftharpoons C_{11}H_{14}O_2(l) + H_2O(l)$			
Initial [ ] / mol dm^{-3}	0.0500	0.0750	0	0
Change in [ ] / mol dm^{-3}	-0.0252	-0.0252	+0.0252	+0.0252
Equilibrium [ ] / mol dm^{-3}	0.0248	0.0498	0.0252	0.0252

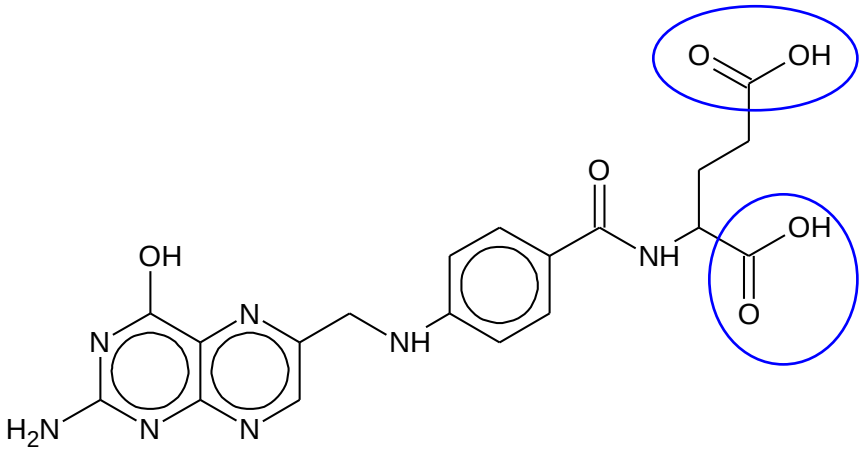
K_c = (0.0252 x 0.0252) / (0.0248 x 0.0498)
= 0.514

[3]

[Total: 11]

3 Folic acid, $C_{19}H_{19}N_7O_6$, is a form of vitamin B_9 needed for many functions in the body, especially in rapid cell division and growth. It is important for pregnant women to have enough folic acid to prevent major birth defects.

The structure of the folic acid molecule is



(a) (i) State the number of sp^2 hybridised carbons in folic acid.

15

[1]

(ii) Circle the acidic groups on the structure of the folic acid molecule above.

Two –COOH groups

[1]

(b) A pharmaceutical company claims the average mass of folic acid in one tablet indicated in the supplement facts, at 5 mg, is correct to 1%.

Supplement Facts

Serving size:	**1 tablet**	
Serving per container:	**60**	
	Amount Per Serving	**% DV***
Folic Acid	5 mg	1250 %

*Percent Daily Values are based on a 2,000 calorie diet (US).
**Daily Value not established

Other ingredients: Dicalcium Phosphate, Microcrystalline Cellulose, Starch, Stearic Acid, Opadry Clear, Magnesium Stearate Vegetable, Silicon Dioxide.

Label on the folic acid bottle

A student wanted to verify the claim made by the company through volumetric analysis. She prepared the following solutions:

FA 1 is a 250 cm^3 solution containing 15 folic acid tablets.
FA 2 is a 1.50 x 10^{-3} mol dm^{-3} sodium hydroxide solution.

It was found that 25.0 cm^3 of **FA 1** required 22.80 cm^3 of **FA 2** for complete reaction.

(i) Calculate the average mass of folic acid present in **one** tablet.

n(NaOH) required = $1.50 \times 10^{-3} \times (22.80/1000)$
= 3.42×10^{-5} mol

Since 1 folic acid ≡ 2 NaOH,
n(folic acid) present in 25.0 cm^3 of FA1 = $3.42 \times 10^{-5} / 2$
= 1.71×10^{-5} mol

n(folic acid) present in 250 cm^3 of FA1 = 1.71×10^{-4} mol

Mass of folic acid in 15 tablets = $1.71 \times 10^{-4} \times 441$
= 0.07541 g

Average mass of folic acid in one tablet = 0.07541 / 15
= 0.00503 g
= 5.03 mg

[4]

(ii) Explain whether the claim made by the company that the average mass of folic acid in one tablet is correct to 1% is valid.

Let *x* be the average mass of folic acid present
Acceptable range of average mass of ascorbic acid present:

99% of 5 mg < *x* <101% of 5 mg
4.95mg < *x* < 5.05 mg

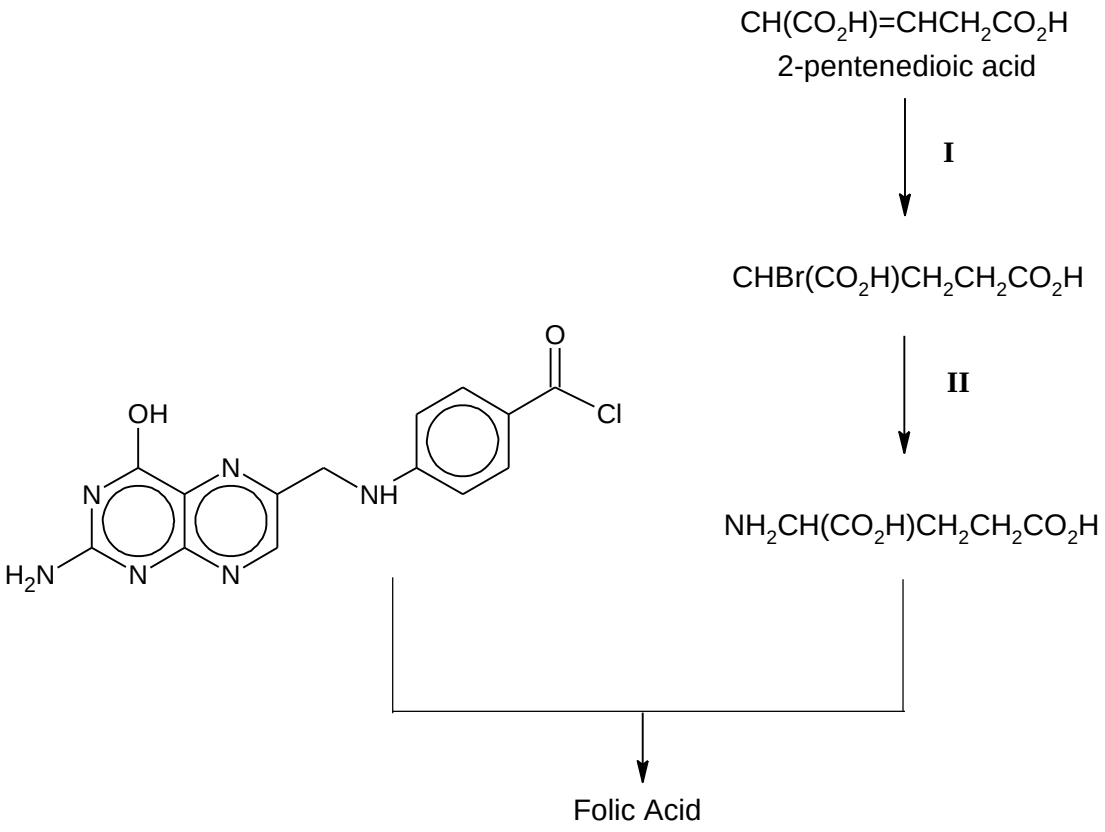
Since 5.03 mg is within the acceptable range, the claim made by the company is valid.

Or

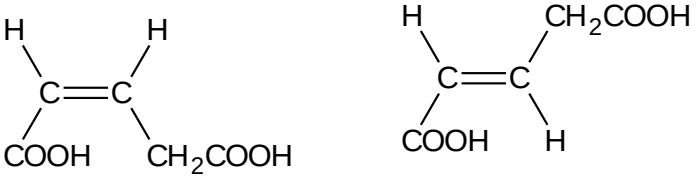
% difference = (5.03 – 5.00) / 5.00 x 100% = 0.6 % (<1%)
Hence, claim made by the company is valid.

[2]

(c) The following shows a possible pathway for the synthesis of folic acid.



(i) 2-pentenedioic acid exhibits geometric isomerism. Draw the two isomers of 2-pentenedioic acid.



[2]

(ii) Write an equation for the reaction occurring in step **I**, and state the reagents and conditions necessary for the reaction to occur.

Equation:
$CH(CO_2H)=CHCH_2CO_2H + HBr \rightarrow CHBr(CO_2H)CH_2CH_2CO_2H$

Reagents and conditions: HBr(g)

[2]

(iii) State the type of reaction in step **II**.

(Nucleophilic) Substitution

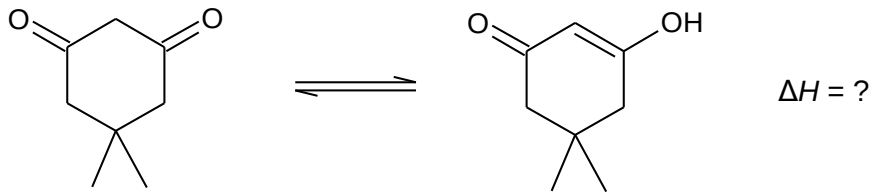
[1]

[Total: 13]

Section B (40 marks)

Answer **two** of the three questions in this section on separate paper.

4 **(a)** Dimedone is an important organic precursor for the synthesis of scented compounds used in perfumes. It exists in dynamic equilibrium with its isomer, enol, through a reaction called enol-keto tautomerisation. This reaction is shown in the equation below.



dimedone enol

(i) Define the term *dynamic equilibrium*.

Dynamic equilibrium is a state of balance in a reversible process where rate of forward reaction is equals to the rate of reverse reaction.

[1]

(ii) Write an expression for the equilibrium constant, K_c, for this reaction.

$K_c = \frac{[enol]_{eqm}}{[dimedone]_{eqm}}$

[1]

(iii) It was experimentally determined using spectrometric techniques that 33% of dimedone was converted to the enol form at room temperature. Calculate the equilibrium constant, K_c, for this reaction.

Let the initial concentration of dimendone be x,

	dimendone ⇌	enol
Initial concentration / mol dm^{-3}	x	0
Change in concentration / mol dm^{-3}	-0.33x	+0.33x
Eqm concentration / mol dm^{-3}	0.67x	0.33x

$K_c = \frac{0.33x}{0.67x}$

$= 0.493$

[2]

(iv) Using suitable bond energy values from the *Data Booklet*, calculate the Δ*H* for the formation of enol from dimedone.

Bonds broken	Energy absorbed / kJ mol^{-1}	Bond formed	Energy released / kJ mol^{-1}
C – H	+410	C = C	-610
C = O	+740	O – H	-460
C – C	+350	C – O	-360
Total	+1500	Total	-1430

Δ*H* = (+1500) + (-1430) = +70.0 kJ mol^{-1}

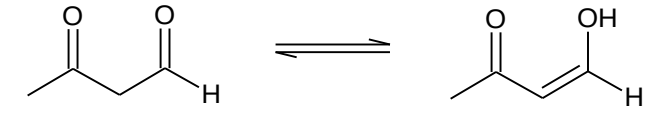
[3]

(v) Using the answer obtained in **(iv)**, suggest what will happen to the equilibrium position and composition when the equilibrium mixture is heated.

By Le Chatelier's Principle, when the equilibrium mixture is heated, the system will reduce the temperature by favoring the forward endothermic reaction to absorb the excess heat. As a result, the equilibrium will shift to the right and the new equilibrium mixture will have more enol and less dimedone.

[4]

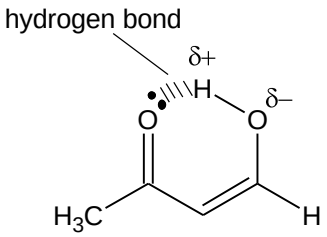
(b) Acetylacetaldehyde can also undergo enol-keto tautomerisation reaction as shown in the equation below.



acetylacetaldehyde ⇌ enol of acetylacetaldehyde

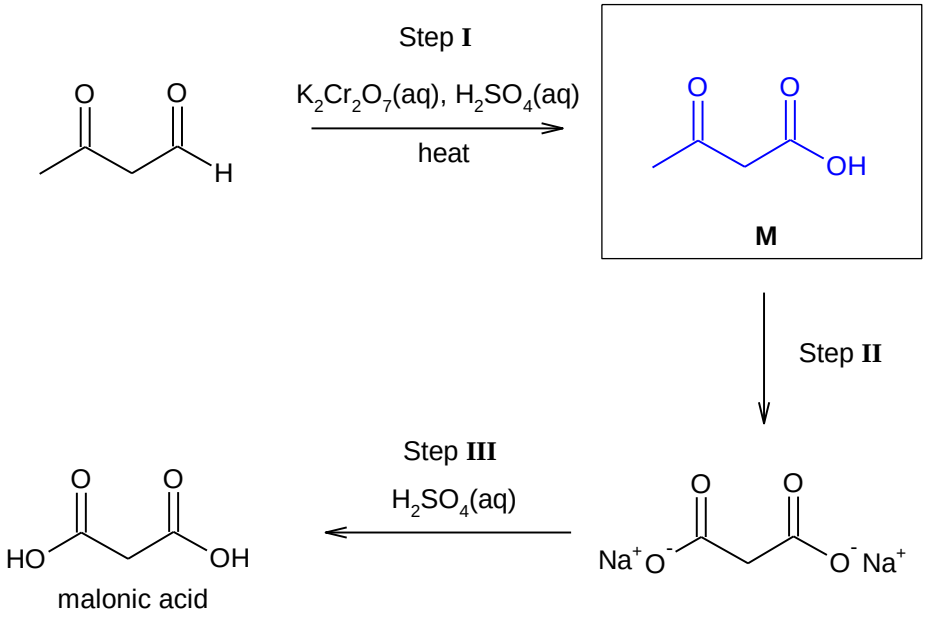
Compared to dimedone, a higher percentage of up to 76% of acetylacetaldehyde was converted to the enol form at room temperature. This can be attributed to the greater stability brought about by the formation of intramolecular hydrogen bonding of the enol of acetylacetaldehyde.

Draw a diagram to show how the intramolecular hydrogen bonding is formed in the enol of acetylacetaldehyde.



[2]

(c) Malonic acid can be synthesised from acetylacetaldehyde by the following reaction scheme.



(i) Draw the intermediate compound **M** and give the reagent and conditions for Step **II**.

Step **II**:
Reagent and Conditions: NaOH(aq), I_2(aq), warm

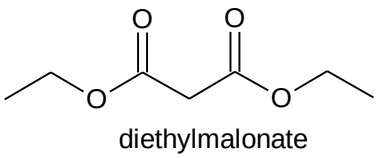
[2]

(ii) Name the type of reaction which occurred in Step **III**.

Acid-base reaction

[1]

(iii) Malonic acid can be converted to diethylmalonate, an ester, which occurs naturally in grapes and strawberries.

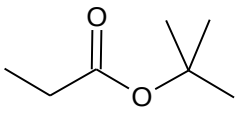


Name the type of reaction when malonic acid is converted to diethylmalonate.

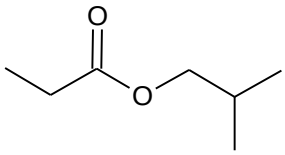
Condensation

[1]

(d) By means of a simple chemical test, suggest how you would distinguish the two esters, **P** and **Q**.



P



Q

State clearly the reagents and conditions you would use and the observations you would make.

Reagents & Conditions: $KMnO_4(aq)$, $H_2SO_4(aq)$, heat
Observation: **P** – Purple $KMnO_4$ solution remained.
Q – Purple $KMnO_4$ solution decolourised.

OR

Reagents & Conditions: $K_2CrO_7(aq)$, $H_2SO_4(aq)$, heat
Observation: **P** – Orange K_2CrO_7 solution remained.
Q – Orange K_2CrO_7 solution turned green.

[3]

[Total: 20]

5 **(a)** Compound **R** has the molecular formula $C_4H_6O_2$.

Data about the reactions of **R** are given in the table.

reaction	reagent	result
1	Br_2(aq)	Aqueous bromine decolourised.
2	Na	1 mol of **R** produced 12 dm^3 of colourless gas, measured at r.t.p.
3	2,4-dinitrophenylhydrazine	Orange solid formed.
4	Hot Tollens' reagent	No visible change observed.
5	Hot acidified $KMnO_4$	Purple $KMnO_4$ decolourised and product **S** formed. When Na_2CO_3(aq) is added to 1 mol of **S**, 24 dm^3 of colourless gas, measured at r.t.p was produced.

(i) Name the functional group that reaction **1** shows to be present in **R**.

Alkene

[1]

(ii) Based on reactions **2**, **3** and **4**, deduce the identity and number of **each** of the functional groups present in **R**. Explain your answer as fully as you can.

R undergoes redox with Na suggesting the presence of alcohol or carboxylic acid.

Mole ratio of **R** : H_2 = 1 : ½
R contains one –OH group or –COOH group.

R undergoes condensation with 2,4-DNPH suggesting the presence of ketone or aldehyde. Since it does not undergo oxidation with Tollens' reagent, ketone is present.

Thus, from the molecular formula and deductions, **R** contains one alcohol and one ketone.

[5]

(iii) Based only on reaction **5**,
(I) identify the colourless gas
(II) name the type of reaction between **R** and hot acidified $KMnO_4$
(III) deduce the identity and the number of the functional group present in **S**

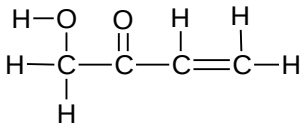
(I): carbon dioxide

(II): oxidation

(III): Mole ratio of **S** : CO_2 = 1 : 1
S contains two –COOH group.

[4]

(iii) From your answers in **(i)**, **(ii)** and **(iii)**, draw the displayed formula of **R**.



[1]

(b) Compound **T**, $CH_3CH=CHCO_2H$, is an isomer of compound **R** from **(a)**.

Aqueous solution of **T** reacts with aqueous sodium hydroxide.

(i) Write a balanced equation for the neutralisation reaction between **T**(aq) and NaOH(aq).

$CH_3CH=CHCO_2H(aq) + NaOH(aq) \rightarrow CH_3CH=CHCOO^-Na^+(aq) + H_2O(l)$

[1]

(ii) The standard enthalpy change of neutralistion between **T**(aq) and NaOH(aq) was determined experimentally by mixing known volumes of 2.0 mol dm^{-3} **T**(aq) and 1.0 mol dm^{-3} NaOH(aq). The following results were obtained.

Volume of **T**(aq) used	= 30.0 cm^3
Volume of NaOH(aq) used	= 60.0 cm^3
Change in temperature	= +8.4 °C

Calculate the standard enthalpy change of the neutralisation reaction.

[Assume specific heat capacity of the solution to be 4.2 J g^{-1} K^{-1} and its density to be 1 g cm^{-3}]

Amount of water formed = 2.0 x 30.0/1000 = 0.0600 mol

$$\Delta H_n = \frac{-\text{heat change}}{n_{H2O}\ formed}$$

$$= \frac{-90 \times 4.2 \times 8.4}{0.0600}$$

$$= -52.9 \text{ kJ mol}^{-1}$$

[3]

(iii) When the experiment is repeated with 2.0 mol dm^{-3} hydrochloric acid instead of 2.0 mol dm^{-3} **T**(aq), would the enthalpy change of neutralisation be more or less exothermic? Explain your answer.

The enthalpy change of neutralisation would be more exothermic.
HC*l* is a strong acid which dissociates completely and no heat is required to dissociate the H^+ ion from the acid unlike **T** which is a weak acid. Thus, more heat would be released to the surrounding.

[2]

(iv) With reference to sodium hydroxide, define the term *lattice energy*.

Lattice energy of NaOH is the heat evolved when one mole of the ionic solid of NaOH is formed from its gaseous Na^+ and OH^- ions under standard conditions of 298 K and 1 atm.

[1]

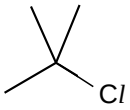
(v) Explain how you would expect the numerical magnitude of the lattice energy of sodium hydroxide to compare with that of magnesium hydroxide.

|Lattice energy| $\propto \left|\frac{q_+ q_-}{r_+ + r_-}\right|$ for ionic compound. Since Mg^{2+} has a bigger ionic charge and smaller ionic radius than Na^+, the magnitude of lattice energy of NaOH should be smaller than that of $Mg(OH)_2$.

[2]

[Total: 20]

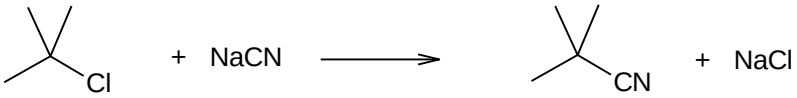
6 **(a)** *t*-butyl chloride is a chloroalkane which is produced industrially as a precursor to other organic compounds.



t-butyl chloride

(i) *t*-butyl chloride reacts with sodium cyanide in ethanol solvent.

Write a balanced equation for the reaction and state the type of reaction.

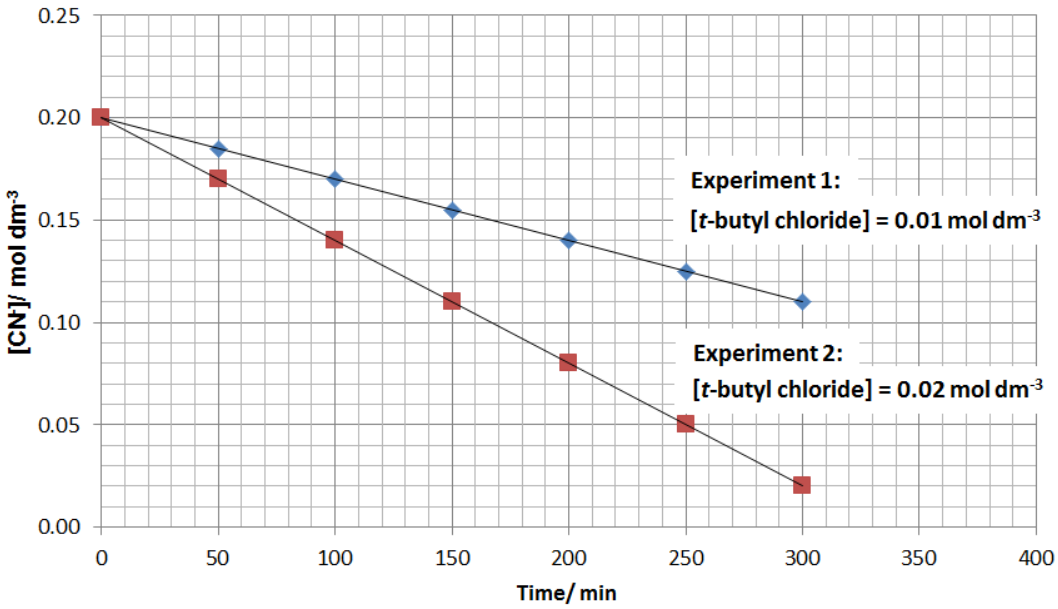


t-butyl chloride

(Nucleophilic) Substitution

[2]

(ii) The kinetics of the reaction in **(i)** can be investigated experimentally. Two separate experiments have been conducted for different concentrations of *t*-butyl chloride and the data collected are used to plot the graphs below.



Use the graphs to show that the order of reaction is zero with respect to CN^- ions.

The shape of the graph is a straight line with constant gradient showing rate is independent of the concentration of CN^-.

[1]

(iii) Use the graph to determine the order of reaction with respect to *t*-butyl chloride. Explain your answer fully, showing all appropriate calculation.

Student shows working and calculation of the initial rate which is negative gradient at time = 0 of both line (0.0003 mol dm^3 min^{-1} and 0.0006 mol dm^3 min^{-1}) correctly.

When the concentration of *t*-butyl chloride doubles, the initial rate also doubles. Hence, order of reaction with respect to *t*-butyl chloride is one.

[3]

(iv) Hence, calculate the rate constant for the reaction, stating its units.

Rate = k [*t*-butyl chloride]

For experiment 1,
0.003 mol dm^3 min^{-1} = k (0.01 mol dm^{-3})
k = 0.0300 min^{-1}

OR
For experiment 2,
0.006 mol dm^3 min^{-1} = k (0.02 mol dm^{-3})
k = 0.0300 min^{-1}

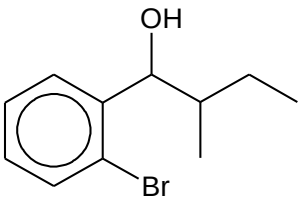
[2]

(v) 1-chlorobutane is an isomer of *t*-butyl chloride. Predict which isomer has a higher boiling point. Explain your answer.

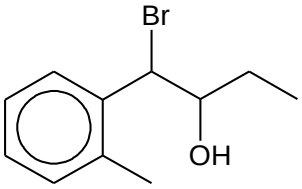
1-chlorobutane has a higher boiling point than *t*-butyl chloride. Both isomers are simple covalent molecules with intermolecular van der Waal's forces of attraction. However, *t*-butyl chloride has more branching / is more spherical in shape with smaller surface area of contact between molecules. Hence, there is weaker van der Waal's forces of attraction between molecules of *t*-butyl chloride and requires less energy to overcome.

[4]

(b) Compounds **V** and **W** are isomers of each other.



Compound **V**



Compound **W**

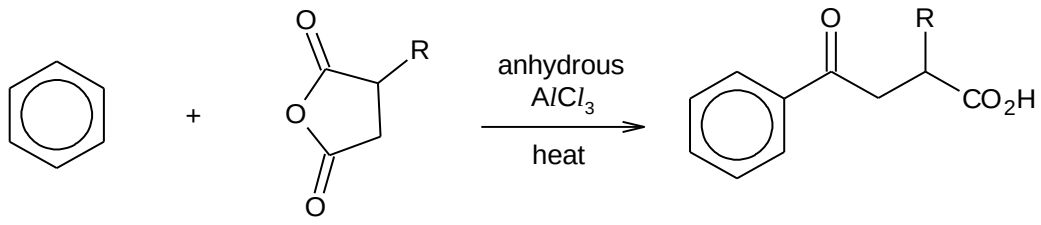
Describe a simple chemical test to distinguish **V** and **W**. State any observations clearly.

Reagents & Conditions: (1) NaOH(aq), heat,
(2) Cool,
(3) Acidify with HNO_3(aq)
(4) $AgNO_3$(aq)

Observations: **V** – No cream ppt seen.
W – Cream ppt seen.

[3]

(c) Friedel-Crafts acylation is a reaction developed by Charles Friedel and James Crafts to attach substituents to an aromatic ring. The general reaction scheme is shown below.



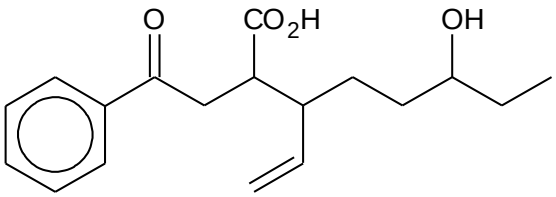
(i) Name the type of reaction for Friedel-Crafts acylation.

(Electrophilic) Substitution

[1]

(ii) 3-(1-vinylhexyl) succinic anhydride reacts with benzene via Friedel-Crafts acylation to form compound **X**.

X is used to produce highly coloured dyes used as biomarkers for livestock exposed to certain carcinogenic pollutants.



X

State the number of sp^2 – sp^3 carbon-carbon overlaps present in **X**.

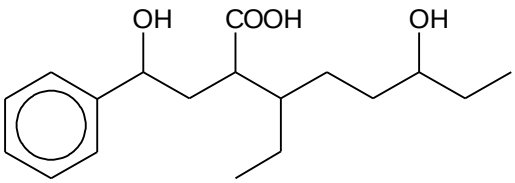
3

[1]

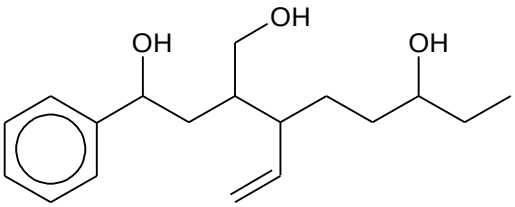
(iii) Draw the organic compounds formed when **X** reacts with:

(I) H_2, Ni, 200 °C
(II) $LiAlH_4$ in dry ether
(III) cold $KMnO_4$(aq), NaOH(aq)

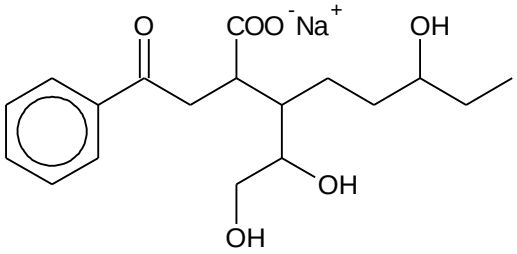
(I):



(II):



(III):



[3]

[Total: 20]

End of Paper