PRELIMINARY EXAMINATIONS

HIGHER 2

CANDIDATE NAME	
CIVICS GROUP	/
CENTER NUMBER	S
INDEX NUMBER	

CHEMISTRY
9729/02

Paper 2 Structured Questions **11 September 2017**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Civics Group, centre number, index number and name on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

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 or part question.

For Examiner's Use	
1	/ 22
2	/ 15
3	/ 21
4	/ 8
5	/ 9
Paper 1	/ 30
Paper 3	/ 80
Total	

This document consists of 18 printed pages

Answer **all** the questions

1 Silver chloride is an important photosensitive inorganic material widely used in photographic applications. It is industrially produced by mixing solutions of silver nitrate and sodium chloride.

$$Ag^{+}(aq) + Cl^{-}(aq) \rightleftharpoons AgCl(s) \qquad \Delta H_{ppt}^{\ominus} = -65.7 \text{ kJ mol}^{-1}, \Delta S_{ppt}^{\ominus} = -34.3 \text{ J mol}^{-1} \text{ K}^{-1}$$

(a) **(i)** Suggest whether a lower or higher temperature should be used to increase the yield of silver chloride. Explain your answer. [2]

(ii) Calculate $\Delta G^{\ominus}$ of the precipitation of $AgCl$. [1]

(iii) In view of your answer in **(a)(ii)**, comment on the solubility of silver chloride in water. [1]

(b) (i) Lattice energies are not measured directly. The value calculated using Hess' Law and the Born-Haber cycle is the experimental lattice energy. [3]

Using $\Delta H_{ppt}^{\ominus}$ of $AgCl(s)$, the following data and relevant data from the *Data Booklet*, calculate the experimental lattice energy of $AgCl(s)$.

standard enthalpy change of formation of $Ag^{+}(aq)$	+106 kJ mol^{-1}
standard enthalpy change of formation of $Cl^{-}(aq)$	–167 kJ mol^{-1}
standard enthalpy change of atomisation of Ag(s)	+285 kJ mol^{-1}
first electron affinity of chlorine	–349 kJ mol^{-1}

The theoretical value of lattice energies are calculated using the distances between the cations and anions in the crystal structure, and the charge on each ion.

The table below shows the numerical values of experimental and theoretical lattice energies for sodium chloride and silver fluoride.

compound	experimental value/ $kJ\ mol^{-1}$	theoretical value/ $kJ\ mol^{-1}$
$NaCl$	-771	-766
AgF	-967	-953

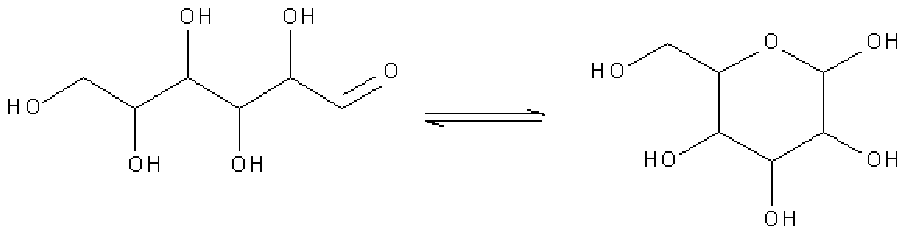
(ii) It can be seen that the experimental and theoretical values for sodium chloride and silver fluoride are quite similar. [1]

However, the theoretical value for the *silver chloride* is significantly less exothermic than the experimental value.

Suggest a reason for this.

(c) Explain, with the aid of equations, why silver chloride is soluble in aqueous ammonia while silver iodide does not dissolve in aqueous ammonia. [3]

(d) (i) Most of the energy our bodies need comes from carbohydrates and fat. Starch is broken down into glucose,$C_6H_{12}O_6$. Glucose exist mainly in cyclic forms with a small percentage in open chains. [1]



open-chain cyclic

State what you would observe when glucose is added to an alkaline solution of ammoniacal silver(I) nitrate.

Glucose is transported to the cells to react with oxygen via a series of steps to form carbon dioxide, water and energy.

(ii) Write a balanced equation for the reaction of glucose with oxygen. [1]

(iii) Using data from the Data Booklet, calculate the amount of energy released per mole of glucose using the **cyclic** structure. [2]

(iv) The literature value for the amount of energy released per mole of glucose is – 2800 kJ. [1]

Apart from bond energies are average values, suggest another reason for the difference between this value and that calculated in **(d)(iii)**.

Like carbohydrates, fats are metabolised into carbon dioxide and water and when subjected to combustion in a bomb calorimeter. The reaction of tristearin, $C_{57}H_{110}O_6$, a typical fat is as follows:

$$C_{57}H_{110}O_6 + \frac{163}{2} O_2 \rightarrow 57\ CO_2 + 55\ H_2O \quad \Delta H^\ominus = -37760 \text{ kJ mol}^{-1}$$

The fuel value is the energy when one gram of the material undergoes combustion. The table below shows the fuel value of carbohydrates and protein and the food label of a cup noodle:

	Fuel value / kJ g^{-1}
Carbohydrate	17
Fat (Tristearin)	To be calculated
Protein	17


Nutrition Facts
Serving Size 1 container (70g)

Amount Per Serving	
Calories 310	Calories from Fat 100
	% Daily Value*
Total Fat 12g	18%
Saturated Fat	25%
Trans Fat	
Cholesterol 0mg	0%
Sodium 1010mg	42%
Total Carbohydrate 44g	15%
Dietary Fiber 4g	16%
Sugars 4g	
Protein 8g	

(v) Determine the fuel value of tristearin and hence deduce if tristearin or carbohydrate is a better source of energy. (M_r of tristearin = 890) [2]

(vi) During reading or watching television, the average adult uses about 7 kJ/min. How many minutes of such activity can be sustained by the energy supplied by a serving of cup noodle (considering only the total fat, total carbohydrate and total protein content)? [1]

(e) In the body, glucose is also converted to energy via alcoholic fermentation. This process has been used in making beer and the side products such as esters contribute greatly to the taste and aroma of the beer. [3]

Ethyl acetate can be formed as follows

$$CH_3CO_2H + CH_3CH_2OH \rightleftharpoons CH_3CO_2CH_2CH_3 + H_2O$$

1.51 mol of CH_3CO_2H and 1.66 mol of CH_3CH_2OH was allowed to reach equilibrium in a 100 cm^3 solution. 10 cm^3 of the equilibrium mixture was extracted and large amounts of cold water was added to quench the reaction. The mixture was then titrated with 22.40 cm^3 of 2 mol dm^{-3} NaOH.

Calculate the K_c for the formation of ethyl acetate.

[Total: 22]

2 **(a)** In 1887, the Swedish scientist Svante Arrhenius postulated that acids and bases dissociate in water to form hydrogen ions, H^+, and hydroxide ions, OH^-, respectively.

(i) Suggest a limitation of the Arrhenius concept of acids and bases. [1]

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A theory proposed by Danish chemist J.N. Brønsted and British chemist T.M. Lowry overcame the shortcomings of the Arrhenius theory.

(ii) Using the Brønsted–Lowry model, nitric acid can be either a Brønsted–Lowry acid or base. Write equations to show how nitric acid *reacts* as a Brønsted–Lowry acid and a Brønsted–Lowry base respectively. [2]

As an acid ____

As a base ____

(b) The following table compares the K_a values of two three-carbon carboxylic acids.

Acid	Formula	K_{a1}	K_{a2}
Propanoic	$CH_3CH_2CO_2H$	1.35×10^{-5}	—
Malonic	$HO_2CCH_2CO_2H$	1.41×10^{-3}	2.00×10^{-6}

Suggest a reason why K_{a1} of malonic acid is higher than

(i) K_a of propanoic acid [1]

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(ii) K_{a2} of malonic acid [1]

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(iii) 25 cm^3 of 0.10 mol dm^{-3} of NaOH is gradually added to 10 cm^3 of 0.10 mol dm^{-3} malonic acid. Calculate the pH of the mixture when the following volumes of NaOH has been added. [3]

- 0 cm^3 [considering only K_{a1} of malonic acid]

- 5 cm^3

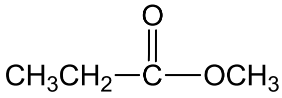
- 15 cm^3

- 25 cm^3

(iv) Using your answers in **(b)(iii)**, sketch the pH-volume added curve when 25 cm^3 of 0.10 mol dm^{-3} NaOH is gradually added to 10 cm^3 of 0.10 mol dm^{-3} malonic acid. [2]

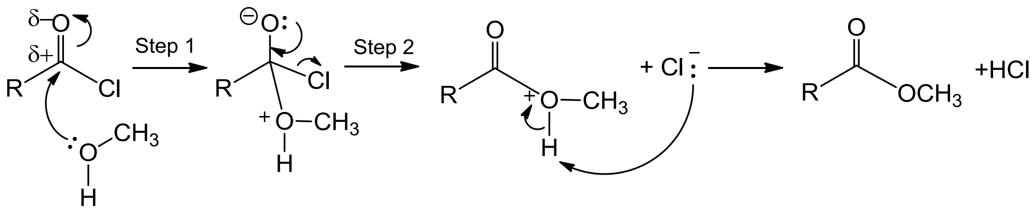
(v) Suggest an indicator for the first equivalence point. [1]

(c) Compound **A** can be directly synthesised from propanoic acid or propanoyl chloride via condensation.



Compound **A**

The formation of compound **A** from propanoyl chloride occurs via the mechanism shown below.



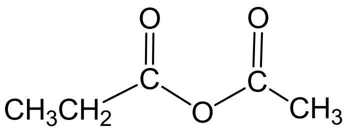
where R = CH_3CH_2—

(i) Name the reactions in step 1 and step 2. [2]

Step 1 ____

Step 2 ____

Compound **B** is a carboxylic acid anhydride that reacts similarly to an acyl chloride.



Compound **B**

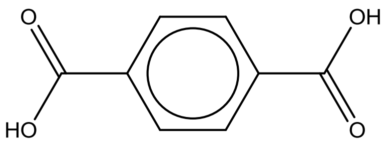
(ii) Compound **B** reacts with methanol that has been labelled with ^{18}O isotope to form compound **A**. [1]

Write an equation for the reaction showing clearly the location of the ^{18}O atom in the product. The formula of methanol can be written as $CH_3{}^{18}OH$.

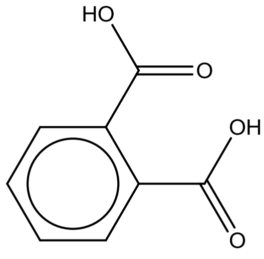
(iii) Draw the structure of another neutral product formed in the reaction. [1]

[Total: 15]

3 Terephthalic acid (TPA) and phthalic acid (PA) both have the molecular formula $C_6H_4(COOH)_2$. While TPA is used principally to make clothing and plastic bottles, PA has limited commercial application. The structures of TPA and PA are shown below.



TPA



PA

Some physical properties of TPA and PA are shown in the table below:

	TPA	PA
Appearance	White crystal	White crystal
Melting point	300 °C	207 °C
Boiling point	Decomposes	Decomposes

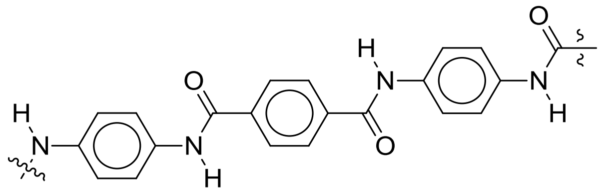
(a) Explain why TPA has a higher melting point than PA. [2]

(b) **(i)** TPA can be reduced to a diol for the synthesis of a renewable polymer.

Draw the structure of this diol and illustrate with a diagram, its interaction with water. [3]

(ii) Hence, explain why the diol in **(i)** is soluble in water. [1]

One common derivative of TPA is terephthaloyl chloride. Terephthaloyl chloride reacts with another monomer in a polymerisation reaction to form a synthetic fiber, commonly known as Kevlar®. A short chain of the Kevlar® polymer is shown below.



A strand of Kevlar® polymer

(c) **(i)** Name the type of reaction for this polymerisation reaction and suggest the structure of the other monomer to form the Kevlar® polymer. [2]

Type of reaction:

Structure of monomer:

(ii) In selecting a suitable material for the manufacture of bulletproof armour, it is necessary to ensure that the material does not shatter upon high impact force from a bullet.

With reference to the structures of gold and fluorite, CaF_2, explain why gold is more suitable for the lining of bulletproof armour. [2]

(d) **(i)** Define second ionisation energy of aluminium. [1]

(ii) Explain why the second ionisation energy of aluminium is higher than that of silicon. [1]

(e) Many chemical reactions such as the reaction between peroxodisulfate and iodide ions occur very slowly at room temperature.

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

One way to speed up rate of reaction is to use a homogeneous catalyst.

(i) Explain why the reaction between $S_2O_8^{2-}$ and I^- has a high activation energy. [1]

(ii) A solution of iron(II) ions can be used to catalyse the reaction between $S_2O_8^{2-}$ and I^-.

Using appropriate equations, outline the catalytic role of Fe^{2+} in the $S_2O_8^{2-}$ and I^- reaction. Hence, explain with the aid of a Boltzmann distribution curve, how Fe^{2+} speeds up the rate of the reaction. [5]

A kinetics study was conducted on the reaction of $S_2O_8^{2-}$ and I^- to determine the rate equation. Varying volumes of $S_2O_8^{2-}$ and I^- were added to a mixture containing sodium thiosulfate and starch indicator, followed by topping up with suitable volume of water.

As the reaction of $S_2O_8^{2-}$ and I^- proceeds, the iodine produced will be consumed by the thiosulfate. When all thiosulfate is reacted, the remaining iodine will react with the starch indicator, forming a blue-black complex. The rate of reaction is determined by the time taken for the blue-black colouration to appear.

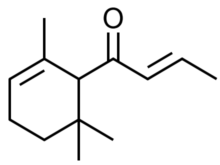
Experiment	Volume of KI / cm^3	Volume of $Na_2S_2O_8$ / cm^3	Volume of $Na_2S_2O_3$ / cm^3	Volume of water / cm^3	Time for blue-black colour / s
1	10	20	10	10	50
2	5	20	10	15	100
3	30	10	10	0	33
4	20	40	20	20	x

(iii) Determine the order of reaction with respect to iodide and peroxodisulfate. [2]

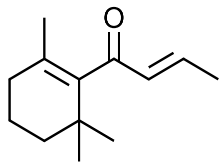
(iv) Hence, deduce the time taken for the blue-black colouration to appear for experiment 4. [1]

[Total: 21]

4 Rose ketones, damascenones, were discovered as active ingredients in the characteristic smell of Bulgarian rose oil. α-damascenone and β-damascenone were later discovered to give female perfumes such as *Dior's Poison* their unusual and distinctive fragrance.

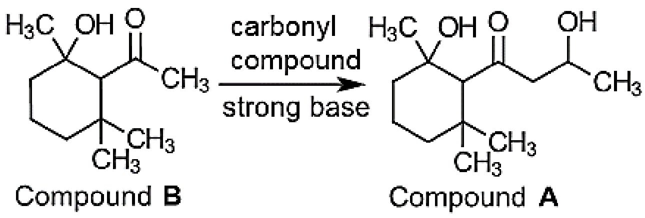


α-damascenone



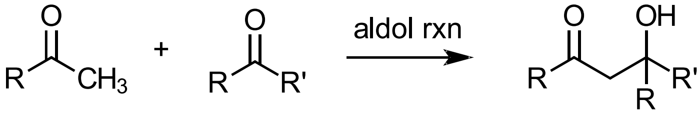
β-damascenone

In the synthesis of damascenones in the laboratory, it was found that compound **A** is a possible precursor which could be synthesised from compound **B** via an aldol reaction.



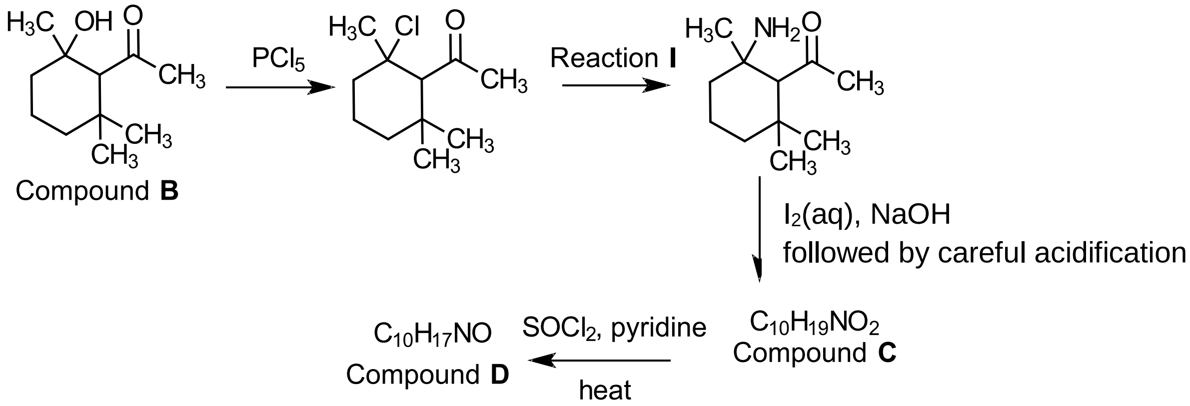
(a) State the reagent and condition required to convert compound **A** to either α-damascenone or β-damascenone. [1]

(b) With reference to an example of aldol reaction shown below, suggest an identity of the carbonyl compound reacting with compound **B** to form compound **A**.



[1]

Compound **B** can undergo a series of chemical reactions as shown in the flow chart below.



(c) State the reagents and conditions for Reaction **I**. [1]

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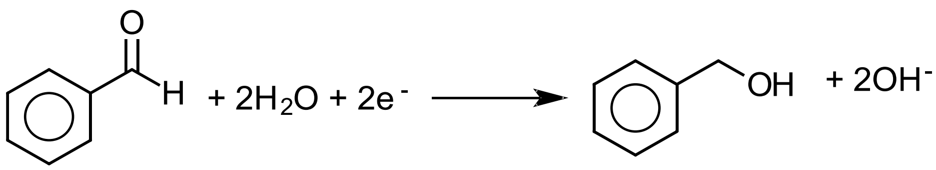
(d) Draw the structural formulae of compounds **C** and **D**. [2]

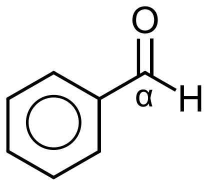
Benzaldehyde, in the presence of sodium hydroxide, undergoes the cannizzaro reaction to give benzoate ion and phenylmethanol.

(e) The ion-electron half-equation of benzaldehyde forming phenylmethanol is shown below.



Construct the ion-electron half equations for the reaction of benzaldehyde forming benzoate ion and hence, construct an overall balanced equation for the reaction. [2]

(f) Using changes in oxidation states of the carbon labelled α in benzaldehyde, state and explain the type of reaction that benzaldehyde undergoes in **(e)**. [1]



[Total: 8]

5 Organic compound **P** (M_r = 144) can be found in most leather products and is used as a mould inhibitor. **P** has the following composition by mass:

C: 50.04%　　H: 5.56%　　O: 44.40%

(a) (i) Determine the molecular formula of **P**. [2]

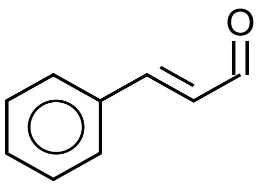
P exhibits stereoisomerism and it decolourises aqueous bromine. On heating one mole of **P** with dilute acid, two organic products **Q**, $C_4H_4O_4$ and **R** (M_r = 32) are obtained. The mole ratio of **Q** to **R** is 1:2. Vigorous effervescence was observed when **Q** reacted completely with sodium carbonate in equimolar proportions.

(ii) Draw the displayed formula of **Q**. [1]

(iii) State the functional groups present in **P**. [1]

(iv) Hence state the type of stereoisomerism exhibited by **P**. Draw and label the stereoisomers. [2]

(b) Another mould inhibitor, cinnamaldehyde has the structure shown below. [3]



Reaction of cinnamaldehyde with HBr produces a mixture that is optically inactive. Explain this observation.

[Total: 9]