



**TEMASEK**  
JUNIOR COLLEGE

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.

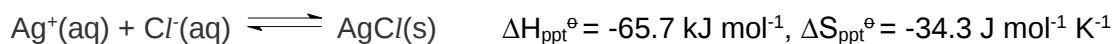
The number of marks is given in brackets [ ] at the end of each question or part question.

| 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.



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

• A lower temperature should be used.  
 • By Le Chatelier's Principle, the system will favour the forward exothermic reaction to counteract the lowered temperature. Hence, the position of equilibrium shifts to the right increasing the yield of silver chloride.

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

$$\begin{aligned} \bullet \Delta G^\ominus &= \Delta H^\ominus - T\Delta S^\ominus \\ &= -65.7 - (298)(-34.3/1000) \\ &= -55.5 \text{ kJ mol}^{-1} \end{aligned}$$

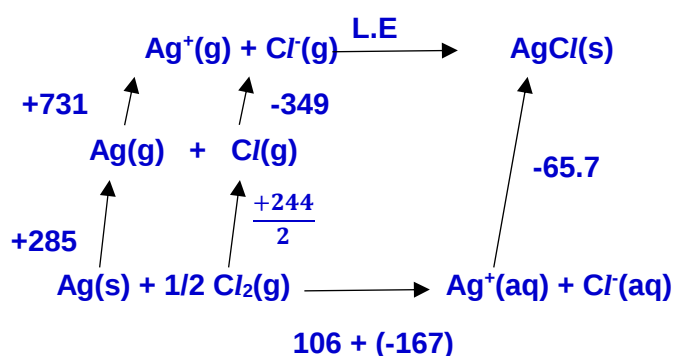
- (iii) In view of your answer in (a)(ii), comment on the solubility of silver chloride in water. [1]

• Since  $\Delta G^\ominus$  is negative, precipitation is spontaneous. Hence, AgCl is insoluble/sparingly soluble in water.

- (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  $\Delta H_{\text{ppt}}^\ominus$  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 $\text{Ag}^+(\text{aq})$ | +106 kJ mol <sup>-1</sup> |
| standard enthalpy change of formation of $\text{Cl}^-(\text{aq})$ | -167 kJ mol <sup>-1</sup> |
| standard enthalpy change of atomisation of Ag(s)                  | +285 kJ mol <sup>-1</sup> |
| first electron affinity of chlorine                               | -349 kJ mol <sup>-1</sup> |



• cycle with state symbols

By Hess' Law,

$$\bullet +285 + 731 + 122 - 349 + \text{L.E} = +106 - 167 - 65.7$$

$$\text{L.E} = \bullet - 916 \text{ kJ mol}^{-1}$$

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/ $\text{kJ mol}^{-1}$ | theoretical value/ $\text{kJ mol}^{-1}$ |
|----------|------------------------------------------|-----------------------------------------|
| 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.

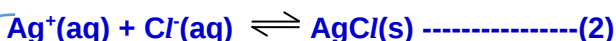
Suggest a reason for this.

• The theoretical value of lattice energy is based on the assumption that AgCl is ionic. However, there is some covalent character in AgCl due to the large size of Cl<sup>-</sup> ion which can be polarised by Ag<sup>+</sup>.

- (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]



• NH<sub>3</sub> forms a stable soluble complex [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> with the free Ag<sup>+</sup> ion causing [Ag<sup>+</sup>(aq)] to decrease.

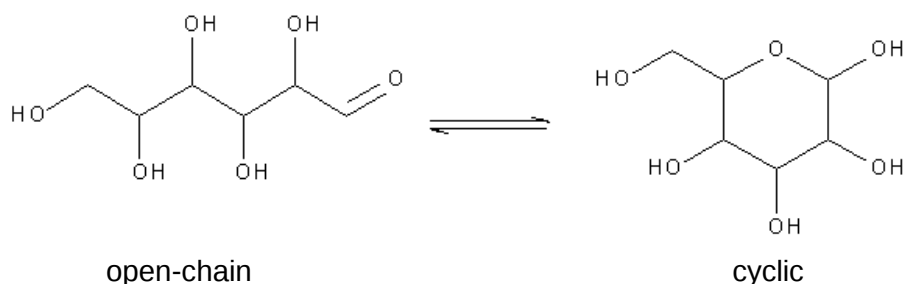


• By Le Chatelier's Principle, the position of equilibrium in (2) shifts left to counteract the decrease in the [Ag<sup>+</sup>(aq)].

• The ionic product [Ag<sup>+</sup>][Cl<sup>-</sup>] decreases to a value lower than the K<sub>sp</sub> of AgCl and AgCl dissolves.

• The K<sub>sp</sub> of AgI is much lower than K<sub>sp</sub> of AgCl. The ionic product is still easily exceeded even with the decrease in [Ag<sup>+</sup>(aq)] and hence it does not dissolve.

- (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]



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

• **Silver mirror is observed.**

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]

•  **$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$**

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

**Using the cyclic structure of glucose,**

**Bond-breaking**

5 x C – C

5 x O – H

7 x C – H

7 x C – O

6 x O = O

• **Energy released**

**$= +(5 \times 350 + 5 \times 460 + 7 \times 410 + 7 \times 360 + 6 \times 496) - (12 \times 805 + 12 \times 460)$**

**$= - 2760 \text{ kJ mol}^{-1}$**

**Bond-Forming**

12 x C = O

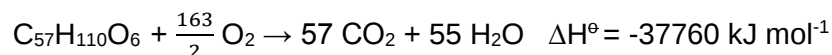
12 x O – H

- (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).

• **The  $\Delta H$  calculated using bond energies applies for the reactants and products in the gaseous phase but the reaction involves liquid  $H_2O$  rather than gaseous  $H_2O$ .**

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:



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 <sup>-1</sup> |
|------------------|---------------------------------|
| 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<sub>r</sub> of tristearin = 890) [2]

No. of moles of tristearin in 1 g =  $1/890 = 1.12 \times 10^{-3} \text{ mol}$   
 • Fuel value of tristearin =  $1.12 \times 10^{-3} \times 37760 = 42.4 \text{ kJ/g}$

OR

Since mass of 1 mol tristearin is 890 g  
 Fuel value =  $-37760/890 = 42.4 \text{ kJ/g}$

• Since more energy is produced per gram, tristearin is a better source of energy than carbohydrate.

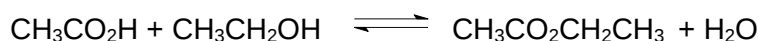
- (vi) During reading or watching television, the average adult uses about 7 kJ/min. How many minutes of such activity can be sustained by the energy supplied by a serving of cup noodle (considering only the total fat, total carbohydrate and total protein content)? [1]

Total energy provided by cup noodle =  $12 \times 42.4 + 44 \times 17 + 8 \times 17$   
 = 1390 kJ

• No. of minutes that can be sustained by energy =  $1390/7$   
 = 199 min

- (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



1.51 mol of  $\text{CH}_3\text{CO}_2\text{H}$  and 1.66 mol of  $\text{CH}_3\text{CH}_2\text{OH}$  was allowed to reach equilibrium in a  $100 \text{ cm}^3$  solution.  $10 \text{ cm}^3$  of the equilibrium mixture was extracted and large amounts of cold water was added to quench the reaction. The mixture was then titrated with  $22.40 \text{ cm}^3$  of  $2 \text{ mol dm}^{-3}$  NaOH.

Calculate the  $K_c$  for the formation of ethyl acetate.

**NaOH  $\equiv$   $\text{CH}_3\text{CO}_2\text{H}$**

**No. of moles of  $\text{CH}_3\text{CO}_2\text{H}$  in  $10 \text{ cm}^3 = (22.40/1000) \times 2$   
= 0.0448 mol**

**• No. of moles of  $\text{CH}_3\text{CO}_2\text{H}$  in  $100 \text{ cm}^3 = 0.0448 \times 10$   
= 0.448 mol**

|                      |                                                                                                                                                         |       |       |       |
|----------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------|-------|-------|-------|
| •                    | $\text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{CH}_2\text{OH} \rightleftharpoons \text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3 + \text{H}_2\text{O}$ |       |       |       |
| Initial amount/mol   | 1.51                                                                                                                                                    | 1.66  | 0     | 0     |
| Change in amount/mol | -1.06                                                                                                                                                   | -1.06 | +1.06 | +1.06 |
| Eqm amount/mol       | 0.448                                                                                                                                                   | 0.600 | 1.06  | 1.06  |

$$\begin{aligned} \bullet K_c &= \frac{[\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{CO}_2\text{H}][\text{CH}_3\text{CH}_2\text{OH}]} \\ &= \frac{\left(\frac{1.06}{0.1}\right)\left(\frac{1.06}{0.1}\right)}{\left(\frac{0.448}{0.1}\right)\left(\frac{0.6}{0.1}\right)} \\ &= 4.18 \end{aligned}$$

[Total: 22]

- 2 (a) In 1887, the Swedish scientist Svante Arrhenius postulated that acids and bases dissociate in water to form hydrogen ions,  $\text{H}^+$ , and hydroxide ions,  $\text{OH}^-$ , respectively.
- (i) Suggest a limitation of the Arrhenius concept of acids and bases. [1]

**Accept any of the answers below**

- It applies only to aqueous solutions.**
- It does not adequately explain why such compounds as ammonia are bases.**
- The hydrogen ion,  $\text{H}^+$ , exists as hydronium ion,  $\text{H}_3\text{O}^+$ , in water.**

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]

- Acting as acid:  $\text{HNO}_3 + \text{NaOH} \rightarrow \text{NaNO}_3 + \text{H}_2\text{O}$
- Acting as base:  $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{NO}_3^+ + \text{HSO}_4^-$

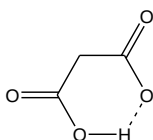
- (b) The following table compares the  $K_a$  values of two three-carbon carboxylic acids.

| Acid      | Formula                                      | $K_{a1}$              | $K_{a2}$              |
|-----------|----------------------------------------------|-----------------------|-----------------------|
| Propanoic | $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$  | $1.35 \times 10^{-5}$ | —                     |
| Malonic   | $\text{HO}_2\text{CCH}_2\text{CO}_2\text{H}$ | $1.41 \times 10^{-3}$ | $2.00 \times 10^{-6}$ |

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

- (i)  $K_a$  of propanoic acid [1]

- This is due to the stabilisation of the monoanion by hydrogen bonding with the unionised  $-\text{CO}_2\text{H}$  group.



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

- The stabilising hydrogen bonding in the monoanion of malonic acid would be destroyed by the ionisation of the second  $-\text{CO}_2\text{H}$  group.

or

- The removal of an  $\text{H}^+$  from  $\text{HO}_2\text{CCH}_2\text{CO}_2^-$  that already carries a negative charge would be electrostatically unfavourable.

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

- 0 cm<sup>3</sup> [considering using  $K_{a1}$  of malonic acid]
- 5 cm<sup>3</sup>
- 15 cm<sup>3</sup>
- 25 cm<sup>3</sup>

Volume of NaOH added = 0 cm<sup>3</sup> (Initial pH)

$K_{a1} = 1.41 \times 10^{-3} \text{ mol dm}^{-3}$

$[\text{H}^+] = \sqrt{1.41 \times 10^{-3} \times 0.10} = 0.0118 \text{ mol dm}^{-3}$

- $\text{pH} = -\lg [\text{H}^+] = -\lg 0.0118 = 1.93$

Volume of NaOH added = 5 cm<sup>3</sup> and 15 cm<sup>3</sup> (Maximum buffering)

- $\text{pH at } 5 \text{ cm}^3 = \text{p}K_{a1} = -\lg 1.41 \times 10^{-3} = 2.85$   
 $\text{pH at } 15 \text{ cm}^3 = \text{p}K_{a2} = -\lg 2.00 \times 10^{-6} = 5.70$

Volume of NaOH added = 25 cm<sup>3</sup> (Excess NaOH added)

Volume of excess NaOH added = 25 - 20 = 5 cm<sup>3</sup>

No. of moles of excess NaOH =  $\frac{5}{1000} \times 0.10 = 5.00 \times 10^{-4}$  mol

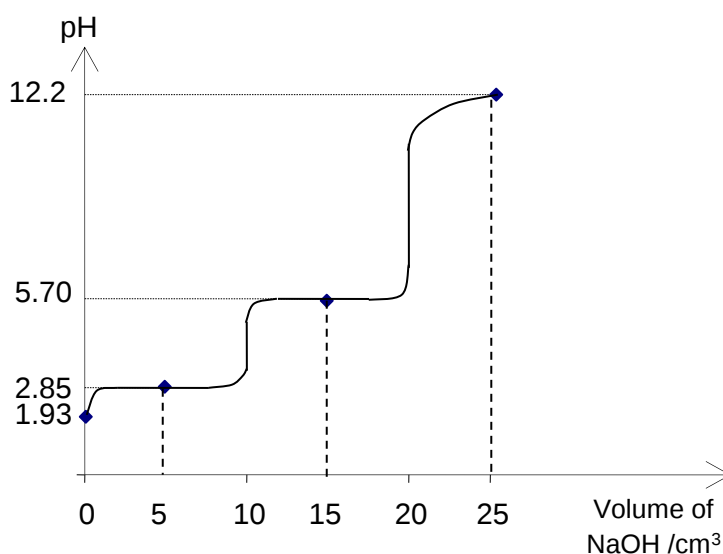
Total volume of solution = 10 + 25 = 35 cm<sup>3</sup>

$[\text{OH}^-] = \frac{5.00 \times 10^{-4}}{\frac{35}{1000}} = 0.0143 \text{ mol dm}^{-3}$

$\text{pOH} = -\log [\text{OH}^-] = 1.85$

•  $\text{pH} = 14 - \text{pOH} = 12.2$

- (iv) Using your answers in (b)(iii), sketch the pH-volume added curve when 25 cm<sup>3</sup> of 0.10 mol dm<sup>-3</sup> NaOH is gradually added to 10 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> malonic acid. [2]

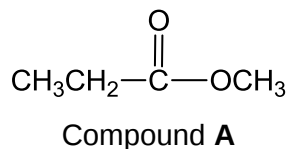


•• Correct shape of graph, correct volumes of NaOH indicated, proper labelling of axes and pH

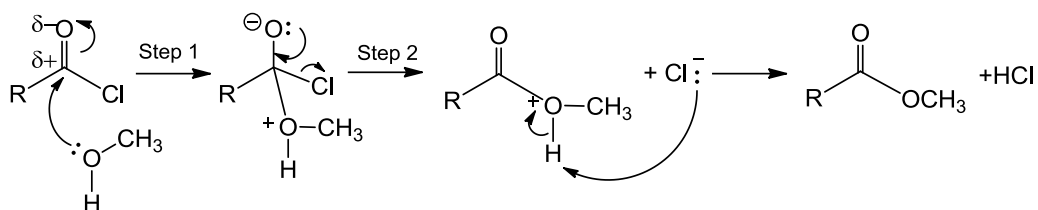
- (v) Suggest an indicator for the first equivalence point. [1]

• Screened methyl orange or methyl orange

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



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



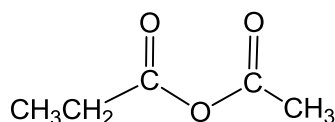
where  $\text{R} = \text{CH}_3\text{CH}_2-$

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

[2]

- **Step 1: Nucleophilic addition**
- **Step 2: Elimination**

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

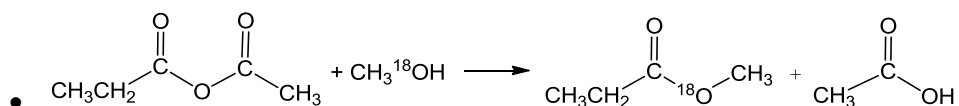


Compound **B**

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

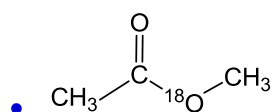
[1]

Write an equation for the reaction showing clearly the location of the  $^{18}\text{O}$  atom in the product. The formula of methanol can be written as  $\text{CH}_3^{18}\text{OH}$ .



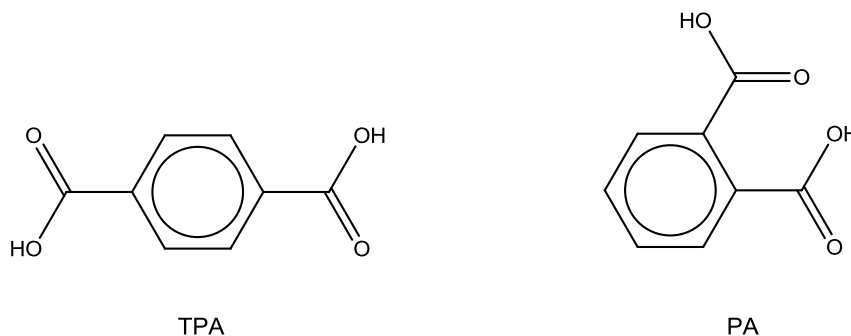
(iii) Draw the structure of another neutral product formed in the reaction.

[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.



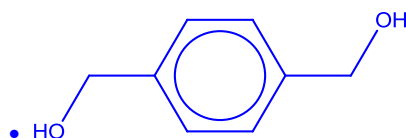
Some physical properties of TPA and PA are shown in the table below:

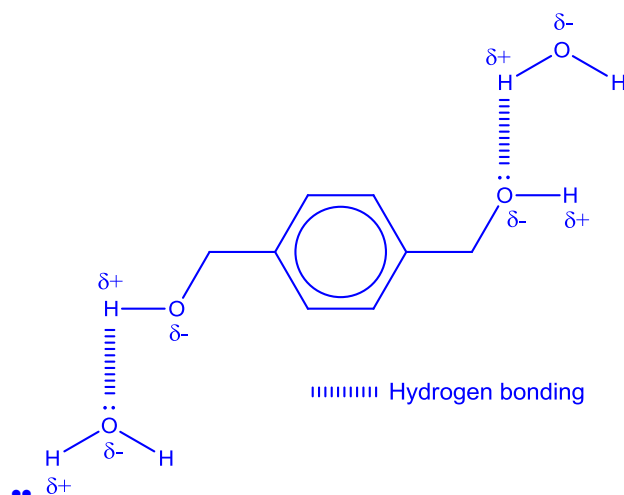
|               | TPA           | PA            |
|---------------|---------------|---------------|
| Appearance    | White crystal | White crystal |
| Melting point | 300 °C        | 207 °C        |
| Boiling point | Decomposes    | Decomposes    |

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

- Due to the close proximity of the 2 -COOH groups in PA, intramolecular hydrogen bonding occurs. This reduces the extent of intermolecular hydrogen bonding between PA molecules.
- In TPA, the 2 -COOH groups are further away hence only intermolecular hydrogen bonding occurs. Thus, more heat energy is needed to overcome the more extensive hydrogen bonding.

- (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]

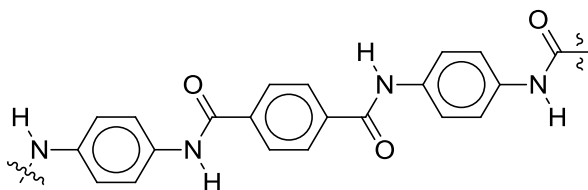




- (ii) Hence, explain why the diol in (i) is soluble in water. [1]

• **Formation of hydrogen bonds between the diol and water releases sufficient energy to overcome the hydrogen bonding between diol molecules and hydrogen bonding between water molecules.**

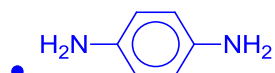
One common derivative of TPA is terephthaloyl chloride. Terephthaloyl chloride reacts with another monomer in a polymerisation reaction to form a synthetic fiber, commonly known as Kevlar®. A short chain of the Kevlar® polymer is shown below.



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]

• **Condensation reaction**



- (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,  $\text{CaF}_2$ , explain why gold is more suitable for the lining of bulletproof armour. [2]

• **When hit with a high impact force, the layers of close-packed gold atoms can slide over one another without breaking the non-directional metallic bonds.**

However, for an ionic compound  $\text{CaF}_2$ , a • high impact force would cause layers of ions to shift and causes ions to same charge to slide next to each other, forcing the layers to come apart and shatter.

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

• 2<sup>nd</sup> IE of aluminium is the minimum amount of energy to completely remove 1 mole of valence electrons from 1 mole of ground state gaseous  $\text{Al}^+$  ions to form 1 mole of gaseous  $\text{Al}^{2+}$  ions.

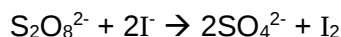
- (ii) Explain why the second ionisation energy of aluminium is higher than that of silicon. [1]

$\text{Al}^+$ :  $[\text{Ne}] 3s^2$

$\text{Si}^+$ :  $[\text{Ne}] 3s^2 3p^1$

Si has a higher nuclear charge than Al. However, • 2<sup>nd</sup> IE of Al involves the removal of 3s electron which is more strongly attracted and closer to the nucleus than the removal of 3p electron for Si. Hence, more energy is needed to remove the 3s electron.

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



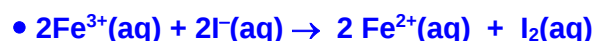
One way to speed up rate of reaction is to use a homogeneous catalyst.

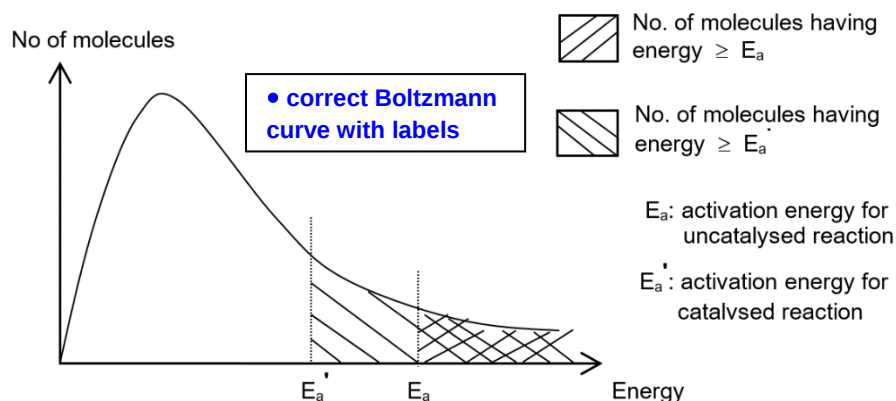
- (i) Explain why the reaction between  $\text{S}_2\text{O}_8^{2-}$  and  $\text{I}^-$  has a high activation energy. [1]

• The reaction involve the collision of 2 anions which would experience electrostatic repulsion upon contact with each other.

- (ii) A solution of iron(II) ions can be used to catalyse the reaction between  $\text{S}_2\text{O}_8^{2-}$  and  $\text{I}^-$ .

Using appropriate equations, outline the catalytic role of  $\text{Fe}^{2+}$  in the  $\text{S}_2\text{O}_8^{2-}$  and  $\text{I}^-$  reaction. Hence, explain with the aid of a Boltzmann distribution curve, how  $\text{Fe}^{2+}$  speeds up the rate of the reaction. [5]





$\text{Fe}^{2+}$  acts as a homogeneous catalyst that provides an alternative pathway of lower activation energy than the uncatalysed reaction, through the formation of an intermediate  $\text{Fe}^{3+}$ .

• The number of reactant molecules having energy greater than or equal to the lower activation energy,  $E_a'$  increases significantly.

Hence the frequency of effective collisions increases and the rate increases.

A kinetics study was conducted on the reaction of  $\text{S}_2\text{O}_8^{2-}$  and  $\text{I}^-$  to determine the rate equation. Varying volumes of  $\text{S}_2\text{O}_8^{2-}$  and  $\text{I}^-$  were added to a mixture containing sodium thiosulfate and starch indicator, followed by topping up with suitable volume of water.

As the reaction of  $\text{S}_2\text{O}_8^{2-}$  and  $\text{I}^-$  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 $\text{KI}$ / $\text{cm}^3$ | Volume of $\text{Na}_2\text{S}_2\text{O}_8$ / $\text{cm}^3$ | Volume of $\text{Na}_2\text{S}_2\text{O}_3$ / $\text{cm}^3$ | Volume of water / $\text{cm}^3$ | 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]

For expt 1 to 3, total volume is kept constant, so volume of reactant  $\propto$  concentration.

Since thiosulfate is the limiting reagent and volume is constant, relative rate  $\propto 1/t$ , so relative rates for expt 1, 2 and 3 are 0.02, 0.01 and 0.03.

• Comparing expt 1 and 2, when conc of  $\text{KI}$  decreases by 2 times, rate decreases by 2 times  $\rightarrow$  1<sup>st</sup> order with respect to  $\text{I}^-$ .

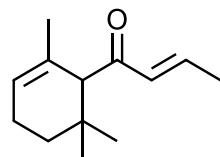
- Comparing expt 1 and 3, when conc of KI increases by 3 times and conc of  $\text{Na}_2\text{S}_2\text{O}_8$  decreases by 2 times, overall rate increases by 1.5 times (from 0.02 to 0.03)  $\rightarrow$  1<sup>st</sup> order with respect to  $\text{S}_2\text{O}_8^{2-}$ .

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

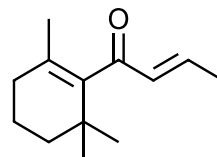
Since volume of all reactants double and total volume of mixture doubles, concentration of KI,  $\text{Na}_2\text{S}_2\text{O}_8$  and  $\text{Na}_2\text{S}_2\text{O}_3$  remain the same. Rate of reaction remains constant, so  $x = 50 \text{ s}$ .

[Total: 21]

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

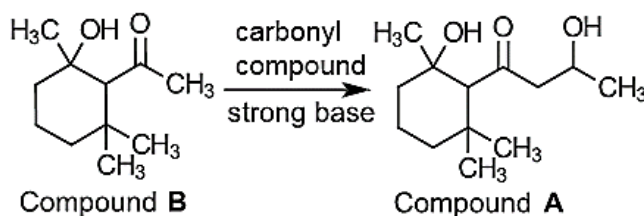


$\alpha$ -damascenone



$\beta$ -damascenone

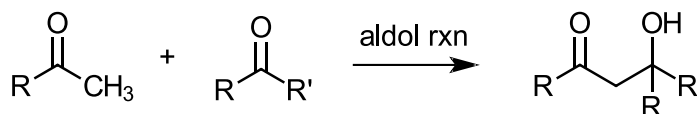
In the synthesis of damascenones in the laboratory, it was found that compound **A** is a possible precursor which could be synthesised from compound **B** via an aldol reaction.



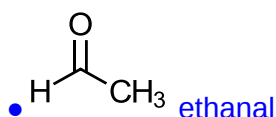
- (a) State the reagent and condition required to convert compound **A** to either  $\alpha$ -damascenone or  $\beta$ -damascenone. [1]

- Excess concentrated sulfuric acid,  $180^\circ\text{C}$

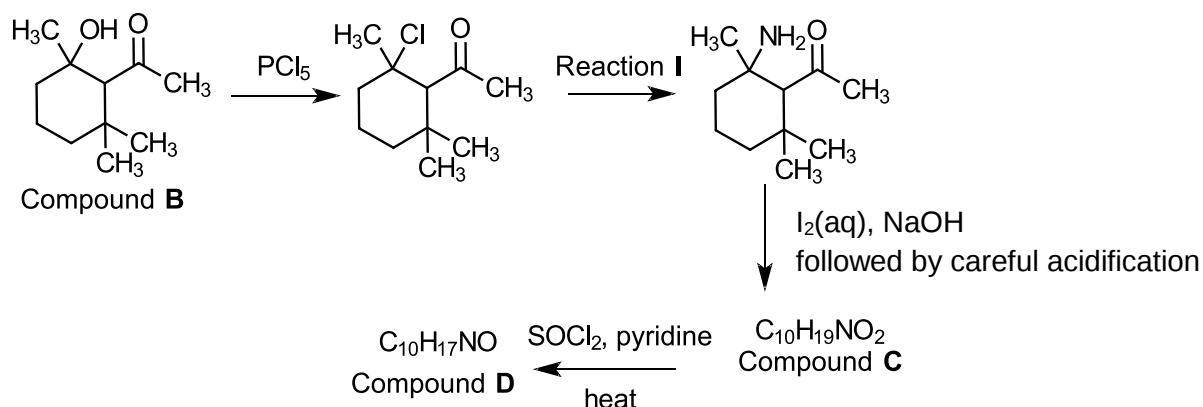
- (b) With reference to an example of aldol reaction shown below, suggest an identity of the carbonyl compound reacting with compound **B** to form compound **A**.



[1]



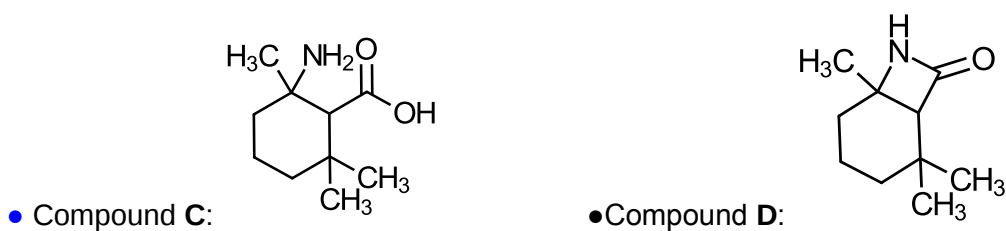
Compound **B** can undergo a series of chemical reactions as shown in the flow chart below.



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

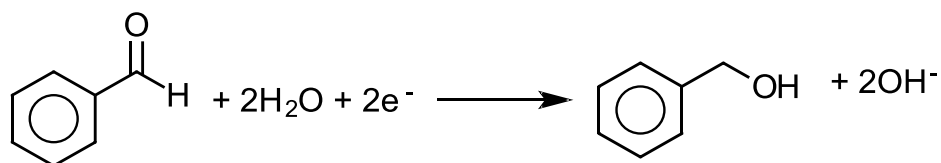
• Excess concentrated  $\text{NH}_3$ , heat in a sealed tube

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

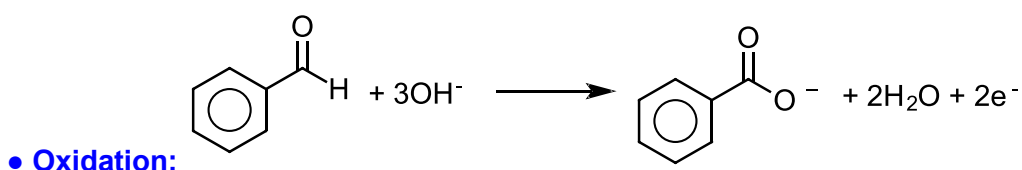


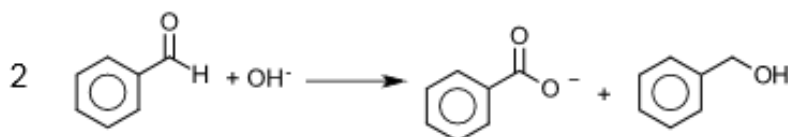
Benzaldehyde, in the presence of sodium hydroxide, undergoes the cannizzaro reaction to give benzoate ion and phenylmethanol.

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



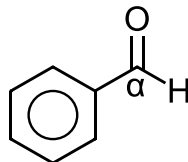
Construct the ion-electron half equations for the reaction of benzaldehyde forming benzoate ion and hence, construct an overall balanced equation for the reaction.





•Overall:

- (f) Using changes in oxidation states of the carbon labelled  $\alpha$  in benzaldehyde, state and explain the type of reaction that benzaldehyde undergoes in (e).



[1]

Disproportionation reaction.

The oxidation state of  $\alpha$ -C in benzaldehyde changes from +1 to +3 (in benzoate ion) and -1 (in phenylmethanol) simultaneously.

[Total: 8]

- 5 (a) 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%

- (i) Determine the molecular formula of **P**.

[2]

|                | C                 | H              | O                 |
|----------------|-------------------|----------------|-------------------|
| Mole ratio     | 50.04/12<br>4.167 | 5.56/1<br>5.56 | 44.40/16<br>2.775 |
| Simplest ratio | 1.50<br>3         | 2.00<br>4      | 1.00<br>2         |

Empirical formula :  $\text{C}_3\text{H}_4\text{O}_2$

$$(\text{C}_3\text{H}_4\text{O}_2)_n = 144$$

$$36n + 4n + 32n = 144$$

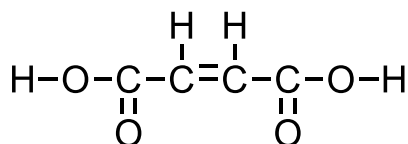
$$n = 2$$

Molecular formula :  $\text{C}_6\text{H}_8\text{O}_4$

**P** exhibits stereoisomerism and it decolourises aqueous bromine. On heating one mole of **P** with dilute acid, two organic products **Q**,  $\text{C}_4\text{H}_4\text{O}_4$  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. Vigorous effervescence was observed when **Q** reacted completely with sodium carbonate in equimolar proportions.

- (ii) Draw the displayed formula of **Q**.

[1]

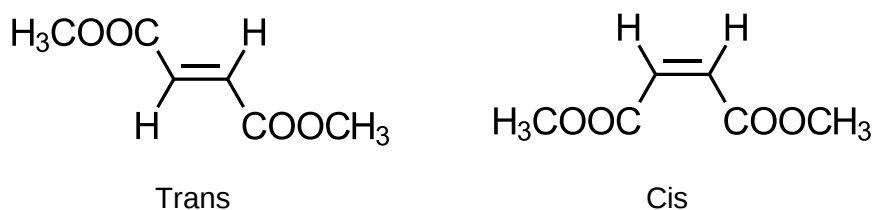


- (iii) State the functional groups present in **P**. [1]

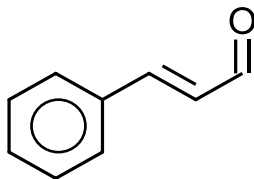
**P** : **alkene, ester**

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

**Cis-trans isomerism**

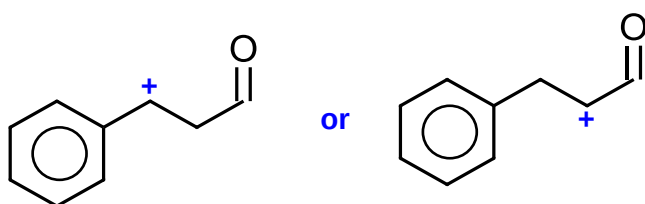


- (b) Another mould inhibitor, cinnamaldehyde has the structure shown below. [3]



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

•Cinnamaldehyde undergoes electrophilic addition with HBr to form the intermediate carbocation,



which is planar about the C with the positive charge.

•The Br<sup>-</sup> ion can then attack from both top and bottom of the plane with equal probability resulting in a racemic mixture.

•The resulting enantiomers rotate plane polarized light to equal extent but in opposite directions giving rise to an optically inactive mixture.

[Total: 9]