

---

# **CHEMISTRY**

**Paper 3 Free Response**

**9647/03**

**Friday 26 August 2016**

**2 hours**

Candidates answer on separate paper.

Additional Materials:      Answer Paper  
                                         Data Booklet

---

## **READ THESE INSTRUCTIONS FIRST**

Write your name and class 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 any **four** questions.

A Data Booklet is provided.

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

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

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.

**ANSWER SCHEME  
&  
EXAMINERS'  
COMMENTS**

---

This documents consists of **17** printed pages and **1** blank pages.

Answer any **four** questions.

1 Use of the Data Booklet is relevant to this question.

- (a) When potassium manganate(VII),  $\text{KMnO}_4$ , is heated with concentrated sodium hydroxide,  $\text{NaOH}$ , bubbles of oxygen are seen and a green solution of  $\text{MnO}_4^{2-}$  is obtained. The addition of barium chloride,  $\text{BaCl}_2$ , to this solution precipitated out a solid **X** with composition by mass of 53.5% barium, 21.5% manganese and 25.0% oxygen.

- (i) Calculate the empirical formula of **X**. [1]

Element	Ba	Mn	O
% mass	53.5	21.5	25.0
$A_r$	137	54.9	16.0
No. of moles	0.391	0.392	1.56
Mole ratio	1	1	4

**Empirical formula of X is  $\text{BaMnO}_4$**

- (ii) When the green solution above is acidified, a brown precipitate in a purple solution is formed.

Suggest the identities of the species formed upon acidification and hence state the type of reaction that has occurred. [3]

**Brown precipitate is  $\text{MnO}_2$**

**Purple solution is  $\text{MnO}_4^-$**

**Disproportionation**

- (b) A solution of acidified potassium manganate(VII),  $\text{KMnO}_4$ , can be standardised through titration against sodium ethanedioate,  $\text{Na}_2\text{C}_2\text{O}_4$ . The ethanedioate ion is oxidised to carbon dioxide in this reaction.

- (i) State the oxidation numbers of C in the ethanedioate ion and in carbon dioxide. [1]

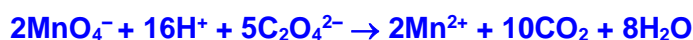
**O.N. of C in  $\text{C}_2\text{O}_4^{2-}$  = +3**

**O.N. of C in  $\text{CO}_2$  = +4**

- (ii) Write the half-equation for the oxidation of the ethanedioate ion. [1]



- (iii) Hence, write the overall balanced equation for the reaction between acidified manganate(VII) and ethanedioate ions. [1]



- (iv) In one such standardisation procedure, 25.0 cm<sup>3</sup> of 0.0150 mol dm<sup>-3</sup> Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution required 28.85 cm<sup>3</sup> of acidified KMnO<sub>4</sub> to reach the end-point.

Determine the concentration of KMnO<sub>4</sub> in the solution. You may assume that  $2\text{MnO}_4^- \equiv 5\text{C}_2\text{O}_4^{2-}$ . [3]

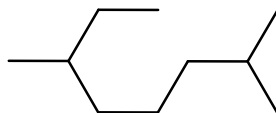
$$\begin{aligned}\text{No. of moles of C}_2\text{O}_4^{2-} &= \frac{25.0}{1000} \times 0.0150 \\ &= 0.000375 \text{ mol}\end{aligned}$$

Since  $2\text{MnO}_4^- \equiv 5\text{C}_2\text{O}_4^{2-}$ ,

$$\begin{aligned}\text{No. of moles of MnO}_4^- &= \frac{2}{5} \times 0.000375 \\ &= 0.000150 \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{Concentration of KMnO}_4 &= \frac{0.000150}{28.85} \times 1000 \\ &= 0.00520 \text{ mol dm}^{-3}\end{aligned}$$

- (c) Myrcene, **A** and ocimene, **B**, are isomers with the molecular formula C<sub>10</sub>H<sub>16</sub>. When subjected to hydrogen with platinum catalyst, both isomers give 2,6-dimethyloctane, C<sub>10</sub>H<sub>22</sub>.

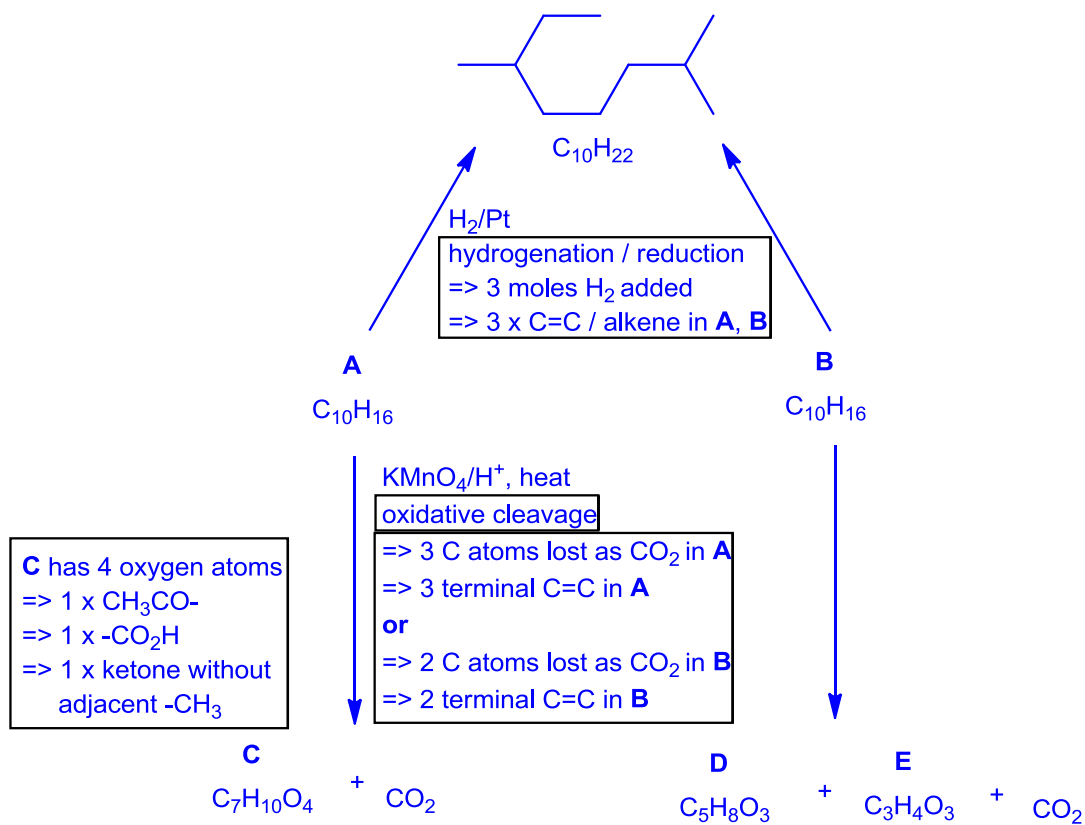


2,6-dimethyloctane

When treated with hot concentrated acidified KMnO<sub>4</sub>, **A** gives CO<sub>2</sub> and compound **C**, C<sub>7</sub>H<sub>10</sub>O<sub>4</sub>; **B** gives CO<sub>2</sub> and compounds **D**, C<sub>5</sub>H<sub>8</sub>O<sub>3</sub>, and **E**, C<sub>3</sub>H<sub>4</sub>O<sub>3</sub>.

Compounds **C**, **D** and **E** give one mole of CHI<sub>3</sub> with alkaline aqueous iodine. On addition of aqueous NaHCO<sub>3</sub>, compounds **C**, **D** and **E** produce effervescence.

Suggest structures for **A-E**, and explain the observations described above. [10]



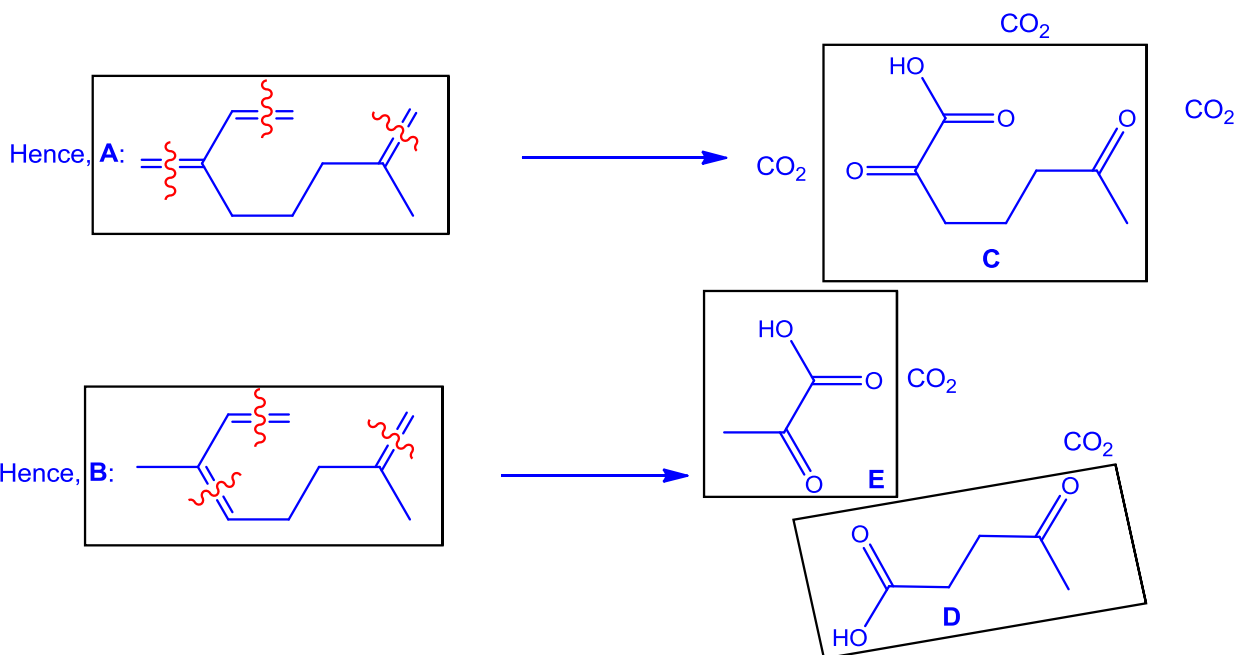
$KMnO_4/H^+$ , heat  
 oxidative cleavage

$\Rightarrow$  **C**, **D** and **E** have ketone and/or carboxylic acid groups

Iodoform/Triiodomethane test  
 $\Rightarrow$  **C**, **D** and **E** have  $CH_3CO-$  groups

$NaHCO_3(aq)$

Acid-carbonate/acid-base/neutralisation reaction  
 $\Rightarrow$  **C**, **D** and **E** produce  $CO_2$   
 $\Rightarrow$  they have carboxylic acid groups



[Total: 20]

- 2 The table below lists the standard enthalpy change of formation of four compounds.

Compound	$\Delta H_f^\circ / \text{kJ mol}^{-1}$
$\text{H}_2\text{O}(\text{l})$	– 286
$\text{HCl}(\text{g})$	– 92.0
$\text{SiO}_2(\text{s})$	– 910
$\text{SiCl}_4(\text{l})$	– 640

- (a) What is meant by the term, standard enthalpy change of formation of a compound? [1]  
**The enthalpy change when 1 mol of a compound is formed from its elements (in its most stable form), under standard conditions (25°C, 1 atm pressure).**

- (b)  $\text{SiCl}_4(\text{l})$  undergoes hydrolysis to give  $\text{SiO}_2(\text{s})$ .

- (i) Write the balanced equation with state symbols for the hydrolysis reaction. [1]  
 **$\text{SiCl}_4(\text{l}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{SiO}_2(\text{s}) + 4\text{HCl}(\text{g})$**

- (ii) Using the above data, calculate the standard enthalpy change for the hydrolysis reaction. State one assumption made in your calculation. [1]

$$\begin{aligned}\Delta H_r^\circ &= \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants}) \\ &= [-910 + 4(-92.0)] - [-640 + 2(-286)] \\ &= -66.0 \text{ kJ mol}^{-1}\end{aligned}$$

**Assumption:**

- **$\text{SiCl}_4(\text{l})$  is in excess. The hydrolysis gives  $\text{HCl}(\text{g})$  instead of  $\text{HCl}(\text{aq})$ .**
- **Hess' Law is followed/obeyed.**

- (iii) Does the hydrolysis have a positive, negative or zero entropy change? Explain your answer. [1]

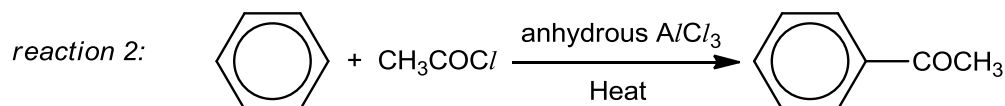
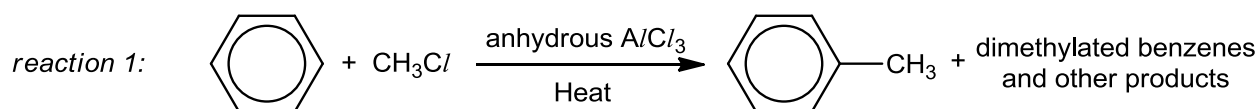
**Positive entropy change. 4 moles of gas (HCl) are produced. There is an increase in disorder of the system as there are more ways of arranging the particles in the system.**

- (iv) Hence, by the use of the Gibbs free energy,  $\Delta G^\circ$ , explain why the hydrolysis of  $\text{SiCl}_4(\text{l})$  is always a spontaneous process. [1]

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

**Since  $\Delta H^\circ$  is negative and  $\Delta S^\circ$  is positive,  $\Delta G^\circ$  is always negative. So the process is spontaneous.**

- (c) Consider reaction 1 and reaction 2 shown below.



- (i) Both *reaction 1* and *reaction 2* proceed via a similar mechanism. Name the type of reaction undergone. [1]  
**Electrophilic substitution.**
- (ii) Suggest why *reaction 1* gives a mixture of organic products while *reaction 2* gives only one mono-substituted product. [2]

### Reaction 1

The  $\text{CH}_3$  is an electron donating or activating group. It activates the benzene ring and so makes the delocalised  $\pi$  electrons more susceptible/available to electrophilic attack/electrophiles. This favours further substitution to give multi-substituted products.

### Reaction 2

The  $\text{C}=\text{O}$  is an electron withdrawing or deactivating group. It deactivates the benzene ring and so makes the delocalised  $\pi$  electrons less susceptible/available to electrophilic attack/electrophiles. Further substitution is less favourable.

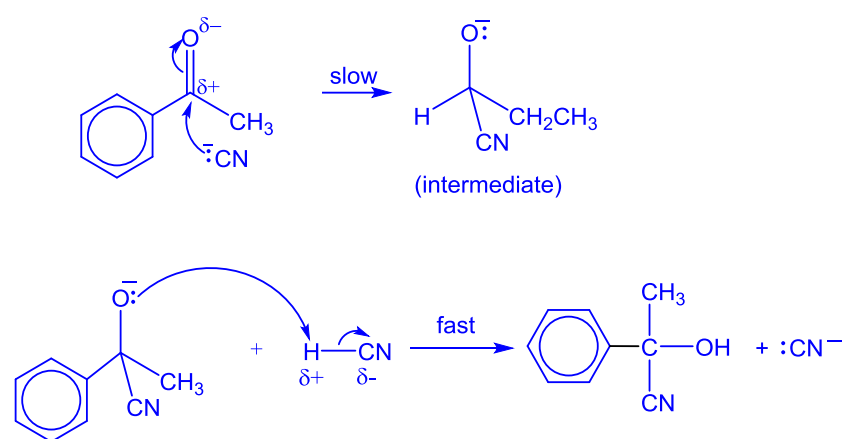
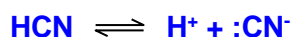
- (d) The organic product in *reaction 2*, phenylethanone,  $\text{C}_6\text{H}_5\text{COCH}_3$ , reacts with  $\text{HCN}$  to produce the corresponding cyanohydrin under certain experimental conditions.

- (i) State the experimental conditions. [1]

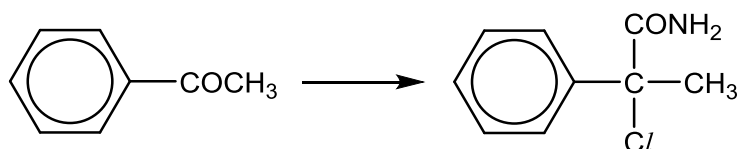
**Trace amount of  $\text{NaOH}/\text{NaCN}$  and  $10 - 20^\circ\text{C}$**

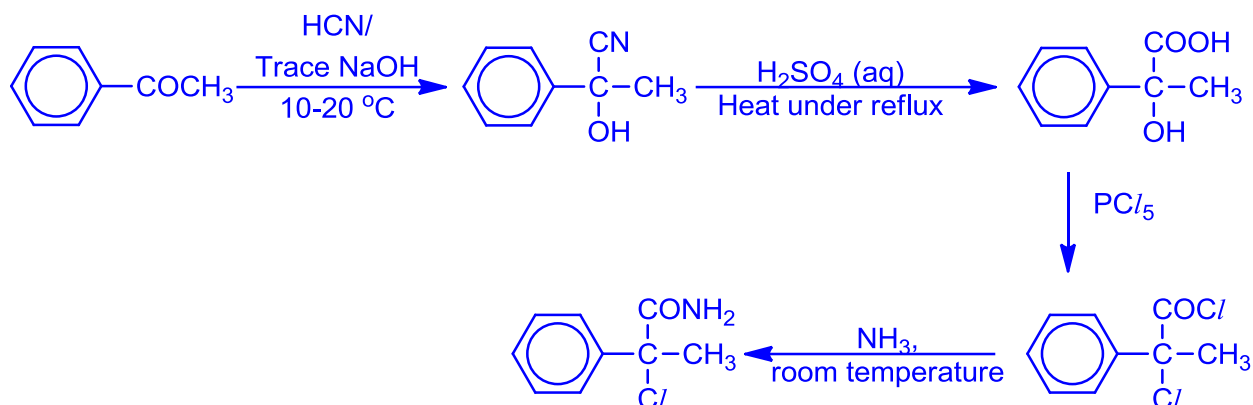
- (ii) Describe the mechanism of reaction, of phenylethanone with  $\text{HCN}$ , showing clearly the curly arrows to indicate the movement of electrons and all charges. [3]


### **Nucleophilic Addition Mechanism.**



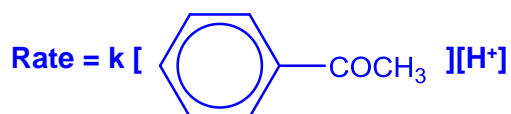
- (iii) Hence, suggest the reagents and conditions used in the following conversion, stating clearly the intermediate products in the process of synthesis. [2]





- (e) The rate of reaction between phenylethanone and iodine in acid medium to give 2-iodo-1-phenylethanone, , is found to be independent of  $[I_2]$ , but directly proportional to  $[H^+]$  and directly proportional to [phenylethanone].

- (i) Write the rate equation for this reaction and state the overall order and the units of the rate constant. [2]



Overall order = 2, units:  $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$

- (ii) The reaction between phenylethanone and bromine proceeds by a similar mechanism. How would you expect the rate of this reaction to compare with that of the above reaction? Explain your answer. [1]

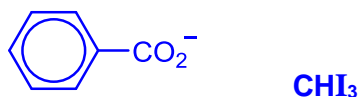
The reaction rate is unchanged as it is also independent of  $[Br_2]$  like  $I_2$ .

- (iii) When a basic medium is used instead for the reaction between phenylethanone and iodine, a different mechanism of reaction is followed and different organic products are produced.

- (I) State the type of reaction undergone. [1]

Triiodomethane/iodoform reaction.

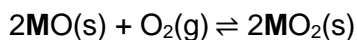
- (II) Give the structures of all the organic products formed in this reaction. [2]



[Total: 20]

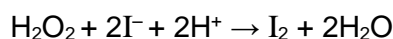
- 3 Fireworks are a traditional part of many celebrations. Their colours can come from heating of Group II metals and their salts. These salts often contain anions such as chlorates, perchlorates, and nitrates which are oxidising agents.

- (a) One of the Group II metals, **M**, when heated with oxygen under pressure, forms a metal peroxide which can be used as an oxidising agent in fireworks to produce a vivid green colour. The equation for the reaction is shown below:

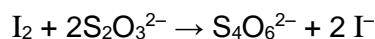


When equilibrium is attained, the mixture of oxides was found to have a mass of 1.60 g, where **MO**<sub>2</sub> has a percentage mass of 18.7%. When the mixture was treated with dilute sulfuric acid, a white solid was precipitated and a solution of hydrogen peroxide was produced.

An excess of acidified potassium iodide was added to the hydrogen peroxide solution. The reaction between hydrogen peroxide and acidified potassium iodide is as follows.



The iodine liberated needed 11.80 cm<sup>3</sup> of 0.300 mol dm<sup>-3</sup> sodium thiosulfate, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, for complete reaction.



- (i) Write a balanced equation to represent the reaction between **MO**<sub>2</sub> and sulfuric acid.[1]  
**MO<sub>2</sub> + H<sub>2</sub>SO<sub>4</sub> → MSO<sub>4</sub> + H<sub>2</sub>O<sub>2</sub>**
- (ii) By determining the amount of **MO**<sub>2</sub> that has reacted, calculate the relative atomic mass of **M** and suggest its identity. [5]



$$\text{Amount of S}_2\text{O}_3^{2-} = 11.8 \times 10^{-3} \times 0.3$$

$$= 3.54 \times 10^{-3} \text{ mol}$$

$$\text{Amount of MO}_2 = 0.5 \times 3.54 \times 10^{-3}$$

$$= 1.77 \times 10^{-3} \text{ mol}$$

Let the relative atomic mass of **M** be  $x$  g

$$\text{Mass of MO}_2 = (x + 2 \times 16.0) \times 1.77 \times 10^{-3}$$

$$\frac{18.7}{100} \times 1.60 = (x + 2 \times 16.0) \times 1.77 \times 10^{-3}$$

$$x = 137$$

Identity of **M**: Barium



- (b) Strontium nitrate,  $\text{Sr}(\text{NO}_3)_2$  is an oxidising agent and is commonly used as a red colouring agent in fireworks.

- (i) Write a balanced equation for the reaction that occurs when  $\text{Sr}(\text{NO}_3)_2$  undergoes thermal decomposition. [1]



- (ii) Predict whether the decomposition temperature of  $\text{Sr}(\text{NO}_3)_2$  will be higher or lower than the decomposition temperature of  $\text{Mg}(\text{NO}_3)_2$ . Explain your answer. [3]

Higher.

cationic radius  $\text{Sr}^{2+}$  is larger than that of  $\text{Mg}^{2+}$  and charge density or polarising power of  $\text{Sr}^{2+}$  is smaller.

electron cloud of  $\text{NO}_3^-$  anion is less distorted, N-O bond weakened to a smaller extent, does not break as easily.

Thus  $\text{Sr}(\text{NO}_3)_2$  is thermally more stable than  $\text{MgNO}_3$ , and decomposition temperature is higher.

- (c) Another oxidising agent used in fireworks is potassium chlorate(V),  $\text{KClO}_3$ . When  $\text{KClO}_3$  undergoes thermal decomposition, two products are obtained, one of which is  $\text{KCl}$ .

- (i) Write a balanced equation to show how  $\text{KClO}_3$  is produced from  $\text{Cl}_2$  gas and hot, aqueous potassium hydroxide. [1]



- (ii) Write a balanced equation for the thermal decomposition of  $\text{KClO}_3$  and hence suggest why  $\text{KClO}_3$  is an important ingredient used in fireworks. [2]



$\text{O}_2$  gas is produced when heat is applied to potassium chlorate.  $\text{O}_2$  gas supports subsequent combustion of fireworks/explosives, therefore it is an important ingredient.

- (d) Fireworks which produce bright sparks, flashes and coloured flames also involve the elements phosphorus, sulfur and chlorine.

The table below gives the melting points of these elements.

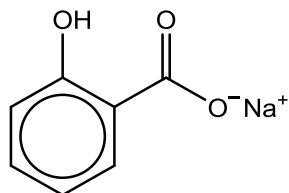
element	phosphorus	sulfur	chlorine
melting point / K	317	392	172

In terms of structure and bonding, explain why sulfur has the highest melting point among the three elements. [2]

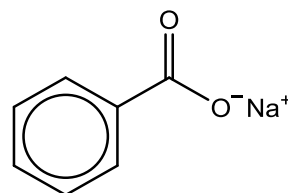
All 3 elements exist as simple covalent molecules with van der Waals' forces between the molecules.

$\text{S}_8$  has the largest number of electrons, compared to  $\text{P}_4$  and  $\text{Cl}_2$ ; it has the strongest van der Waals' forces, hence it needs the largest amount of energy to overcome these attractions during melting.

- (e) Sodium salicylate and sodium benzoate are used as whistle mixes in fireworks. Both are white crystalline powder.



sodium salicylate



sodium benzoate

- (i) Suggest methods by which sodium salicylate and sodium benzoate can be distinguished from each other by a simple chemical test. State the reagents and conditions used and the expected observations for each compound. [2]

**Method 1**

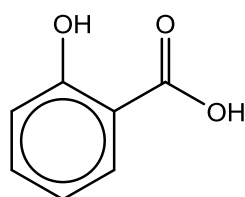
To 2 separate test tubes containing sodium salicylate and sodium benzoate, add neutral  $\text{FeCl}_3(\text{aq})$ . A violet colouration will be observed in the test tube containing sodium salicylate. No violet colouration is seen in the test tube containing sodium benzoate.

OR

**Method 2**

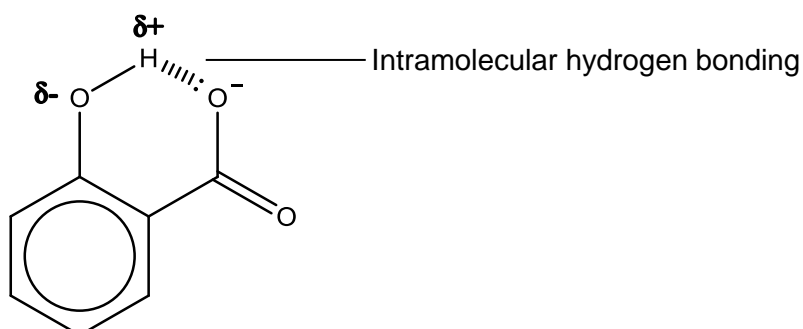
To 2 separate test tubes containing sodium salicylate and sodium benzoate, add aqueous  $\text{Br}_2$  and shake. White precipitate formed in test tube containing sodium salicylate and orange bromine water decolourises. Orange aqueous bromine water remains orange in test tube containing sodium benzoate.

- (ii) The  $\text{p}K_{\text{a}}$  values of the two acidic groups in salicylic acid are  $\text{p}K_{\text{a}1} = 2.98$  and  $\text{p}K_{\text{a}2} = 13.6$ .



salicylic acid

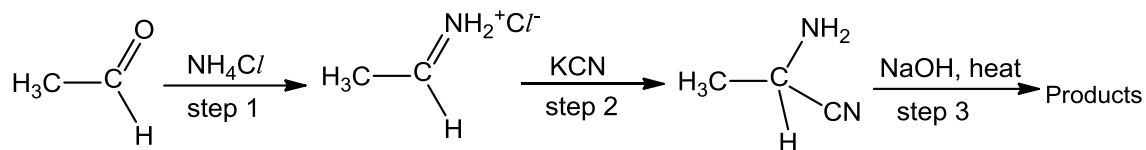
Draw the displayed formula of the mono-anion produced after the dissociation of the carboxylic acid group and use your formula to explain why the dissociation of the phenol group is unlikely to occur. [3]



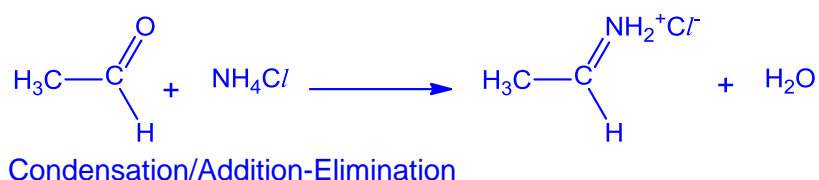
[Total: 20]

- 4 Strecker synthesis is a method used for the synthesis of amino acids. It is often studied due to the simplicity of the process.

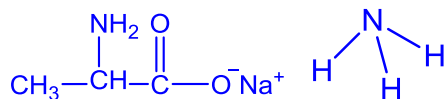
(a) Alanine, an amino acid, can be formed using this method as shown below.



- (i) Construct a balanced equation for step 1 and suggest the type of reaction that has occurred. [2]



- (ii) Give the structural formulae for all the products formed in step 3. [2]



- (b) Insulin is a hormonal protein which was first discovered in 1921. In 1959, it became the first protein to have its primary structure determined. These led to the award of two Nobel Prizes, in Physiology/Medicine and Chemistry respectively.

The basic unit of insulin consists of two polypeptides, A-chain and B-chain. A-chain has 21 amino acid residues, and some of these are listed in the following table (You may use the abbreviations for your answers).

amino acid	abbreviation	formula of R group side chain at pH 7.4 (physiological pH)	number of amino acid residues in A-chain
cysteine	cys	$-\text{CH}_2\text{SH}$	4
glutamic acid	glu	$-\text{CH}_2\text{CH}_2\text{CO}_2^-$	2
glutamine	gln	$-\text{CH}_2\text{CH}_2\text{CONH}_2$	2
glycine	gly	$-\text{H}$	1
isoleucine	ile	$-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	2
threonine	thr	$-\text{CH}(\text{OH})\text{CH}_3$	1
valine	val	$-\text{CH}(\text{CH}_3)\text{CH}_3$	1

In order to determine the sequence of the A-chain, partial hydrolysis was carried out with two separate methods to obtain several polypeptide fragments. One method of hydrolysis involves the use of  $6 \text{ mol dm}^{-3} \text{ HCl}$  or  $\text{NaOH}$ , while the other method causes hydrolysis at specific peptide bonds.

- (i) State what may be used in the method for the hydrolysis at specific peptide bonds.[1]  
**Enzyme**

- (ii) One of the polypeptides was isolated and subjected for further hydrolysis giving the following smaller tri-peptide fragments.

cys-cys-thr, ile-val-glu, glu-gln-cys, gly-ile-val

Using the same abbreviations, write out the amino acid sequence of the **smallest** polypeptide that could produce the above fragments. [2]

**gly-ile-val-glu-gln-cys-cys-thr**

- (iii) Describe the tertiary structure of insulin A-chain, include the type of bondings or interactions with reference to all the relevant amino acid residues listed in the above table. [4]

**The tertiary structure of insulin A-chain is the overall 3-dimensional shape of the protein resulting from folding or coiling of the chains due to various R-group interactions within a polypeptide chain. These may be hydrogen bonding between R-groups of gln and thr residues, covalent disulfide linkages between sulfur of cys residues and van der Waals' between R-groups of gly,ile and val residues.**

- (iv) In further confirmation of structures of insulin, chemicals can be used to affect the structures. Suggest one type of bond or interaction from your answer in (b)(iii) that can be broken by chemicals and state the chemicals that can be used. [2]

**Disulfide linkage can be broken by heavy metal ions, such as  $\text{Ag}^+$  or  $\text{Hg}^{2+}$ , hence either  $\text{AgNO}_3$  or  $\text{Hg}(\text{NO}_3)_2$  can be used.**

- (v) Zinc has an important role in the the production, storage and use of insulin. Zinc cation can bind to insulin through interactions with the amino acids. Suggest the type of interaction and state an amino acid that may be involved. [1]

**Ionic interactions with glutamic acid (glu); OR ion-dipole attractions with threonine (thr) or glutamine (gln); OR Covalent dative bonds with glutamic acid (glu), threonine (thr) or glutamin (gln).**

- (c) Zinc compounds are often used in paints for various purposes. The properties of some of these compounds are given below.

compound	solubility product, $K_{sp}$	use in paints
$\text{Zn(OH)}_2$	$3.00 \times 10^{-17}$	White pigment
$\text{ZnS}$	$3.21 \times 10^{-23}$	Luminous pigment
$\text{ZnCO}_3$	$1.46 \times 10^{-10}$	Fire Retardant

- (i) Write an expression for  $K_{sp}$  for  $\text{Zn(OH)}_2$  and determine its solubility. Hence, calculate the pH of a saturated solution of  $\text{Zn(OH)}_2$ . [4]



$$K_{sp} = [\text{Zn}^{2+}][\text{OH}^-]^2$$

Let solubility of  $\text{Zn(OH)}_2$  be  $x \text{ mol dm}^{-3}$

$$K_{sp} = (x)(2x)^2$$

$$3.00 \times 10^{-17} = 4x^3$$

$$x = \sqrt[3]{\frac{3.00 \times 10^{-17}}{4}} = 1.96 \times 10^{-6} \text{ mol dm}^{-3}$$

$$[\text{OH}^-] = 2x = 2(1.96 \times 10^{-6}) = 3.92 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\text{pOH} = -\lg (3.92 \times 10^{-6}) = 5.41$$

$$\text{pH} = 14 - 5.41 = 8.59$$

- (ii) In preparation of a water-based luminous paint mixture, all 3 of the above compounds have to be precipitated. Given that concentration of  $\text{Zn}^{2+}$  is  $2.00 \times 10^{-7} \text{ mol dm}^{-3}$ , calculate the minimum amount of  $\text{S}^{2-}$  that must be present in  $250 \text{ cm}^3$  of this mixture. [2]

For precipitation,  $[\text{Zn}^{2+}][\text{S}^{2-}] > K_{sp}$

$$[\text{S}^{2-}] > 3.21 \times 10^{-23} / 2.00 \times 10^{-7}$$

$$[\text{S}^{2-}] > 1.605 \times 10^{-16}$$

$$\text{Minimum amount of } \text{S}^{2-} = 1.605 \times 10^{-16} \times 250/1000$$

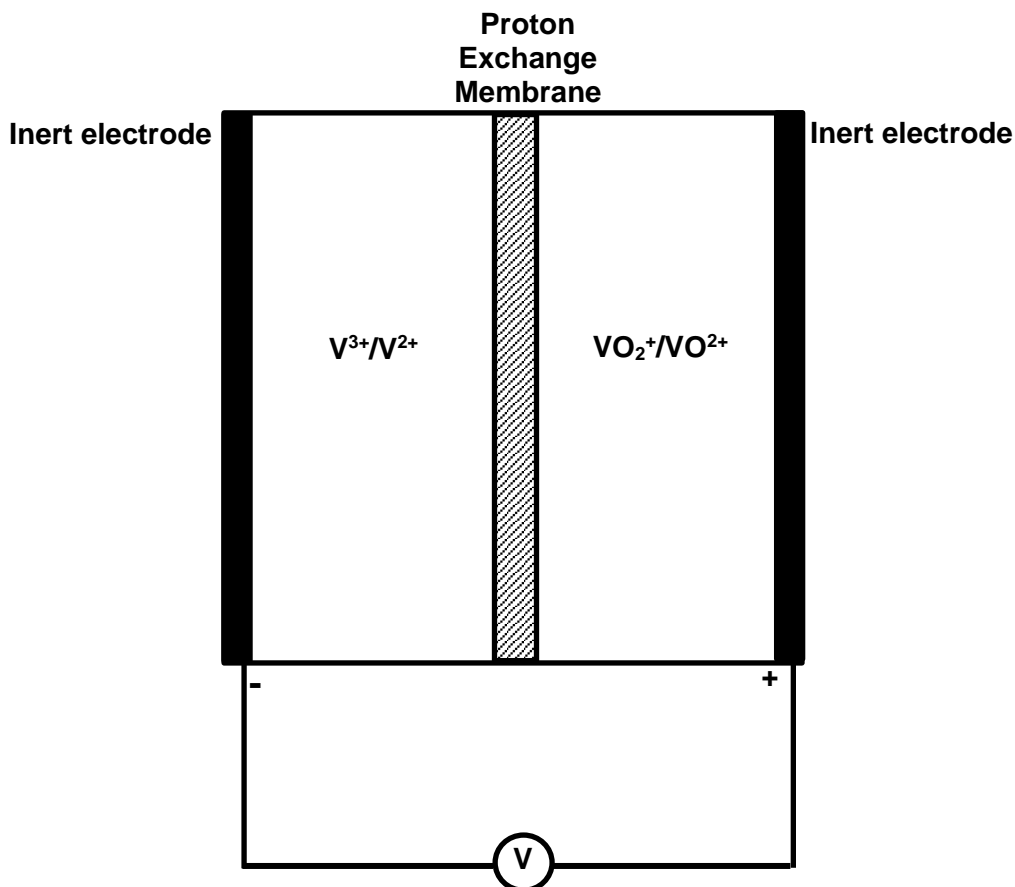
$$= 4.0125 \times 10^{-17} \text{ mol} = 4.02 \times 10^{-17} \text{ mol}$$

[Total: 20]

5 Use of the Data Booklet is relevant to this question.

A redox flow battery is a type of rechargeable battery where rechargeability is provided by two chemical components dissolved in liquids contained within the system. The two half-cells are separated by a ion-exchange membrane instead of a salt bridge. A typical redox flow battery uses vanadium ions and inert electrodes.

- (a) Vanadium flow battery stores energy using vanadium redox couples. During the discharge cycle,  $V^{2+}$  loses an electron to the external circuit to form  $V^{3+}$  in the negative half-cell and acidified  $VO_2^+$  accepts an electron from the external circuit to form  $VO^{2+}$  in the positive half-cell.



- (i) Write out the two half-equations for the electrode processes that occur at the two half-cells. [2]  
**Negative half-cell:**  $V^{2+} \rightarrow V^{3+} + e^-$   
**Positive half-cell:**  $VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$
- (ii) Calculate the e.m.f. of the cell. [1]  
 $E^\circ_{\text{cell}} = E^\circ_{\text{red}} - E^\circ_{\text{oxi}} = (+1.00) - (-0.26) = +1.26V$
- (iii) Suggest why vanadium ions can be used in this redox flow battery. [1]  
**Ability to exist in different oxidation states**
- (iv) Suggest the role of a proton exchange membrane. [1]  
**To maintain electrical neutrality**

- (b) Calcium hydride is used in the synthesis of proton exchange membrane used in the vanadium flow battery. Data about calcium and vanadium are given below.

	Calcium	Vanadium
Electronic configuration	[Ar]4s <sup>2</sup>	[Ar]3d <sup>3</sup> 4s <sup>2</sup>
Relative atomic mass	40.1	50.9
Atomic radius/ nm	0.197	0.122
Density/ g cm <sup>-3</sup>	1.54	6.07

- (i) Using relevant data from the table, suggest why the density of vanadium is significantly greater than that of calcium. [2]

Both vanadium and calcium have a metallic structure. The relative atomic mass of vanadium is higher than that of calcium. The atomic volume ( $V = \frac{4}{3}\pi r^3$ ) of vanadium is lower than that of calcium due to its smaller atomic radius.

With the greater  $A_r$  of vanadium and its smaller atomic volume, the density of vanadium is significantly higher since density = mass/volume.

- (ii) Explain why vanadium compounds are usually coloured whereas calcium compounds are usually colourless. [4]

Vanadium compounds are usually coloured because they have incompletely filled d- orbitals. In the presence of ligands, the 3d orbitals become non-degenerate and split into two groups with slightly different energy (d-d\* splitting). When a d-electron from the lower energy group is promoted to the higher energy group (d-d\* electronic transition), radiation in the visible region of the electromagnetic spectrum is absorbed. The complementary colour not absorbed will be seen.

Calcium compounds are usually colourless because they have no d-electrons and so, d-d\* electronic transition cannot take place.

- (c) Compounds of calcium contain the Ca<sup>2+</sup> ion. The corresponding ion of vanadium is V<sup>2+</sup>.

- (i) Write an equation to show the third ionization energy for calcium. [1]  
 $\text{Ca}^{2+}(\text{g}) \rightarrow \text{Ca}^{3+}(\text{g}) + \text{e}^-$

- (ii) Hence explain why Ca<sup>3+</sup> compounds do not exist whilst V<sup>3+</sup> compounds do. [2]

Formation of Ca<sup>3+</sup> involves removing an electron from the inner principal quantum shell (3p subshell) which is more strongly attracted by the nucleus and this requires a large amount of energy to remove the electron. Hence Ca<sup>3+</sup> compounds do not exist.

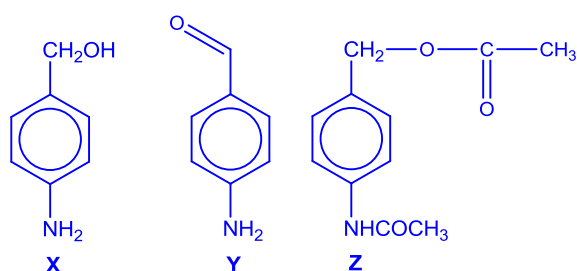
Formation of V<sup>3+</sup> involves removal of electrons from the 3d orbital which has a comparable energy with that of 4s orbital. Therefore, it is less strongly attracted by the nucleus and this requires much less energy to remove the electron. Hence V<sup>3+</sup> compounds can be formed.

(d) The following properties and reactions are exhibited by Compound **X**,  $C_7H_9ON$ .

- Compound **X** is insoluble in dilute NaOH, but dissolves in dilute HCl(aq).
- On reaction with acidified potassium dichromate(VI) under certain condition, compound **X** forms compound **Y**,  $C_7H_7ON$ .
- On reaction with ethanoyl chloride,  $CH_3COCl$ , **X** forms compound **Z**,  $C_{11}H_{13}NO_3$ .

Deduce the structures of compounds **X**, **Y** and **Z**. Explain the chemistry of the reactions described. Write an equation for the formation of compound **Z**. [6]

Structures of **X**, **Y** and **Z** are:

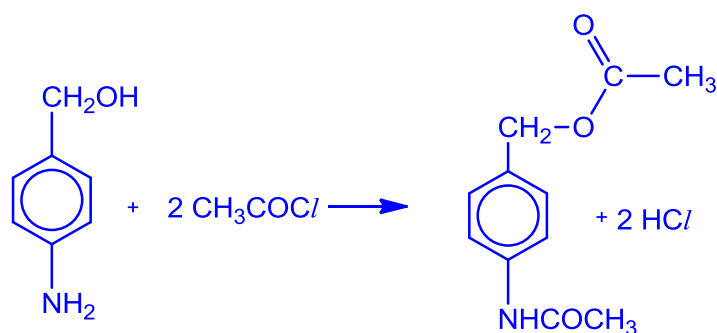


Compound **X** dissolves in HCl(aq) shows that it contains a basic group.

Compound **X** does not dissolve in NaOH(aq), Hence, it does not contain a phenol group.

Compound **X** undergo oxidation with acidified potassium dichromate (VI) and therefore, it is a (primary/secondary) alcohol.

Compound **X** undergo condensation/ acylation/ addition-elimination with ethanoyl chloride to give compound **Z**.



[Total: 20]