H

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE NAME

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| CT GROUP | **1** | **7** | **S** |  |  |

INDEX NUMBER

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**CHEMISTRY** **9729/01**

Paper 1 Multiple Choice **21 September 2018**

**1 hour**

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

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**READ THESE INSTRUCTIONS FIRST**

Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.
Write your name, Centre number and index number on the Answer Sheet in the spaces provided unless this has been done for you.

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

**Read the instructions on the Answer Sheet very carefully.**

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.

This document consists of **14** printed pages

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

**1** In an experiment, 25.0 $cm^3$ of 0.02 mol $dm^{-3}$ of vanadium(II) ions was found to react with 15.00 $cm^3$ of 0.02 mol $dm^{-3}$ of acidified $KMnO_4$. The half equation for the reduction of $MnO_4^-$ is:

$$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$$

What is the final oxidation state of vanadium?

**A** +3

**B** +4

**C** +5

**D** +6

**2** Sulfur dichloride dioxide, $SO_2Cl_2$, reacts with water to give a mixture of sulfuric acid and hydrochloric acid.

How many moles of calcium hydroxide, $Ca(OH)_2$, would be needed to neutralise the solution formed by adding one mole of $SO_2Cl_2$ to an excess of water?

**A** 1

**B** 2

**C** 3

**D** 4

**3** *The use of Data Booklet is relevant to this question.*

An ion $\mathbf{E}^{2+}$ contains 24 protons.

Which of the following statements about $\mathbf{E}^{2+}$ is **incorrect**?

**A** The enthalpy change for the reaction $\mathbf{E}(g) \rightarrow \mathbf{E}^{2+}(g) + 2e$ is +2243 kJ $mol^{-1}$.

**B** The removal of the two electrons from **E** to form $\mathbf{E}^{2+}$ is from the 4s subshell.

**C** The angle of deflection of $\mathbf{E}^{2+}$ in an electric field is smaller than that of $\mathbf{E}^{3+}$.

**D** $\mathbf{E}^{2+}$ is isoelectronic with $Mn^{3+}$.

**4** Which of the following statements explain why aluminium chloride, $Al_2Cl_6$, sublime at a relatively low temperature?

**1** Intermolecular forces between the $Al_2Cl_6$ molecules are weak.

**2** The dative bonds between $Al$ and $Cl$ atoms are weak.

**3** The covalent bonds between $Al$ and $Cl$ atoms are weak.

**A** 1 only

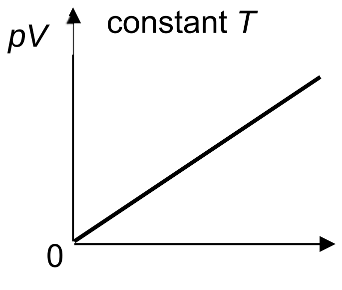
**B** 1 and 2 only

**C** 2 and 3 only

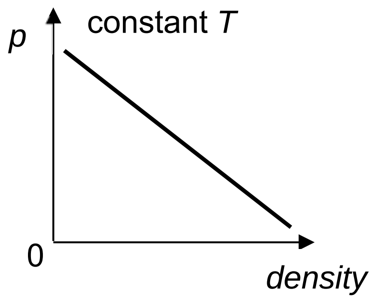
**D** 3 only

**5** Which of the following diagrams correctly describes the behavior of a fixed mass of an ideal gas? ($T$ is measured in K)

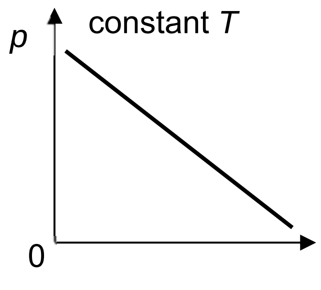
**A**



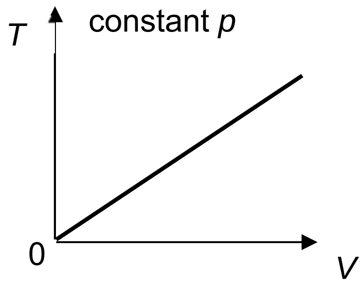
**B**



**C**



**D**



**6** The enthalpy change of reaction between hydrogen sulfide and oxygen is $\Delta H_1$.

$$H_2S(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(g) + S(s) \qquad \Delta H_1$$

What information is **not** needed to calculate $\Delta H_1$?

**A** enthalpy change of vaporisation of $H_2O(l)$

**B** enthalpy change of formation of $H_2S(g)$

**C** enthalpy change of formation of $H_2O(l)$

**D** enthalpy change of combustion of $S(s)$

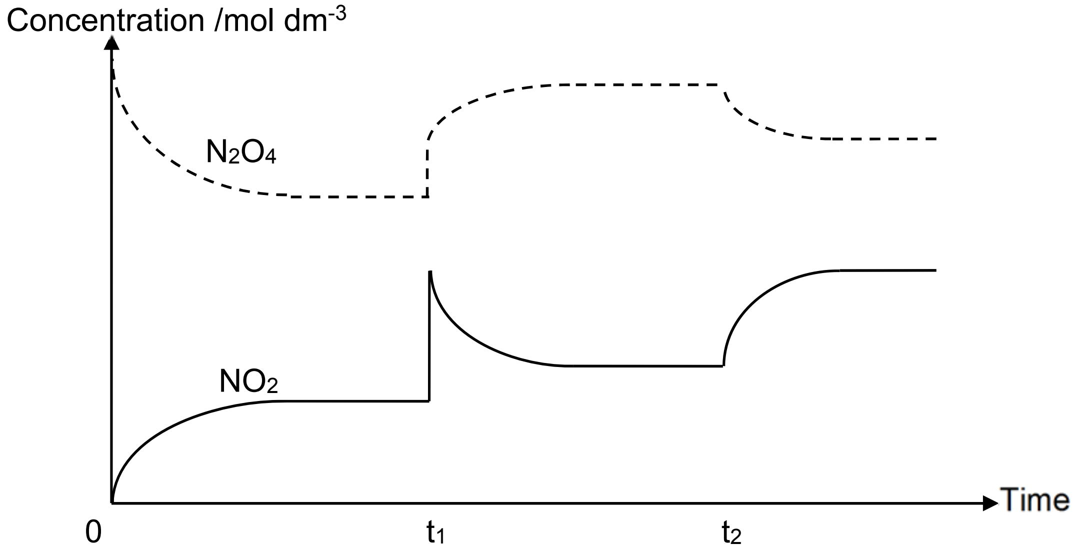
**7** Which suggested mechanism is consistent with the experimentally determined rate equations?

| | **Rate equation** | **Suggested mechanism** | |
|---|---|---|---|
| **A** | Rate = $k[NO]^2[O_2]$ | $2NO(g) \rightarrow N_2O_2(g)$<br>$N_2O_2(g) + O_2(g) \rightarrow 2NO_2(g)$ | (fast)<br>(slow) |
| **B** | Rate = $k[H_2][I_2]$ | $H_2(g) \rightarrow 2H(g)$<br>$2H(g) + I_2(g) \rightarrow 2HI(g)$ | (slow)<br>(fast) |
| **C** | Rate = $k[HBr][O_2]$ | $2HBr(g) + O_2(g) \rightarrow 2HBrO(g)$<br>$HBrO(g) + HBr(g) \rightarrow H_2O(g) + Br_2(g)$ | (slow)<br>(fast) |
| **D** | Rate = $k[H_2O_2][I^-]$ | $2H^+(aq) + 2I^-(aq) \rightarrow 2HI(aq)$<br>$2HI(aq) + H_2O_2(aq) \rightarrow I_2(aq) + 2H_2O(l)$ | (fast)<br>(slow) |

**8** An amount of $N_2O_4$ was placed in a closed vessel and allowed to reach equilibrium as shown below.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = +57 \text{ kJ mol}^{-1}$$

Two changes were made to the equilibrium system at $t_1$ and $t_2$.



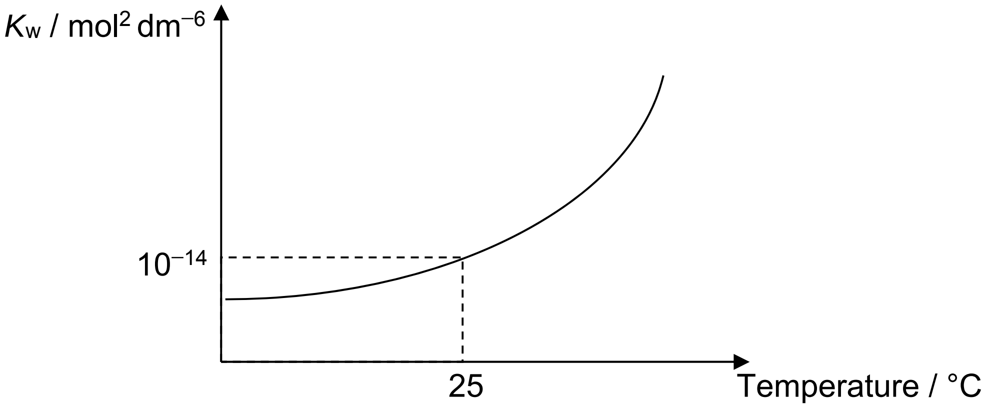
Which are the changes made at $t_1$ and $t_2$?

| | $t_1$ | $t_2$ |
|---|---|---|
| **A** | More $NO_2$ was added | Temperature was increased |
| **B** | An inert gas was added at constant volume | Temperature was decreased |
| **C** | Volume of the system was decreased | Temperature was increased |
| **D** | Volume of the system was increased | Temperature was decreased |

**9** Water dissociates as shown:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

The ionic product of water, $K_w$, varies with temperature as shown in the graph below.



Which statements about the above equilibrium system are correct?

**1** The pH of water decreases as temperature increases.

**2** The concentrations of $H^+$ and $OH^-$ are equal at all temperatures.

**3** The dissociation of water is exothermic.

**A** 2 only

**B** 3 only

**C** 1 and 2 only

**D** 2 and 3 only

**10** The pH range and colour changes for two acid-base indicators are given below:

| Indicator | Colour in acidic solution | pH range | Colour in basic solution |
|---|---|---|---|
| **P** | Violet | 3.0-5.0 | red |
| **Q** | Yellow | 5.7-7.6 | blue |

Which solution will appear red in **P** and yellow in **Q**?

**A** 0.1 mol dm$^{-3}$ of $HCl$

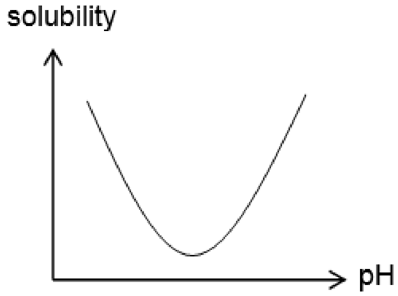
**B** 0.1 mol dm$^{-3}$ of NaOH

**C** 0.1 mol dm$^{-3}$ of $CH_3CO_2H$ ($K_a$ = 1.8 x $10^{-5}$ mol dm$^{-3}$)

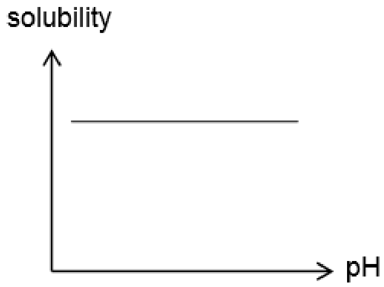
**D** 0.1 mol dm$^{-3}$ of HX ($K_a$= 2.5 x $10^{-10}$ mol dm$^{-3}$)

**11** The solubility product of calcium carbonate, $CaCO_3$, is 4.81 x $10^{-9}$ $mol^2\ dm^{-6}$. Which of the following graphs shows how the solubility of $CaCO_3$ will vary with pH at constant temperature?

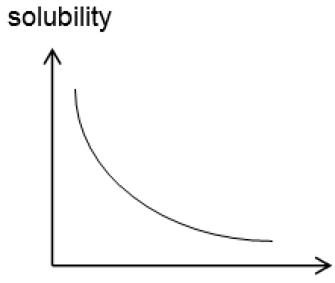
**A**



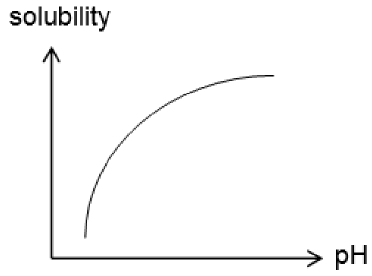
**B**



**C**



**D**



**12** The equilibrium between $Ag_2CO_3$, a sparingly soluble salt, and its saturated solution is as shown below.

$$Ag_2CO_3(s) + aq \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$$

$K_{sp}$ of $Ag_2CO_3 = 8.2 \times 10^{-12}\ mol^3\ dm^{-9}$

Which one of the following is correct?

**1** Adding NaC*l*(aq) will cause more $Ag_2CO_3$ solid to dissolve.

**2** Upon the addition of sodium carbonate, solubility of $Ag_2CO_3$ increases.

**3** $K_{sp}$ of $Ag_2CO_3$ decreases as $AgNO_3$ solution is added to it.

**A** 1 only

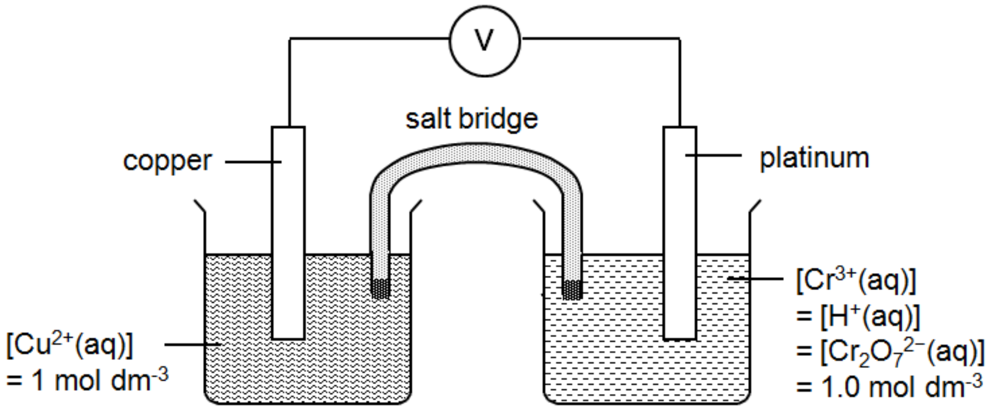
**B** 1 and 2 only

**C** 2 and 3 only

**D** 1, 2 and 3

**13** *Use of the Data Booklet is relevant to this question.*

A cell is set up by connecting a $Cu^{2+}/Cu$ half-cell and an acidified $Cr_2O_7^{2-}/Cr^{3+}$ half-cell under standard conditions.

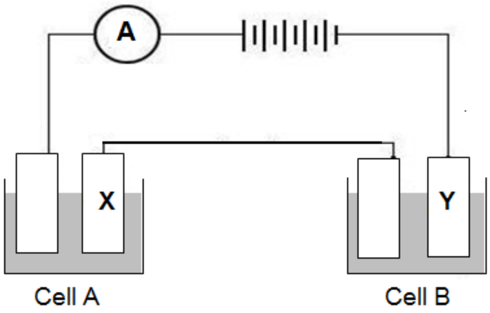


Which of the following correctly describes the effect on the e.m.f of the cell when the respective change is made?

| | change | effect on e.m.f of cell |
|---|---|---|
| **A** | using a larger copper electrode | increases |
| **B** | addition of concentrated $H_2SO_4$ into reduction half-cell | decreases |
| **C** | addition of dilute NaOH into oxidation half-cell | decreases |
| **D** | addition of water into oxidation half-cell | increases |

**14** *Use of the Data Booklet is relevant to this question.*

A student carried out an experiment involving the electrolysis of aqueous copper(II) sulfate in cell **A** and aqueous chromium(III) sulfate in cell **B**.



Given that 6.35 g of copper was deposited at electrode **X** at the end of the experiment, what is the mass of chromium deposited at electrode **Y**?

**A** 0.87 g

**B** 1.74 g

**C** 3.47 g

**D** 10.4 g

**15** ***P*****,** ***Q*** and ***R*** are elements of the third period of the Periodic Table. The oxide of ***P*** is amphoteric, the oxide of ***Q*** is basic and oxide of ***R*** is acidic.

What is the order of increasing ionic radius?

**A** ***RQP***

**B** ***QPR***

**C** ***PRQ***

**D** ***PQR***

**16** Which of the following statements about Group 2 elements and their compounds is correct?

**1** Magnesium hydroxide decomposes on heating to give magnesium oxide and steam.

**2** 1 mole of strontium carbonate, on heating over a short period of time, decomposes to give more carbon dioxide gas than 1 mole of magnesium carbonate

**3** Magnesium has a higher melting point than strontium.

**A** 1 only

**B** 1 and 3 only

**C** 2 and 3 only

**D** 1, 2 and 3

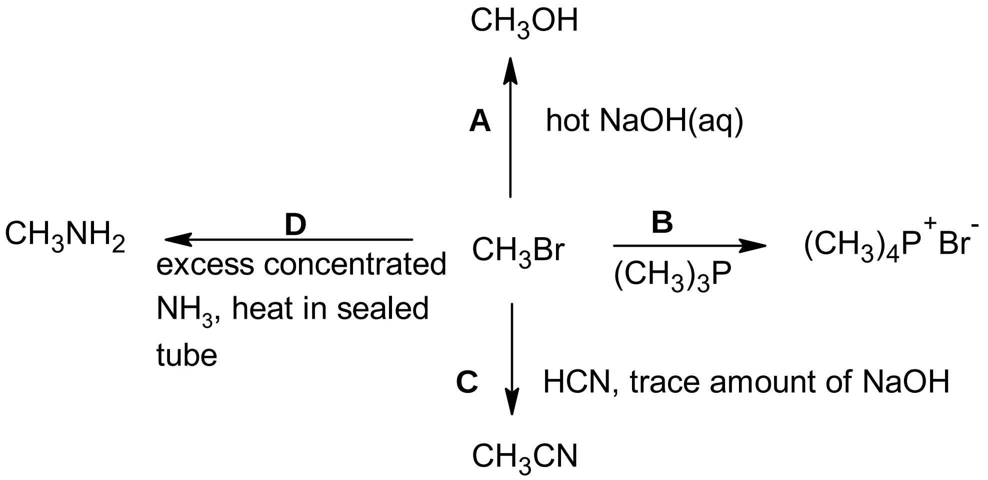
**17** Adding KSCN (aq) to FeNO$_3$(aq) causes the colour of the solution to change from yellow to blood red.

Which of the following row correctly shows the number of d-electrons and the energy gap between the d-orbitals, before and after the reaction?

| | number of d-electrons | energy gap between the d-orbitals |
|---|---|---|
| **A** | changes | changes |
| **B** | changes | remains the same |
| **C** | remains the same | changes |
| **D** | remains the same | remains the same |

**18** A reaction scheme involving bromomethane is given below.

Which of the reactions does **not** take place?



**19** 3-ethylpentane can react with bromine in the presence of sunlight to give two monosubstituted halogenoalkanes:

1-bromo-3-ethylpentane and 3-bromo-3-ethylpentane.

Given the relative rates of abstracting H atoms are:

| Type of H atom | primary | secondary | Tertiary |
|---|---|---|---|
| Relative rate of abstraction | 1 | 4 | 6 |

What is the expected ratio of 1-bromo-3-ethylpentane to 3-bromo-3-ethylpentane formed?

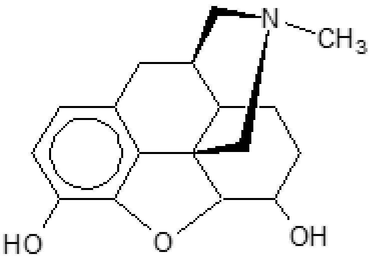
**A** 9 : 1

**B** 6 : 1

**C** 3 : 2

**D** 1 : 6

**20** Morphine is an effective pain killer.



morphine

Which of the following statements about morphine is correct?

**A** It contains 10 chiral centers.

**B** It does not decolourise $Br_2$(aq).

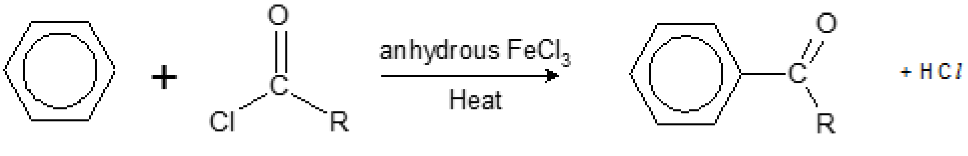
**C** It turns cold alkaline $KMnO_4$ from purple to colourless.

**D** One mole of morphine reacts with excess sodium to give 1 mole of $H_2$ gas.

**21** Under suitable conditions, ethene may undergo a reaction with an interhalogen compound, I*Cl*. Which of the following shows the structure of the intermediate formed?

**A** $[CH_3CH_2]^+$ **B** $[CH_3CHI]^+$ **C** $[CH_2CH_2I]^+$ **D** $[CH_2CH_2Cl]^+$

**22** Anhydrous iron(III) chloride is made by passing chlorine gas over heated iron. It can be used as a catalyst in the acylation of benzene, a process called Friedel-Crafts acylation, to produce carbonyl compounds.



The mechanism of the above reaction is similar to that of chlorination of benzene. Which of the following statements is **not** correct about the mechanism?

**A** The organic intermediate has a ring with one $sp^3$ hybridised carbon.

**B** The overall order of reaction is 1.

**C** The mechanism involves $RCO^+$ as an electrophile.

**D** $FeCl_3$ is a homogeneous catalyst.

**23** Some chlorobutanes were separately treated with hot ethanolic sodium hydroxide. Two of these gave the same hydrocarbon, $C_4H_6$.

From which pair of chlorobutanes was this hydrocarbon obtained?

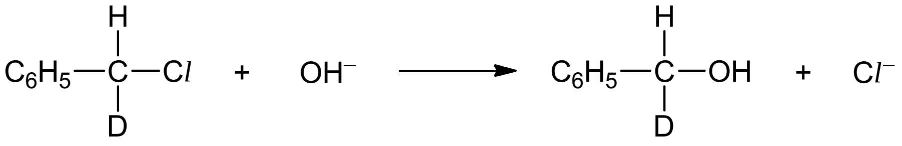
**A** $CH_3CH_2CH_2CH_2Cl$ and $CH_3CH_2CH_2CHCl_2$

**B** $CH_3CHClCHClCH_3$ and $ClCH_2CH_2CH_2CH_2Cl$

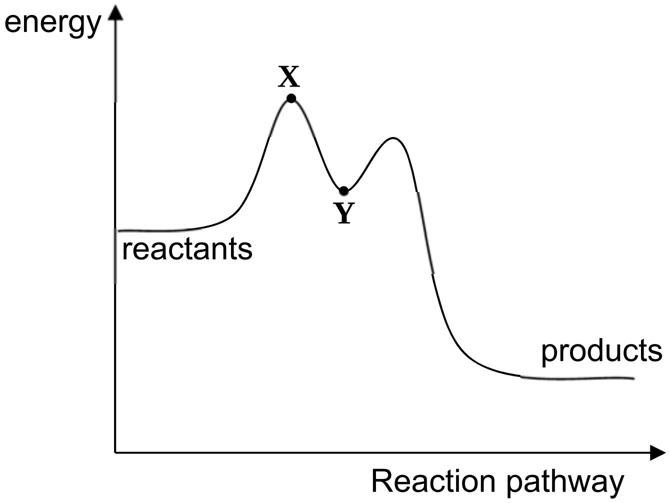
**C** $CH_3CH_2CH_2CH_2Cl$ and $ClCH_2CH_2CH_2CH_2Cl$

**D** $CH_3CH_2CH_2CH_2Cl$ and $CH_3CH_2CHClCH_3$

**24** The energy profile for the following reaction is shown below. [D = $^2H$]



$$C_6H_5CHDCl + OH^- \longrightarrow C_6H_5CHDOH + Cl^-$$

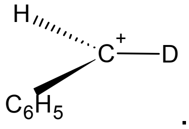


Which of the following conclusions can be drawn?

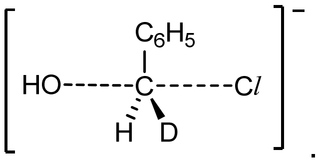
**A** The product has no effect on the rotation of plane polarised light.

**B** The rate of reaction can be increased by increasing concentration of $OH^-$.

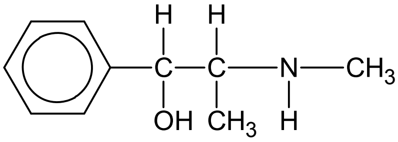
**C** The structure of the species at point **X** is



**D** The structure of the species at point **Y** is



**25** Ephedrine is a drug that is widely used in cold and allergy medications.

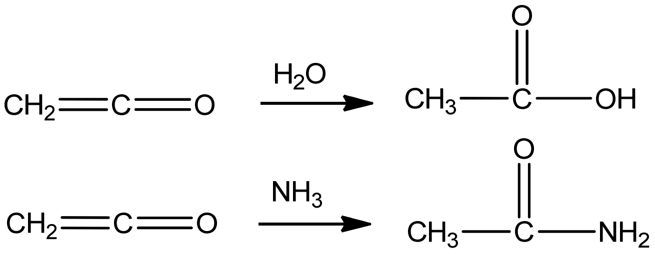


Ephedrine

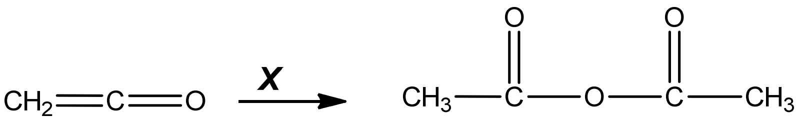
Which of the following pairs of reagents consists of one which reacts with ephedrine and one which does **not** react with ephedrine?

| | | |
|---|---|---|
| **A** | $CH_3CO_2H$ | $CH_3COCl$ |
| **B** | $HCl(aq)$ | $SOCl_2$ |
| **C** | $CH_3Br$ | $NaOH(aq)$ |
| **D** | $[Ag(NH_3)_2]^+$ | 2,4-dinitrophenylhydrazine |

**26** Ketene ($CH_2{=}C{=}O$) can combine with nucleophiles such as $H_2O$ or $NH_3$ to make ethanoic acid and ethanamide respectively, as shown below.



Which of the following is the correct nucleophile ***X*** for the reaction below?



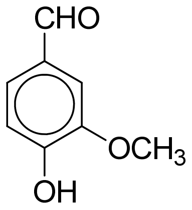
**A** $HCO_2CH_3$

**B** $CH_3CHO$

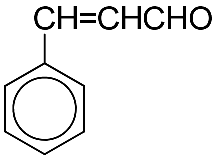
**C** $CH_3COCH_3$

**D** $CH_3CO_2H$

**27** Vanillin and cinnamaldehyde are found in natural products and have very pleasant fragrances.



**vanillin**



**cinnamaldehyde**

Which of the following reagents could be used to distinguish between the two compounds? You may assume that the –$OCH_3$ group in vanillin is inert.

**1** Fehling's solution

**2** hot acidified aqueous $KMnO_4$

**3** 2, 4-dinitrophenylhydrazine

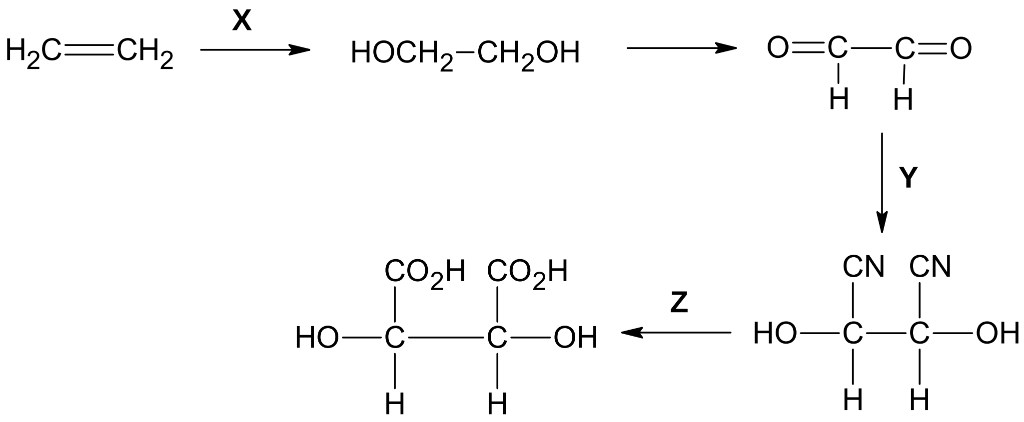
**A** 1 only

**B** 2 only

**C** 1 and 2 only

**D** 1, 2 and 3

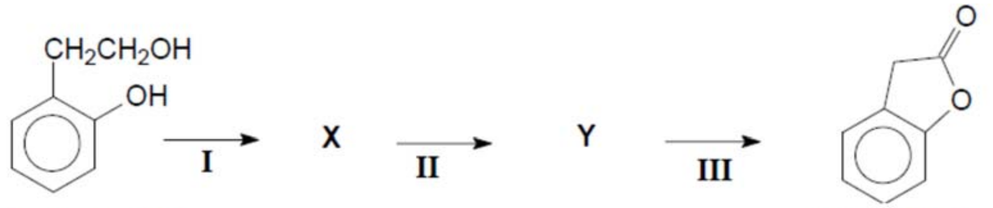
**28** The following is a method of synthesising tartaric acid, a compound found in wine.



Which set of reagents and conditions can be used for the synthesis?

| | stage **X** | stage **Y** | stage **Z** |
|---|---|---|---|
| **A** | cold $KMnO_4$, NaOH(aq) | cold HCN, trace KCN(aq) | hot $K_2Cr_2O_7$, $H_2SO_4$(aq) |
| **B** | cold $KMnO_4$, NaOH(aq) | ethanolic KCN, heat | HC*l*(aq), heat |
| **C** | cold $KMnO_4$, $H_2SO_4$(aq) | ethanolic KCN, heat | hot $K_2Cr_2O_7$, $H_2SO_4$(aq) |
| **D** | cold $KMnO_4$, $H_2SO_4$(aq) | cold HCN, trace KCN(aq) | HC*l*(aq), heat |

**29** Compound **B** can be converted to compound **C** as shown below.



Compound **B**

Compound **C**

Which of the following statements regarding the reaction scheme is correct?

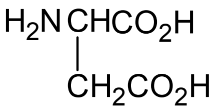
**A** Step **I** may involve the use of $PCl_5$.

**B** Step **I** may involve the use of hot acidified $KMnO_4$.

**C** Step **III** may involve the use of aqueous NaOH.

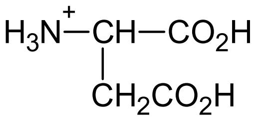
**D** Step **III** may involve the use of hot concentrated $H_2SO_4$.

**30** Which structure will be present when the amino acid aspartic acid,

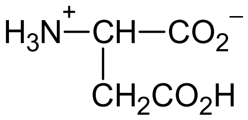

$$\begin{array}{l} H_2N\,CHCO_2H \\ \quad\;\;\, | \\ \quad\;\; CH_2CO_2H \end{array}$$

is in aqueous solution at pH 10?

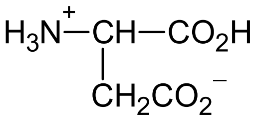
**A**


$$\begin{array}{l} H_3\overset{+}{N}-CH-CO_2H \\ \qquad\;\; | \\ \qquad\; CH_2CO_2H \end{array}$$

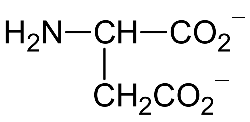
**B**


$$\begin{array}{l} H_3\overset{+}{N}-CH-CO_2^{\;-} \\ \qquad\;\; | \\ \qquad\; CH_2CO_2H \end{array}$$

**C**


$$\begin{array}{l} H_3\overset{+}{N}-CH-CO_2H \\ \qquad\;\; | \\ \qquad\; CH_2CO_2^{\;-} \end{array}$$

**D**


$$\begin{array}{l} H_2N-CH-CO_2^{\;-} \\ \qquad\;\; | \\ \qquad\; CH_2CO_2^{\;-} \end{array}$$

**End of paper**

2018 P1 Prelim answers

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

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE NAME

CT GROUP | 1 | 7 | S | | |

INDEX NUMBER | | | | |

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**CHEMISTRY** **9729/02**

Paper 2 Structured **11 September 2018**

**2 hours**

Additional Materials: Data Booklet

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**READ THESE INSTRUCTIONS FIRST**

Write your class, index number and name on all work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough workings.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.

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** | | | |
|---|---|---|---|
| **Paper 1** | | **/ 30** | |
| **Paper 2** | | | |
| 1 | / 9 | 4 | /12 |
| 2 | / 8 | 5 | / 10 |
| 3 | / 18 | 6 | / 18 |
| Penalty | | sf | unit |
| **Paper 2** | | **/ 75** | |
| **Paper 3** | | **/ 80** | |
| **Paper 4** | | **/ 55** | |
| Total | | | |

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This document consists of **21** printed pages.

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

**1** **(a)** Water hardness is determined by the concentration of multivalent cations in the water. Common cations found in hard water include $Ca^{2+}$ and $Mg^{2+}$. Lime softening is a type of water treatment where aqueous $Na_2CO_3$ is added to remove $Ca^{2+}$ ion as $CaCO_3$ is precipitated. These precipitates are then removed by sedimentation and filtration, where $X^{2+}$ can be $Ca^{2+}$ and $Mg^{2+}$.

$$X^{2+}(aq) + Na_2CO_3(aq) \rightarrow XCO_3(s) + 2Na^{+}(aq)$$

In the laboratory, 1 $cm^3$ of 0.50 mol $dm^{-3}$ $Na_2CO_3$ is added to 10 $cm^3$ of a raw water sample. What is the minimum concentration of $Ca^{2+}$ in the original raw water sample, which would cause a white precipitate to be observed?

The value of $K_{sp}$ for $CaCO_3$ is $4.81 \times 10^{-9}$ $mol^2\ dm^{-6}$.

[2]

**(b)** A saturated solution of raw water containing both $CaF_2$ and $Ca(OH)_2$ has a pH of 12 at 25°C.

| calcium compound | numerical value of $K_{sp}$ |
|---|---|
| $CaF_2$ | $3.2 \times 10^{-11}$ |
| $Ca(OH)_2$ | $6.4 \times 10^{-6}$ |

**(i)** Calculate the concentration of hydroxide ions in the solution.

[1]

**(ii)** Hence, calculate the solubility of $CaF_2$ in the raw water sample. Show your working clearly.

[2]

**(c)** Using the following data, construct an energy cycle to calculate the enthalpy change for the thermal decomposition of calcium carbonate.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

| | $\Delta H$ / kJ mol$^{-1}$ |
|---|---|
| $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ | −57.1 |
| $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$ | −63.7 |
| $H_2SO_4(aq) + CaCO_3(s) \rightarrow CaSO_4(aq) + H_2O(l) + CO_2(g)$ | −151.5 |

[4]

[Total: 9]

**2** The reaction of ethanal with iodine occurs in the presence of acid catalyst, HC*l*. . The reaction is given below.

$$I_2 + CH_3CHO \xrightarrow{HCl} CH_2ICHO + HI \qquad \text{Reaction 1}$$

The table shows the results obtained when the concentrations of $I_2$, $CH_3CHO$ and HC*l* were varied.

| Experiment | Initial [HC*l*] / mol dm$^{-3}$ | Initial [$I_2$] / mol dm$^{-3}$ | Initial [$CH_3CHO$] / mol dm$^{-3}$ | Initial rate / mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|---|---|
| 1 | 0.10 | 0.20 | 0.20 | $1.6 \times 10^{-6}$ |
| 2 | 0.10 | 0.40 | 0.30 | $2.4 \times 10^{-6}$ |
| 3 | 0.40 | 0.40 | 0.20 | $6.4 \times 10^{-6}$ |
| 4 | 0.10 | 0.20 | 2.00 | $1.6 \times 10^{-5}$ |

**(a) (i)** Deduce the orders of reaction with respect to $I_2$, $CH_3CHO$ and HC*l*. Hence, determine the rate equation.

[3]

**(ii)** The half-life of ethanal in experiment 1 was 60 seconds. Predict the half-life of ethanal in experiments 2 and 3. Explain your answer.

……………………………………………………………………………………………

……………………………………………………………………………………………

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…………………………………………………………………………………………… .[2]

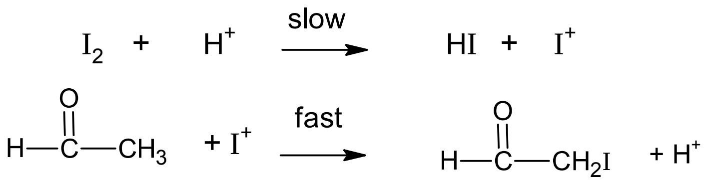
**(iii)** Sketch the graph of concentration of iodine against time for experiment 4.

| Experiment | Initial [HC*l*] / mol dm$^{-3}$ | Initial [I$_2$] / mol dm$^{-3}$ | Initial [CH$_3$CHO] / mol dm$^{-3}$ | Initial rate / mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|---|---|
| 4 | 0.10 | 0.20 | 2.00 | 1.6 x 10$^{-5}$ |

[1]

**(b)** The following mechanisms **A** and **B** are proposed for the reaction of ethanal, iodine and acid catalyst in Reaction 1.

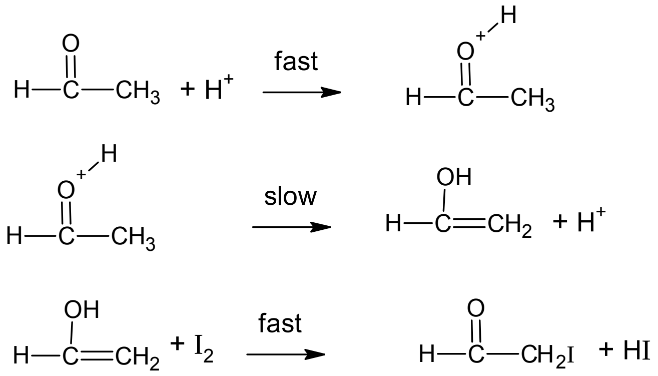
**Mechanism A**



$$I_2 + H^+ \xrightarrow{\text{slow}} HI + I^+$$

$$H{-}\overset{\overset{O}{\|}}{C}{-}CH_3 + I^+ \xrightarrow{\text{fast}} H{-}\overset{\overset{O}{\|}}{C}{-}CH_2I + H^+$$

**Mechanism B**



$$H{-}\overset{\overset{O}{\|}}{C}{-}CH_3 + H^+ \xrightarrow{\text{fast}} H{-}\overset{\overset{{}^{+}O{-}H}{\|}}{C}{-}CH_3$$

$$H{-}\overset{\overset{{}^{+}O{-}H}{\|}}{C}{-}CH_3 \xrightarrow{\text{slow}} H{-}\overset{\overset{OH}{|}}{C}{=}CH_2 + H^+$$

$$H{-}\overset{\overset{OH}{|}}{C}{=}CH_2 + I_2 \xrightarrow{\text{fast}} H{-}\overset{\overset{O}{\|}}{C}{-}CH_2I + HI$$

Which of the above mechanisms best agrees with the experimentally determined rate equation in **(a)(i)**? Explain your answer.

……………………………………………………………………………………………

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…………………………………………………………………………………………… [2]

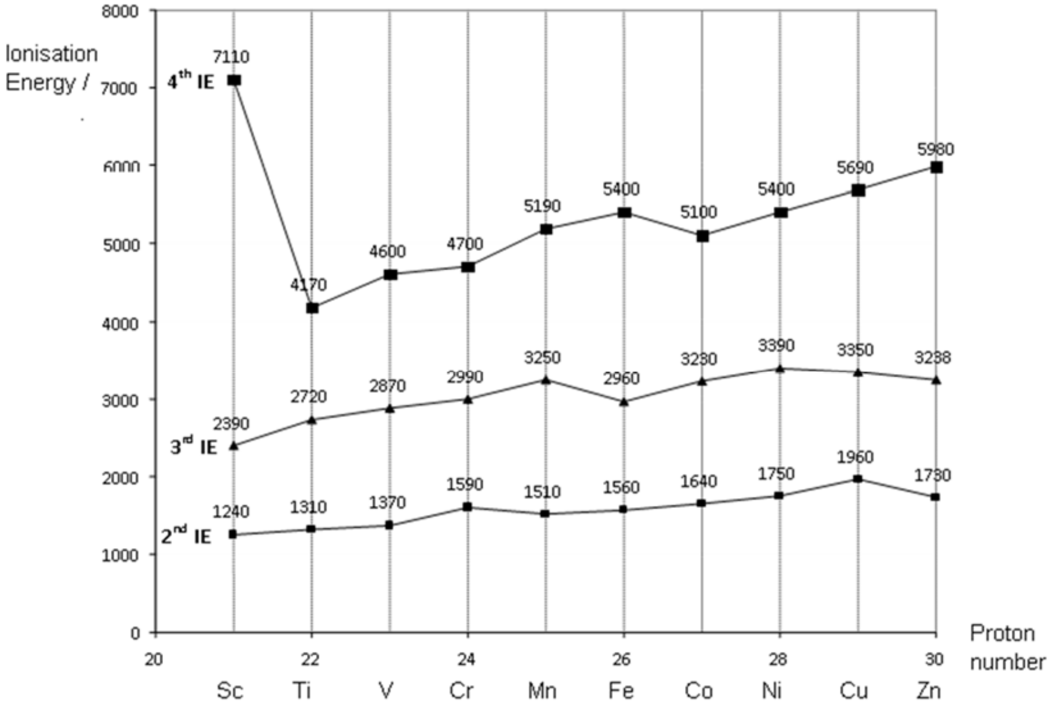
[Total: 8]

**3** Transition metal is "an element whose atom has a partially filled d sub-shell, or which can give rise to cations with an incompletely filled d sub-shell". Chromium and vanadium, both transition metals, have found a number of industrial uses due to their toughness and resistance to heat and corrosion.

The table below shows some information of a Group 2 metal calcium, vanadium and chromium.

| | **Vanadium** | **Chromium** | **Calcium** |
|---|---|---|---|
| Melting point/ $^oC$ | 1910 | 1875 | 843 |
| Atomic radius/ nm | 0.135 | 0.129 | 0.197 |
| Common Oxidation Number | +2, +3, +4, +5 | +2, +3, +6 | +2 |

The graph below shows the second to fourth ionisation energies for the first row d block elements scandium to zinc.



**(a)** **(i)** Although the vanadium atom has more electrons than the calcium atom, the atomic radius of vanadium is smaller than that of calcium. Suggest an explanation for this.

…………………………………………………………………………………………………

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…………………………………………………………………………………………………

…………………………………………………………………………………………………[2]

**(ii)** Explain why the second ionisation energies of transition elements from Ti to Cu are relatively invariant.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

………………………………………………………………………………………… [2]

**(iii)** Explain why the second ionisation energy of chromium is higher than that of manganese.

…………………………………………………………………………………………

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…………………………………………………………………………………………

………………………………………………………………………………………… [2]

**(b)** **(i)** State the **full** electronic configuration of $Cr^{3+}$ ion.

………………………………………………………………………………………… [1]

**(ii)** The complex ion $[Cr(H_2O)_6]^{3+}$ is green, and it is an octahedral complex. On the Cartesian axes shown in Fig. 2.1, draw **fully-labelled** diagrams of the following:

- One of the d orbitals at the lower energy level in an octahedral complex- Label this diagram 'lower'.
- One of the d orbitals at the upper energy level in an octahedral complex. Label this diagram 'upper'.

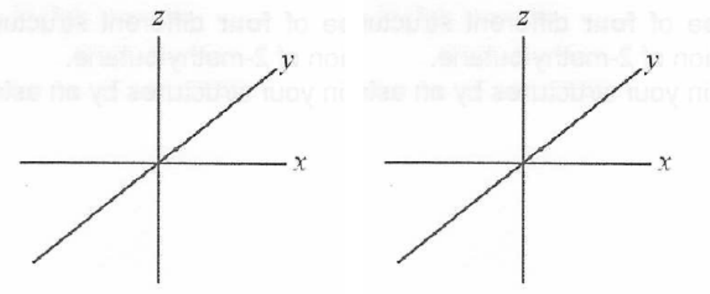

Fig. 3.1

[2]

**(iii)** Suggest which of the two compounds chromium(III) oxide, $Cr_2O_3$, and chromium(III) carbonate, $Cr_2(CO_3)_3$, would have a more exothermic lattice energy. Explain your answer.

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

……………………………………………………………………………………………… [2]

**(iv)** The compound $K_3CrO_4$ is a green solid. When mixed with dilute $H_2SO_4$, it undergoes disproportionation to yield $Cr^{3+}$(aq) and $Cr_2O_7^{2-}$(aq) ions.

By writing appropriate half-equations, write an overall balanced equation for the disproportionation of $CrO_4^{3-}$ in acid.

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………………………………………………………………………………………………

………………………………………………………………………………………………

……………………………………………………………………………………………… [2]

**(v)** Purification of chromium can be achieved by electro-refining chromium from an impure chromium anode onto a pure chromium cathode in an electrolytic cell. How many hours will it take to plate 130 g of chromium onto the cathode if the current passed through the cell is held constant at 34.0 A?

Assume the chromium in the electrolytic solution is present as $Cr^{3+}$.

[2]

**(c)** The reaction between $S_2O_8^{2-}$ ions and $I^-$ ions is very slow:

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

If a small amount of aqueous manganese(II) ions, $Mn^{2+}$, is added to the mixture, the rate of reaction increases rapidly.

State the property, typical of transition metals, which allow manganese (II) ions to behave as a homogeneous catalyst in this reaction.

By considering the data given below, write relevant chemical equations to support your answer.

$$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$$

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

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…………………………………………………………………………………………………… [3]

[Total:18]

**4** **(a)** Citric acid is commonly found in citrus fruits such as lemons. Mixtures of citric acid and its salt, sodium citrate, are often used as “acidity regulators”. These are food additives that have a buffering action on the pH of foodstuffs.

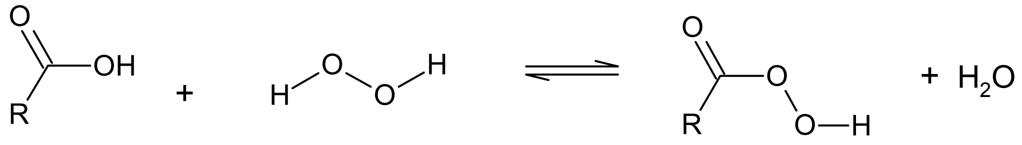
$$\underset{\text{citric acid}}{C_5H_7O_4CO_2H} \rightleftharpoons \underset{\text{citrate}}{C_5H_7O_4CO_2^-} + H^+$$

$K_a$ of citric acid = $7.4 \times 10^{-4}$ mol dm$^{-3}$

A typical citric acid / sodium citrate buffer mixture is prepared by mixing 0.100 mol dm$^{-3}$ citric acid and 0.200 mol dm$^{-3}$ sodium citrate in a volume ratio 2:3 respectively. Calculate the pH of the buffer solution.

[2]

**(b)** The reaction between carboxylic acids and hydrogen peroxides produce peroxyacids.



The p*K*a values of four compounds are listed in the table below.

| **name** | **formula** | ***pK*a** |
|---|---|---|
| Water | $H_2O$ | 14.0 |
| Hydrogen peroxide | $H_2O_2$ | 11.7 |
| Methanoic acid | $HCO_2H$ | 3.7 |
| Peroxymethanoic acid | $HCO_3H$ | 7.1 |

Suggest an explanation for why

**(i)** The p*K*a of $H_2O_2$ is less than that for water

..........................................................................................................................

.......................................................................................................................... [1]

**(ii)** the p*K*a of HCO$_3$H is more than that for HCO$_2$H

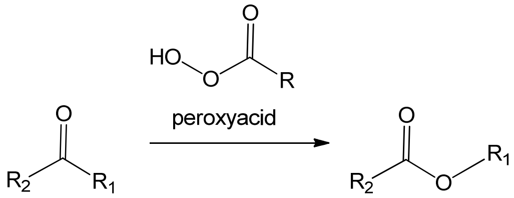
……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

…………………………………………………………………………………………… [2]

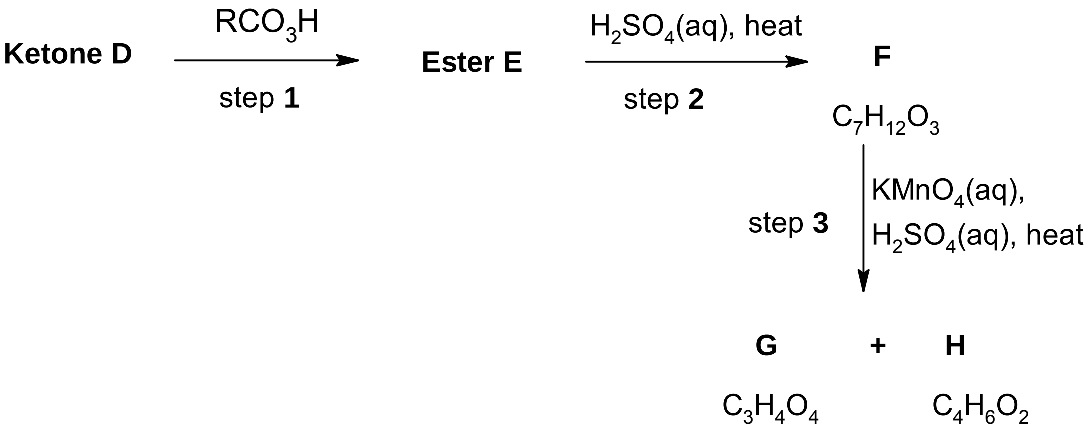
**(c)** The Baeyer-Villiger oxidation is an organic reaction in which peroxyacids react with ketones to give esters, as shown in the equation below.



In the following scheme, ketone **D** **(**C$_7$H$_{10}$O) undergoes Baeyer-Villiger oxidation in step **1** to form ester **E**. Ketone **D** also decolourises orange aqueous Br$_2$.

**F** is the **only** product formed, from treating ester **E** with hot H$_2$SO$_4$(aq).

Hot acidified KMnO$_4$ oxidises several classes of organic compounds to ketones, carboxylic acids and carbon dioxide. By this means, the structures of compounds can be determined. The scheme below shows the oxidation products of **F**.



**(i)** State the type of reaction Ester **E** undergoes with hot H$_2$SO$_4$(aq) in step 2.

Type of reaction: ………………………………………………………………… [1]

**(ii)** 1 mole **H** reacted with alkaline aqueous iodine to form 2 moles of $CHI_3$ yellow ppt. Suggest the structure of **H**.
Give the product of the reaction of **H** with alkaline aqueous iodine.
Structure of **H:**

Product**:**

[2]

**(iii)** **G** ($C_3H_4O_4$) was found to react with $Na_2CO_3$(aq). Suggest the structure of **G**.

[1]

**(iv)** From your answer in **(ii)** and **(iii)**, deduce and suggest the structure of **F**.

[1]

**(v)** Hence, suggest the structures of ketone **D** and ester **E**.

[2]

[Total: 12]

**5** **(a)** **(i)** Oleic acid, $CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$ is a fatty acid found in oils and fats, which has C=C double bond in the cis configuration.

The trans isomer of oleic acid is known as *elaidic acid*, which is found in partially hydrogenated vegetable oils.

Draw the skeletal formula for the ***trans*** isomer of oleic acid, $CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$, which is also known as *elaidic acid*.

[1]

**(ii)** Suggest a brief explanation for the differences in melting points between oleic acid and its *trans* isomer, elaidic acid.

| **Compound** | ***Mr*** | **Melting point / °C** |
|---|---|---|
| oleic acid (cis-isomer) | 282 | 4.0 |
| elaidic acid (trans-isomer) | 282 | 45.0 |

……………………………………………………………………………………………...........

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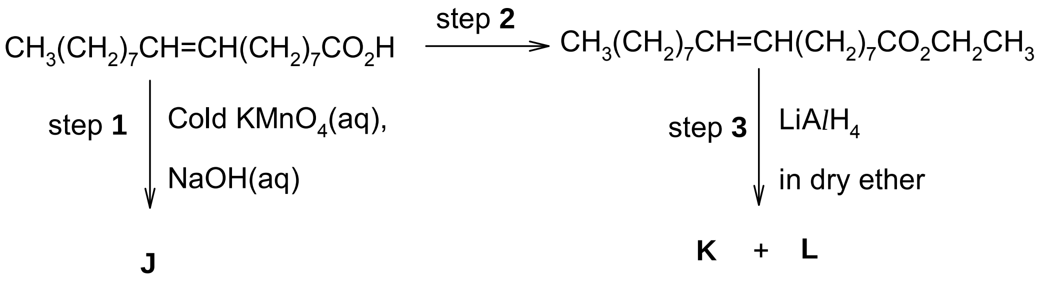
……………………………………………………………………………………………....... [1]

**(iii)** Below outlines a reaction scheme involving oleic acid.



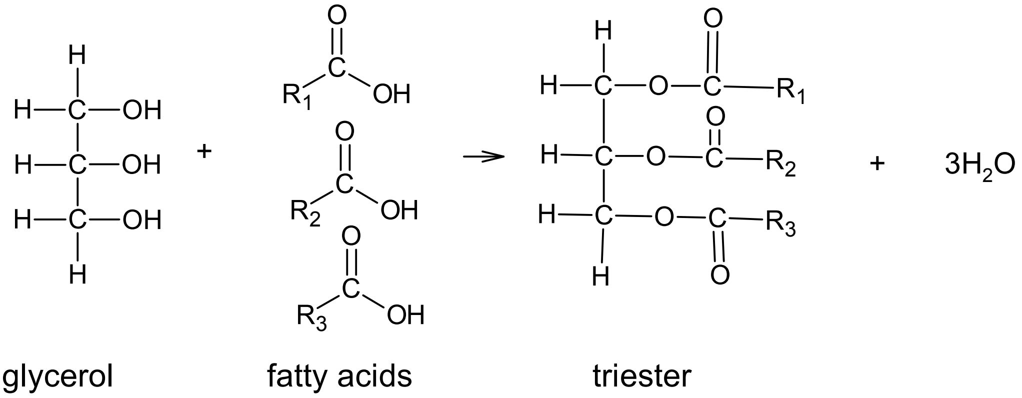
Give the reagents and conditions for step 2, and draw the structures of compounds **J**, **K** and **L** in the boxes provided below.

Step **2:** ……………………………………………………………………………………

| **J** | **K** | **L** |
|---|---|---|

[4]

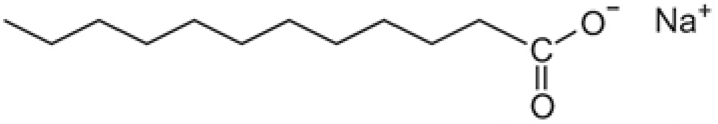
**(b)** Avocado oil consists mainly of triesters formed from glycerol (propane-1,2,3-triol) and long-chain carboxylic acids (fatty acids) as shown by the general equation.



The major component of avocado oil is triolein, the triester formed from glycerol and three units of oleic acid (fatty acid).

**(i)** A student tried to flush his cup with water to wash away the avocado oil, but was not successful. The student then tried using soap to wash away the avocado oil in the cup, and was successful.

The following compound, sodium stearate is a typical soap for washing.



By reference to the type of intermolecular forces formed between the soap, avocado oil and water, explain why sodium stearate is able to wash away the avocado oil in the cup.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………[2]

**(ii)** Below shows the nutrition content of fats, carbohydrates and protein present in one serving of avocado milkshake.

| | Mass present in 1 serving of milkshake | Fuel value/ kJ $g^{-1}$ |
|---|---|---|
| **Total Fat** | 30 g | |
| Saturated fat (tristearin) | 6 g | 42.4 |
| Unsaturated fat (triolein) | 24 g | $x$ |
| Trans fat | 0 g | - |
| **Carbohydrates** | 18g | 17 |
| **Protein** | 2g | 17 |
| **Dietary Fiber** | 16g | 8 |
| **Potassium** | 850 mg | - |

Fats constitute the bulk of the milkshake, and are metabolised into carbon dioxide and water when subjected to combustion in a bomb calorimeter. There are two types of fats in the milkshake, saturated versus unsaturated fat.

You may assume that the unsaturated fat and saturated fat in the milkshake are triolein and tristearin respectively.

The combustion of triolein, $C_{57}H_{104}O_6$, the unsaturated fat is as follows:

$$C_{57}H_{104}O_6 + 80O_2 \rightarrow 57\ CO_2 + 52\ H_2O \quad \Delta H_c^{\ominus} = -35100\ \text{kJ mol}^{-1}$$

The **fuel value** of a substance is defined as the heat energy released, when **one gram** of the substance undergoes combustion.

Calculate $x$, the fuel value of triolein, the unsaturated fat, and hence deduce if triolein or tristearin is a better source of energy ($M_r$ of triolein = 884).

[2]
[Total: 10]

**6** Aluminium oxide is frequently used in organic reactions and is also a common component in cosmetics. It is primarily used in the production of aluminium.

**(a)** Aluminium oxide reacts with aqueous sodium hydroxide to give a homogeneous solution. Similarly, aluminium reacts with aqueous sodium hydroxide to give the same homogeneous solution and a gas that pops with a lighted splint.

**(i)** Write a balanced equation for the reaction of a piece of aluminium foil when it is placed into aqueous sodium hydroxide.

……………………………………………………………………………………........ [1]

**(ii)** In reaction **(a)(i)**, a white solid layer was first seen on the aluminium foil before the homogeneous solution was formed. Identify the solid and write an equation to explain how the homogeneous solution was formed from the solid.

Solid: ………………………………

……………………………………………………………………………………..

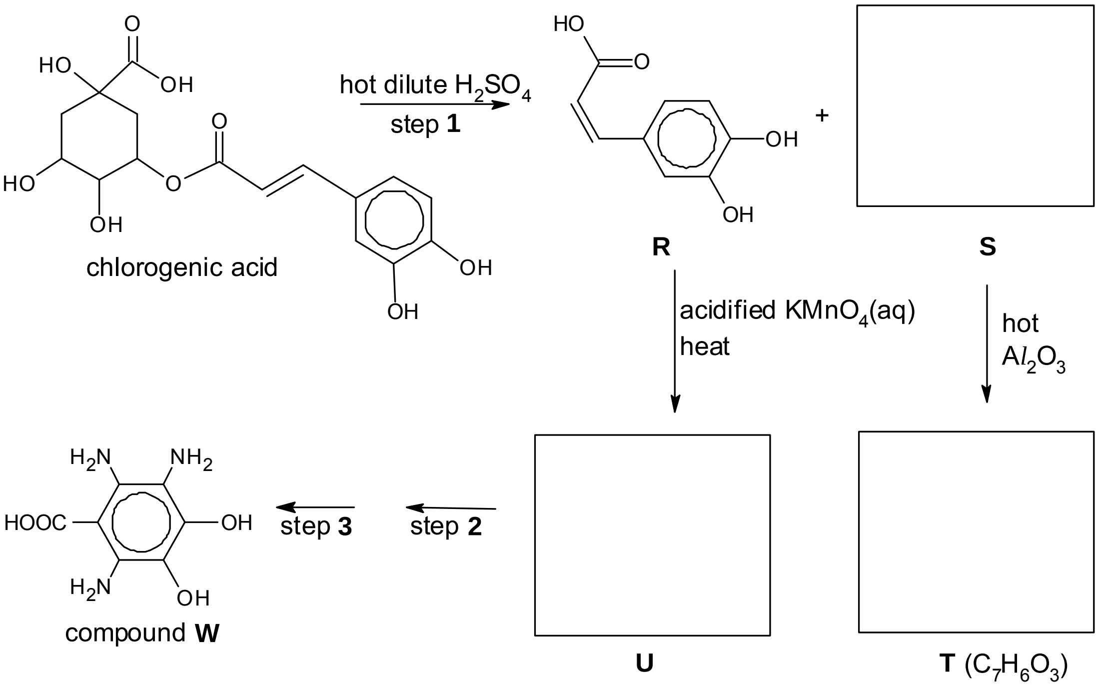
……………………………………………………………………………………..

…………………………………………………………………………………… [2]

**(b)** Polyphenols are often reducing agents known as antioxidants.

An example of a polyphenol is chlorogenic acid.

The structure of chlorogenic acid and its reaction scheme is shown below. In the reaction scheme, compound **T**, $C_7H_6O_3$, is formed from compound **S** and heated $Al_2O_3$. Compound **T** reacts with neutral aqueous iron(III) chloride to form a violet solution.



**(i)** Draw the structures of organic compounds **S**, **T** and **U** in the boxes provided in the scheme above. [3]

**(ii)** Compound **U** can be converted to compound **W** in two steps.

Suggest reagents and conditions for steps **2** and **3**.

Step 2: ........................................................................................ [1]

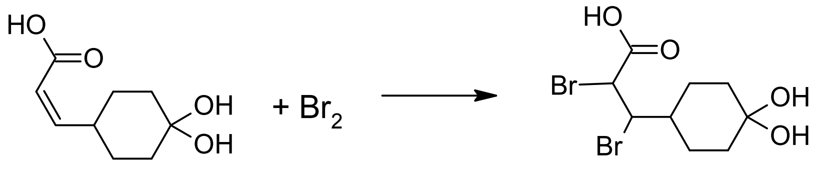
Step 3: ........................................................................................ [1]

**(iii)** If hot dilute sodium hydroxide was used to react with chlorogenic acid, state the number of moles of NaOH that would be required to react with one mole of chlorogenic acid.

Number of mol of NaOH: ………......... [1]

**(iv)** Compound **X** shown below is an analog of compound **R** in the scheme. When compound **X** is added to bromine in CC*l*₄ in the dark, there is a rapid reaction 2, that decolourises the bromine.

reaction 2:



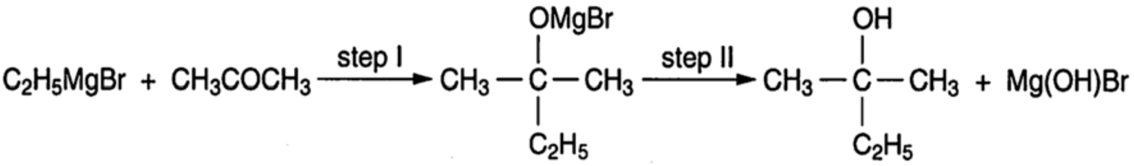
**X**

The product of this reaction 2, exists as a mixture of four stereoisomers. State the type of isomerism exhibited and draw all the stereoisomers.

[3]

**(c)** In a Grignard reaction, the Grignard reagent, RMgBr (alkyl or aryl magnesium halide), may be added to a carbonyl compound for the formation of an alcohol.

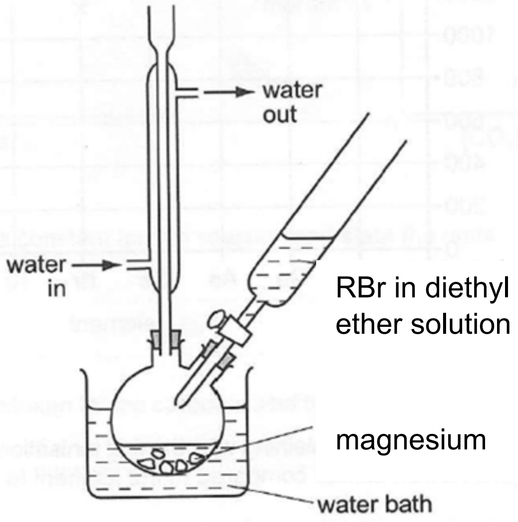
A typical example of the use of a Grignard reagent is the two-step reaction of $C_2H_5MgBr$ with propanone, $CH_3COCH_3$, to form 2-methylbutan-2-ol.



$$C_2H_5MgBr + CH_3COCH_3 \xrightarrow{\text{step I}} CH_3-\overset{OMgBr}{\underset{C_2H_5}{C}}-CH_3 \xrightarrow{\text{step II}} CH_3-\overset{OH}{\underset{C_2H_5}{C}}-CH_3 + Mg(OH)Br$$

**(i)** Draw the structural formula of the Grignard reagent that will react with propanone to form 2–methylhexan–2–ol in a similar two–step reaction. [1]

**(ii)** To prepare 2–methylhexan–2–ol, the following set-up and procedure was used.



**Preparation of the Grignard reagent:**

1. Several small pieces of Mg was placed in a round-bottomed flask.
2. 9.6 g of an appropriate bromoalkane, RBr, was dissolved in anhydrous diethyl ether. It is important to exclude water as Grignard reagent undergoes acid-base reaction with water rapidly to form an alkane, destroying the Grignard reagent.
3. To initiate the reaction, add just enough RBr/ ether solution from the dropping funnel to cover the magnesium. Start stirring with a magnetic stir bar and use a water bath to heat the reaction flask as the RBr/ ether solution is slowly added dropwise into the metal.
4. The mixture was heated under reflux for about 15 minutes and cooled in an ice-bath.

**Reaction of Grignard reagent with propanone:**

5. Add 1.2 g of anhydrous propanone in the dropping funnel and add propanone dropwise to the Grignard reagent.
6. Allow the reaction mixture to stand at room temperature for 30 minutes.
7. The mixture was then slowly poured with vigorous stirring into an ice-cold substance **Z** in a beaker. Almost immediately, a solid precipitate is seen.
8. Filter the mixture and collect the ethereal solution in a clean and dry conical flask.
9. Add anhydrous magnesium sulfate to the ethereal solution, cork the flask tightly and leave the mixture to stand for a while.
10. Filter and collect the filtrate in a round-bottom flask which is then placed on a rotary dryer to evaporate all the solvent diethyl ether away.

**I.** Assuming that 1.9 g of 2–methylhexan–2–ol was prepared using the procedure, calculate the percentage yield for this synthesis. [2]

**II.** During the preparation of the Grignard reagent, anhydrous diethyl ether was used as the solvent in step 2, as the Grignard reagent can be destroyed in the presence of water.

Write an equation to show the reaction of the Grignard reagent with water.

……………………………………………………………………………………....... [1]

**III.** Identify substance **Z** in step 7, in the beaker.

……………………………………………………………………………………....... [1]

**IV.** Suggest what is removed when anhydrous magnesium sulfate is added to the ethereal solution in step 9.

……………………………………………………………………………………....... [1]

[Total: 18]

**End of paper**

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

| | | | | | | |
|---|---|---|---|---|---|---|
| CANDIDATE NAME | | | | | | |
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# CHEMISTRY

**9729/02**

Paper 2 Structured

**11 September 2018**

**2 hours**

Additional Materials: Data Booklet

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**READ THESE INSTRUCTIONS FIRST**

Write your class, index number and name on all work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough workings.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.

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 | | | |
|---|---|---|---|
| **Paper 1** | | | **/ 30** |
| **Paper 2** | | | |
| 1 | / 9 | 4 | /12 |
| 2 | / 8 | 5 | / 10 |
| 3 | / 18 | 6 | / 18 |
| Penalty | | sf | unit |
| **Paper 2** | | | **/ 75** |
| **Paper 3** | | | **/ 80** |
| **Paper 4** | | | **/ 55** |
| Total | | | |

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

**1** **(a)** Water hardness is determined by the concentration of multivalent cations in the water. Common cations found in hard water include $Ca^{2+}$ and $Mg^{2+}$. Lime softening is a type of water treatment where aqueous $Na_2CO_3$ is added to remove $Ca^{2+}$ ion as $CaCO_3$ is precipitated. These precipitates are then removed by sedimentation and filtration, where $X^{2+}$ can be $Ca^{2+}$ and $Mg^{2+}$.

$$X^{2+}(aq) + Na_2CO_3(aq) \rightarrow XCO_3(s) + 2Na^+(aq)$$

In the laboratory, 1 $cm^3$ of 0.50 mol $dm^{-3}$ $Na_2CO_3$ is added to 10 $cm^3$ of a raw water sample. What is the minimum concentration of $Ca^{2+}$ in the original raw water sample, which would cause a white precipitate to be observed?

The value of $K_{sp}$ for $CaCO_3$ is $4.81 \times 10^{-9}$ $mol^2\ dm^{-6}$.

[2]

$Ca^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow CaCO_3(s)$

Let original concentration of $Ca^{2+}$ be y mol $dm^{-3}$

Upon mixing

$[Ca^{2+}] = \dfrac{10\times10^{-3}\times y}{11\times10^{-3}} = 0.9091y$ mol $dm^{-3}$

$[CO_3^{2-}] = \dfrac{1\times10^{-3}\times0.5}{11\times10^{-3}} = 0.04545$ mol $dm^{-3}$

Both $[Ca^{2+}]$ and $[CO_3^{2-}]$ correct

$IP = [Ca^{2+}][CO_3^{2-}] \geq K_{sp}$

$(0.9091y)(0.04545) = 4.81 \times 10^{-9}$

$y = 1.16 \times 10^{-7}$ mol $dm^{-3}$

**(b)** A saturated solution of raw water containing both $CaF_2$ and $Ca(OH)_2$ has a pH of 12 at 25°C.

| calcium compound | numerical value of $K_{sp}$ |
|---|---|
| $CaF_2$ | $3.2 \times 10^{-11}$ |
| $Ca(OH)_2$ | $6.4 \times 10^{-6}$ |

**(i)** Calculate the concentration of hydroxide ions in the solution. [1]

pH = 12

pOH = 2

$[OH^-] = 10^{-2} = 1.00 \times 10^{-2}$ mol $dm^{-3}$

**(ii)** Hence, calculate the solubility of $CaF_2$ in the raw water sample. Show your working clearly. [2]

$K_{sp}$ of $Ca(OH)_2 = [Ca^{2+}]_{total}[OH^-]^2$

$6.4 \times 10^{-6} = [Ca^{2+}]_{total}(1.00 \times 10^{-2})^2$

$[Ca^{2+}]_{total} = 0.0640$ mol dm$^{-3}$

$[Ca^{2+}]_{total}[F^-]^2 = 3.2 \times 10^{-11}$

$(0.0640)[F^-]^2 = 3.2 \times 10^{-11}$

$[F^-] = 2.24 \times 10^{-5}$ mol dm$^{-3}$

Solubility of $CaF_2 = (2.24 \times 10^{-5})/2 = 1.12 \times 10^{-5}$ mol dm$^{-3}$

[2]

**(c)** Using the following data, construct an energy cycle to calculate the enthalpy change for the thermal decomposition of calcium carbonate.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

| | $\Delta H$ / kJ mol$^{-1}$ |
|---|---|
| $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ | −57.1 |
| $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$ | −63.7 |
| $H_2SO_4(aq) + CaCO_3(s) \rightarrow CaSO_4(aq) + H_2O(l) + CO_2(g)$ | −151.5 |

$$\begin{tikzcd}
H_2O(l) + H_2SO_4(aq) + CaCO_3(s) \arrow[r, "\Delta H_r"] \arrow[dd, "-151.5"'] & CaO(s) + H_2O(l) + CO_2(g) + H_2SO_4(aq) \arrow[d, "-63.7"] \\
 & Ca(OH)_2(aq) + CO_2(g) + H_2SO_4(aq) \arrow[dl, "2(-57.1)"] \\
CaSO_4(aq) + CO_2(g) + 2H_2O(l) &
\end{tikzcd}$$

By Hess' Law,

$\Delta H_r = -151.5 - (2)(-57.1) - (-63.7)$

$\Delta H_r = +26.4$ kJ mol$^{-1}$

[Total: 9]

**2** The reaction of ethanal with iodine occurs in the presence of acid catalyst, HC*l*. . The reaction is given below.

$$I_2 + CH_3CHO \xrightarrow{HCl} CH_2ICHO + HI \qquad \text{Reaction 1}$$

The table shows the results obtained when the concentrations of $I_2$, $CH_3CHO$ and HC*l* were varied.

| Experiment | Initial [HC*l*] / mol dm$^{-3}$ | Initial [$I_2$] / mol dm$^{-3}$ | Initial [$CH_3CHO$] / mol dm$^{-3}$ | Initial rate / mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| 1 | 0.10 | 0.20 | 0.20 | $1.6 \times 10^{-6}$ |
| 2 | 0.10 | 0.40 | 0.30 | $2.4 \times 10^{-6}$ |
| 3 | 0.40 | 0.40 | 0.20 | $6.4 \times 10^{-6}$ |
| 4 | 0.10 | 0.20 | 2.00 | $1.6 \times 10^{-5}$ |

**(a)** **(i)** Deduce the orders of reaction with respect to $I_2$, $CH_3CHO$ and HC*l*. Hence, determine the rate equation.

[3]

Comparing expt 1 and 4

[HC*l*] and [$I_2$] are kept constant, when [$CH_3CHO$] is 10 times, initial rate is 10 times.

Hence reaction is first order wrt $CH_3CHO$.

Let rate = $k\,[HCl]^m\,[I_2]^n\,[CH_3CHO]$

Comparing expt 1 and 2

$$\text{When } \frac{(2)}{(1)},\quad \frac{(\text{rate})_2}{(\text{rate})_1} = \frac{2.4 \times 10^{-6}}{1.6 \times 10^{-6}} = \frac{k\,(0.10)^m\,(0.40)^n\,(0.3)}{k\,(0.10)^m\,(0.20)^n\,(0.2)}$$

n = 0

Hence reaction is zero order wrt $I_2$.

Comparing expt 2 and 3

$$\text{When } \frac{(2)}{(3)},\quad \frac{(\text{rate})_2}{(\text{rate})_3} = \frac{2.4 \times 10^{-6}}{6.4 \times 10^{-6}} = \frac{k\,(0.10)^m\,(0.3)}{k\,(0.40)^m\,(0.2)}$$

m = 1

Hence reaction is first order wrt HC*l*.

Hence rate = $k\,[HCl]\,[CH_3CHO]$

**(ii)** The half-life of ethanal in experiment 1 was 60 seconds. Predict the half-life of ethanal in experiments 2 and 3. Explain your answer.

HC*l* functions as a catalyst. Hence, [HC*l*] remains constant in each expt. Therefore, for each experiment, the reaction becomes a pseudo-first order reaction.

Rate = $k$ [ethanal] [HC*l*]

= $k^*$ [ethanal] where $k^* = k\,[HCl]$

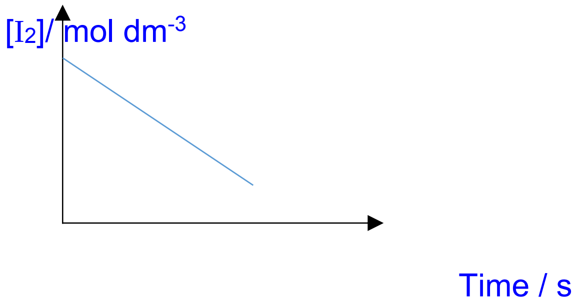
For a first order reaction, $t_{1/2} = \ln 2 / k^* = \ln 2 / k\,[HCl]$

**In expt 2, when [HC*l*] is the same as in expt 1, $t_{1/2}$ = 60 s**

**In expt 3,** when [HC*l*] is four times compared to expt 1**, $t_{1/2}$ = 60/4 = 15 s**

**(iii)** Sketch the graph of concentration of iodine against time for experiment 4.

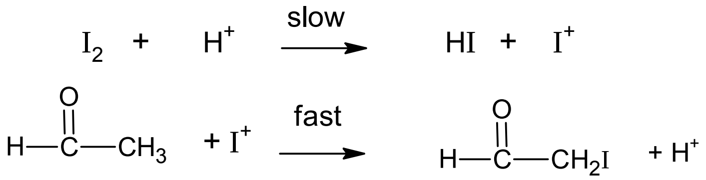
| Experiment | Initial [HC*l*] / mol dm$^{-3}$ | Initial [$I_2$] / mol dm$^{-3}$ | Initial [$CH_3CHO$] / mol dm$^{-3}$ | Initial rate / mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|---|---|
| 4 | 0.10 | 0.20 | 2.00 | 1.6 x 10$^{-5}$ |



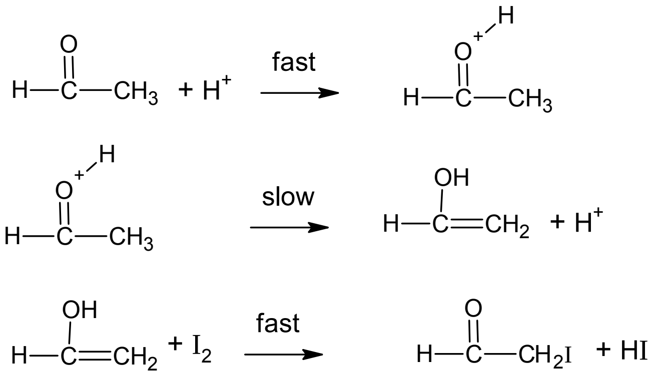
[1]

**(b)** The following mechanisms **A** and **B** are proposed for the reaction of ethanal, iodine and acid catalyst in Reaction 1.

**Mechanism A**



**Mechanism B**



Which of the above mechanisms best agrees with the experimentally determined rate equation in **(a)(i)**? Explain your answer.

Mechanism B

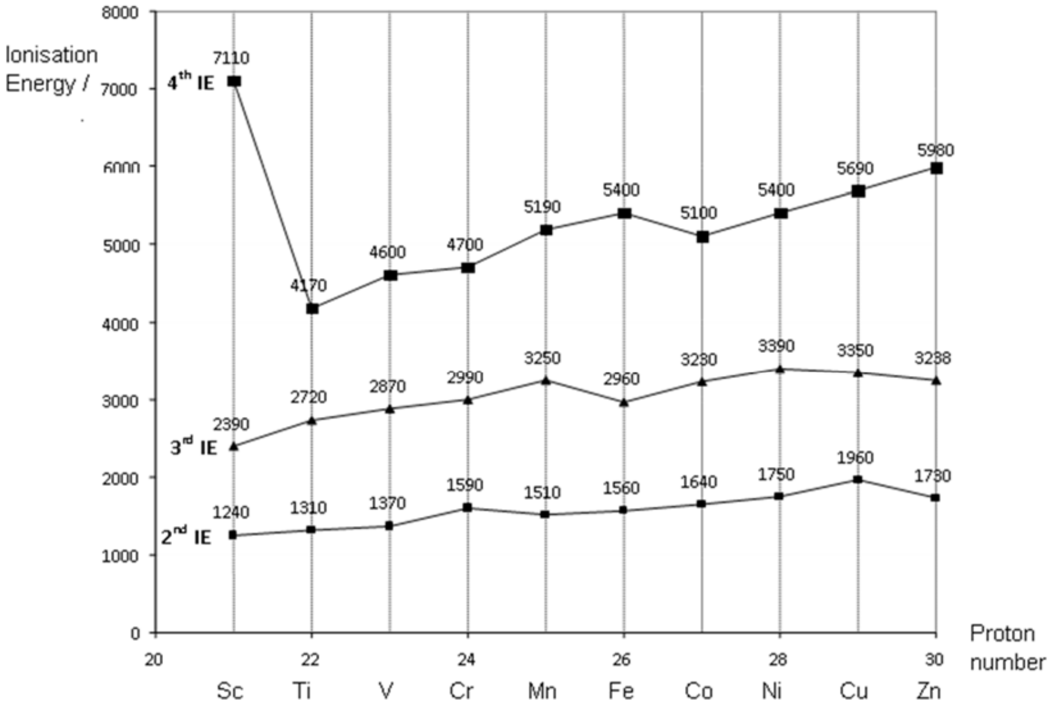
The slow (rate-determining) step involves one molecule of ethanal and colliding with one molecule of hydrochloric acid.

3 Transition metal is "an element whose atom has a partially filled d sub-shell, or which can give rise to cations with an incompletely filled d sub-shell". Chromium and vanadium, both transition metals, have found a number of industrial uses due to their toughness and resistance to heat and corrosion.

The table below shows some information of a Group 2 metal calcium, vanadium and chromium.

| | **Vanadium** | **Chromium** | **Calcium** |
|---|---|---|---|
| Melting point/ °C | 1910 | 1875 | 843 |
| Atomic radius/ nm | 0.135 | 0.129 | 0.197 |
| Common Oxidation Number | +2, +3, +4, +5 | +2, +3, +6 | +2 |

The graph below shows the second to fourth ionisation energies for the first row d block elements scandium to zinc.



**(a)** **(i)** Although the vanadium atom has more electrons than the calcium atom, the atomic radius of vanadium is smaller than that of calcium. Suggest an explanation for this.

Atomic radius of vanadium is smaller than that of calcium because vanadium has <u>higher nuclear charge and the 3d electrons shield the 4s electrons poorly</u>.

These result in a greater effective nuclear charge attraction in Vanadium, for the valence electrons, than calcium.

**(ii)** Explain why the second ionisation energies of transition elements from Ti to Cu are relatively invariant.

Effective nuclear charge increase very slightly or almost constant invariant. There is increase in nuclear charge but shielding effect increases due to electrons added to the 3d penultimate (inner) shell.

**(iii)** Explain why the second ionisation energy of chromium is higher than that of manganese.
$Cr^+$ = [Ar]$3d^5$, $Mn^+$ = [Ar]$3d^5 4s^1$

The second electron removed from manganese is a 4s−electron while the second electron removed from chromium is a 3d−electron.

Since a 3d−electron is (is in inner shell) closer to the nucleus and has lower energy, more energy is required to remove it, causing second ionisation energy of Cr to be higher than that of Mn.

**(b)** **(i)** State the **full** electronic configuration of $Cr^{3+}$ ion.

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$

**(ii)** The complex ion $[Cr(H_2O)_6]^{3+}$ is green, and it is an octahedral complex. On the Cartesian axes shown in Fig. 2.1, draw **fully-labelled** diagrams of the following:

- One of the d orbitals at the lower energy level in an octahedral complex-Label this diagram 'lower'.
- One of the d orbitals at the upper energy level in an octahedral complex. Label this diagram 'upper'. [2]

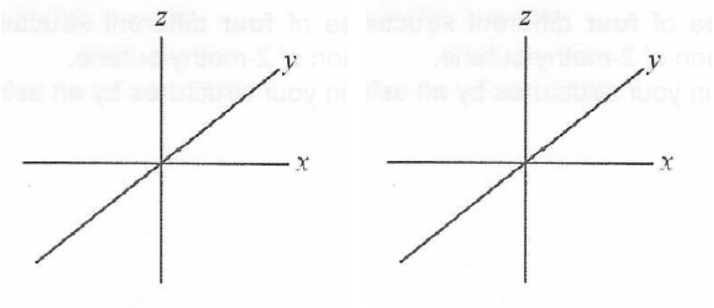
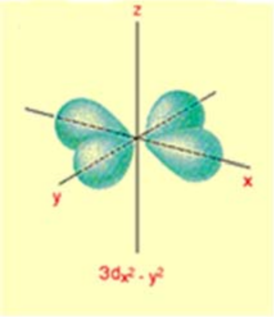
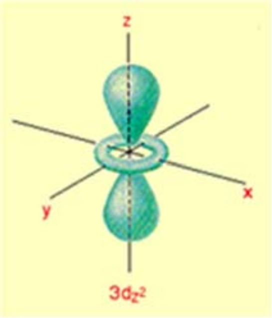


Fig. 3.1

Upper

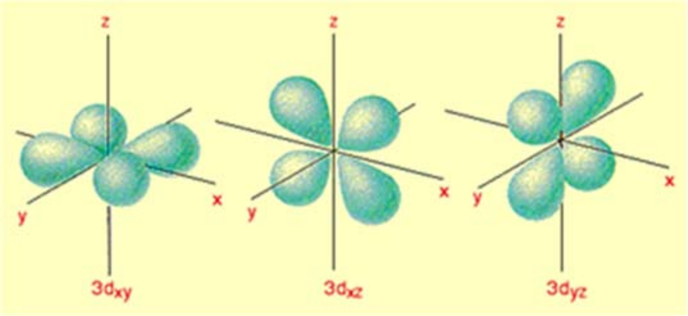


or



**Lower**

**Any of the 3 orbitals (labelled) below**



**(iii)** Suggest which of the two compounds chromium(III) oxide, $Cr_2O_3$, and chromium(III) carbonate, $Cr_2(CO_3)_3$, would have a more exothermic lattice energy. Explain your answer.

All ions have same charges. $O^{2-}$ has smaller ionic radius than $CO_3^{2-}$, thus magnitude of lattice energy is bigger, $Cr_2O_3$ so more exothermic .

**(iv)** The compound $K_3CrO_4$ is a green solid. When mixed with dilute $H_2SO_4$, it undergoes disproportionation to yield $Cr^{3+}$(aq) and $Cr_2O_7^{2-}$(aq) ions.

By writing appropriate half-equations, write an overall balanced equation for the disproportionation of $CrO_4^{3-}$ in acid.

$$\overset{(+5)}{CrO_4^{3-}} + 8H^+ + 2e^- \rightarrow \overset{(+3)}{Cr^{3+}} + 4H_2O$$

$$\overset{2(+5)}{2CrO_4^{3-}} + 2H^+ \rightarrow \overset{2(+6)}{Cr_2O_7^{2-}} + 2e^- + H_2O$$

Overall equation: $3CrO_4^{3-} + 10H^+ \rightarrow Cr^{3+} + Cr_2O_7^{2-} + 5H_2O$

**(v)** Purification of chromium can be achieved by electro-refining chromium from an impure chromium anode onto a pure chromium cathode in an electrolytic cell. How many hours will it take to plate 130 g of chromium onto the cathode if the current passed through the cell is held constant at 34.0 A?

Assume the chromium in the electrolytic solution is present as $Cr^{3+}$.

n(Cr) = 130/ 52.0 = 2.50 mol

n(e) = 2.50 x 3 = 7.50 mol

96500 C for 1 mol of e.

No of charges = 96500 x 7.50 = $7.238 \times 10^5$C

(96500 x 7.50) = 34 x t

t = 5.91 h

[2]

**(c)** The reaction between $S_2O_8^{2-}$ ions and $I^-$ ions is very slow:

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

If a small amount of aqueous manganese(II) ions, $Mn^{2+}$, is added to the mixture, the rate of reaction increases rapidly.

State the property, typical of transition metals, which allow manganese (II) ions to behave as a homogeneous catalyst in this reaction.

By considering the data given below, write relevant chemical equations to support your answer.

$$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$$

Property: $Mn^{2+}$, a transition metal ion, can exist as variable oxidation states.

*Step 1: Formation of intermediate ($Mn^{2+}$ reacting with $S_2O_8^{2-}$)*

$Mn^{2+} \rightleftharpoons Mn^{3+} + e^-$ $E^\ominus_{oxd} = -1.54V$

$S_2O_8^{2-} + 2e^- \rightleftharpoons SO_4^{2-}$ $E^\ominus_{red} = +2.01$ V

$2Mn^{2+} + S_2O_8^{2-} \longrightarrow 2Mn^{3+} + SO_4^{2-}$

$E^\ominus_{cell} = E^\ominus_{oxd} + E^\ominus_{red} = +2.01 + -1.54 = +0.47V > 0$, thus reaction is energetically feasible.

*Step 2: Regeneration of catalyst*

$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$ $E^\ominus_{red} = +1.54$

$2I^- \rightleftharpoons I_2 + 2e^-$ $E^\ominus_{oxd} = -0.54$ V

$2I^- + 2Mn^{3+} \longrightarrow I_2 + 2Mn^{2+}$

$E^\ominus_{cell} = E^\ominus_{oxd} + E^\ominus_{red} = +1.00V > 0$, thus reaction is energetically feasible

[Total:18]

**4** **(a)** Citric acid is commonly found in citrus fruits such as lemons.

Mixtures of citric acid and its salt, sodium citrate, are often used as “acidity regulators”. These are food additives that have a buffering action on the pH of foodstuffs.

$$\underset{\text{citric acid}}{C_5H_7O_4CO_2H} \rightleftharpoons \underset{\text{citrate}}{C_5H_7O_4CO_2^{-}} + H+$$

$K_a$ of citric acid = $7.4 \times 10^{-4}$ mol dm$^{-3}$

A typical citric acid / sodium citrate buffer mixture is prepared by mixing 0.100 mol dm$^{-3}$ citric acid and 0.200 mol dm$^{-3}$ sodium citrate in a volume ratio 2:3 respectively.

Calculate the pH of the buffer solution. [2]

$[C_5H_7O_4CO_2H] = \frac{2}{5}\times 0.100$

$= 0.040$ mol dm$^{-3}$

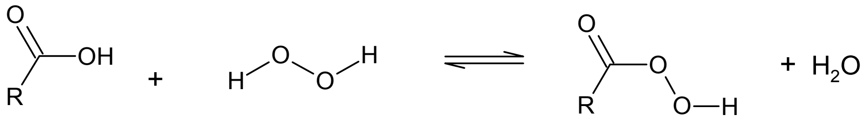
$[C_5H_7O_4CO_2Na] = \frac{3}{5}\times 0.200$

$= 0.120$ mol dm$^{-3}$

pH of the buffer = $-\lg(7.46 \times 10^{-4}) + \lg\left(\frac{0.120}{0.040}\right)$

$= 3.60$

**(b)** The reaction between carboxylic acids and hydrogen peroxides produce peroxyacids.



The p$K$a values of four compounds are listed in the table below.

| **Name** | **formula** | ***pK*a** |
|---|---|---|
| Water | $H_2O$ | 14.0 |
| Hydrogen peroxide | $H_2O_2$ | 11.7 |
| Methanoic acid | $HCO_2H$ | 3.7 |

| | | |
|---|---|---|
| Peroxymethanoic acid | $HCO_3H$ | 7.1 |

Suggest an explanation for why

**(i)** The p*K*a of $H_2O_2$ is less than that for water [1]

Lower p*K*a of $H_2O_2$ means $H_2O_2$ is stronger acid than $H_2O$.

Stability of anion: H-O-O$^-$ > HO$^-$

H-O-O$^-$ has additional O atom bonded to negatively charged O$^-$, this additional electronegative O helps to disperse the negative charge more (via inductive effect), stabilising H-O-O$^-$ relative to HO$^-$

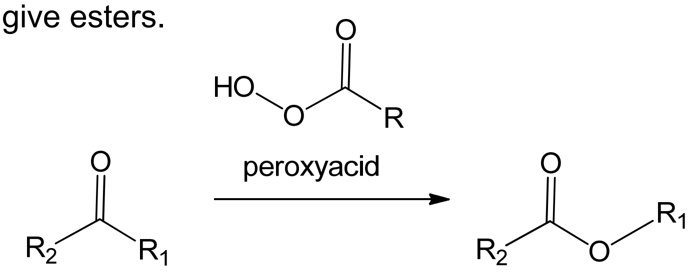
A **(ii)** The p*K*a of $HCO_3H$ is more than that for $HCO_2H$ [2]

Lower p*K*a of $HCO_2H$ means $HCO_2H$ is stronger acid than $HCO_3H$

In $HCO_2^-$, the p orbitals of the 3 atoms of $–CO_2^-$ are all adjacent to each other, overlap sideways, allowing the delocalisation of the negative charge across the 3 atoms of –COO$^-$, thus $HCO_2^-$ is much more stable than $HCO_3^-$.

In $HCO_3^-$, the negative charge cannot be delocalised thus $HCO_3^-$ is less stable.

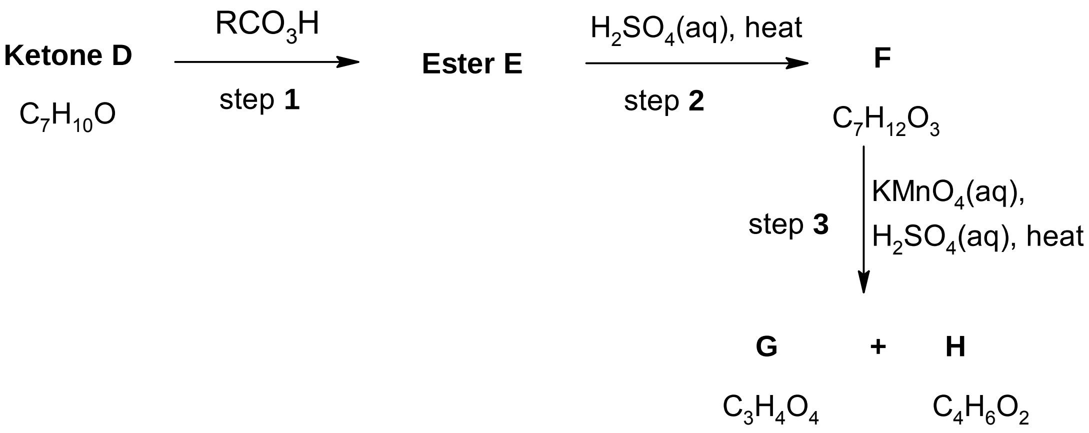
**(c)** The Baeyer-Villiger oxidation is an organic reaction in which peroxyacids react with ketones to give esters.



In the following scheme, ketone **D** ($C_7H_{10}O$) undergoes Baeyer-Villiger oxidation in step **1** to form ester **E**. Ketone **D** also decolourises orange aqueous $Br_2$.

**F** is the **only** product formed, from treating ester **E** with hot $H_2SO_4$(aq).

Hot acidified $KMnO_4$ oxidises several classes of organic compounds to ketones, carboxylic acids and carbon dioxide. By this means, the structures of compounds can be determined. The scheme below shows the oxidation products of **F**.



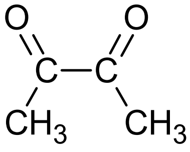
**(i)** State the type of reaction Ester **E** undergoes with hot $H_2SO_4$(aq) in step 2.

Hydrolysis

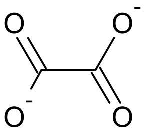
**(ii)** 1 mole **H** reacted with alkaline aqueous iodine to form 2 moles of $CHI_3$ yellow ppt. Draw the structure of **H**.

Give the product of the reaction of **H** with alkaline aqueous iodine. [2]

**H:**



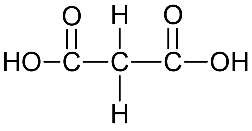
**Product:**



or $C_2O_4^{2-}$

K **(iii)** **G** ($C_3H_4O_4$) was found to react with $Na_2CO_3$(aq). Suggest the structure of **G**.

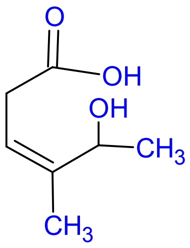
**G:**



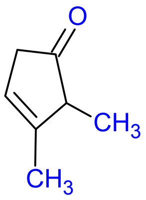
$$\mathrm{HO-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-OH}$$

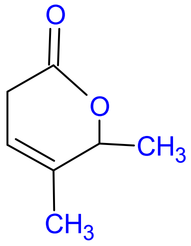
**(iv)** From your answer in **(ii)** and **(iii)**, deduce and suggest the structure of **F**. [1]

**F:**



**(v)** Hence, suggest the structures of ketone **D** and ester **E**.





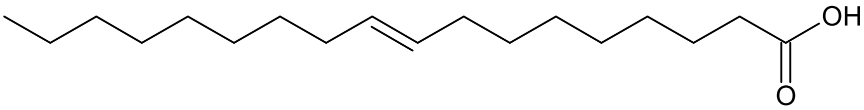
D:$C_7H_{10}O$ E: $C_7H_{10}O_2$

[Total: 12]

**5 (a) (i)** Oleic acid, $CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$ is a fatty acid found in oils and fats, which has C=C double bond in the cis configuration.

The trans isomer of oleic acid is known as *elaidic acid*, which is found in partially hydrogenated vegetable oils.

Draw the skeletal formula for the ***trans*** isomer of oleic acid, $CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$, which is also known as *elaidic acid*.



[1]

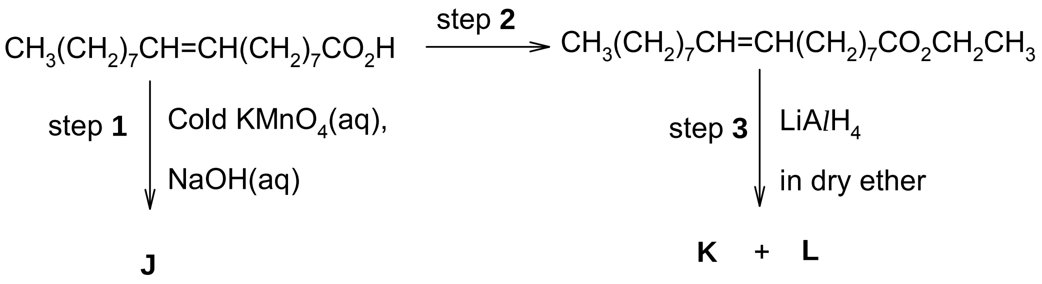
**(ii)** Suggest a brief explanation for the differences in melting points between oleic acid and its *trans* isomer, elaidic acid.

| **Compound** | ***Mr*** | **Melting point / °C** |
|---|---|---|
| oleic acid (cis-isomer) | 282 | 4.0 |
| elaidic acid (trans-isomer) | 282 | 45.0 |

[1]

The trans-double bond isomer of oleic acid, elaidic acid, has a more symmetrical shape and is thus able to pack more closely together, thus more energy to overcome the stronger instantaneous dipole-induced dipole forces of attraction which cause it to have a higher melting point.

**(iii)** Below outlines a reaction scheme involving oleic acid.

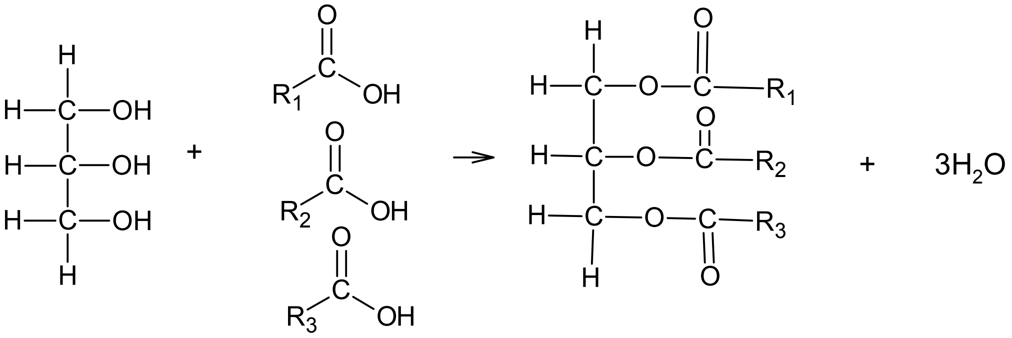


Give the reagents and conditions for step 2, and draw the structures of compounds **J**, **K** and **L** in the boxes provided below.

| | |
|---|---|
| step **2**: | $CH_3CH_2OH$, concentrated $H_2SO_4$, heat |
| **J**: | $CH_3(CH_2)_7CH(OH)CH(OH)(CH_2)_7CO_2^- Na^+$<br>If student wrote $CH_3(CH_2)_7CH(OH)CH(OH)(CH_2)_7COO^-$ |
| **K**: | $CH_3(CH_2)_7CH=CH(CH_2)_7CH_2OH$ |
| **L**: | $CH_3CH_2OH$(K and L are inter-changeable) |

[4]

**(b)** Avocado oil consists mainly of triesters formed from glycerol (propane-1,2,3-triol) and long-chain carboxylic acids (fatty acids) as shown by the general equation.

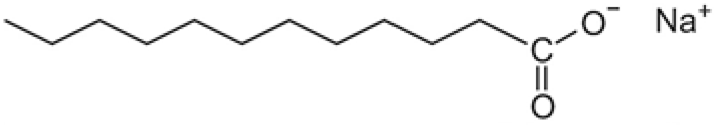


glycerol fatty acids triester

The major component of avocado oil is triolein, the triester formed from glycerol and three units of oleic acid (fatty acid).

**(i)** A student tried to flush his cup with water to wash away the avocado oil, but was not successful. The student then tried using soap to wash away the avocado oil in the cup, and was successful.

The following compound, sodium stearate is a typical soap for washing.



By reference to the type of intermolecular forces formed between the soap, avocado oil and water, explain why sodium stearate is able to wash away the avocado oil in the cup.

The alkyl group of the soap is non-polar and able to form instantaneous dipole – induced dipole attraction with the non-polar avocado oil, while the -COO$^-$ part of the soap is able to form ion-dipole interaction with water molecules, these allow the avocado oil to be washed away by the water, in the presence of the soap.

**(ii)** Below shows the nutrition content of fats, carbohydrates and protein present in one serving of avocado milkshake.

| | Mass present in 1 serving of milkshake | Fuel value/ kJ g$^{-1}$ |
|---|---|---|
| **Total Fat** | 30 g | |
| Saturated fat (tristearin) | 6 g | 42.4 |
| Unsaturated fat (triolein) | 24 g | $x$ |
| Trans fat | 0 g | - |
| **Carbohydrates** | 18g | 17 |
| **Protein** | 2g | 17 |
| **Dietary Fiber** | 16g | 8 |
| **Potassium** | 850 mg | - |

Fats constitute the bulk of the milkshake, and are metabolised into carbon dioxide and water when subjected to combustion in a bomb calorimeter. There are two types of fats in the milkshake, saturated versus unsaturated fat.

You may assume that the unsaturated fat and saturated fat in the milkshake are triolein and tristearin respectively.

The combustion of triolein, $C_{57}H_{104}O_6$, the unsaturated fat is as follows:

$$C_{57}H_{104}O_6 + 80O_2 \rightarrow 57\ CO_2 + 52\ H_2O \quad \Delta H_c^{\ominus} = -35100\ \text{kJ mol}^{-1}$$

The **fuel value** of a substance is defined as the heat energy released, when **one gram** of the substance undergoes combustion.

Calculate $x$, the fuel value of triolein, the unsaturated fat, and hence deduce if triolein or tristearin is a better source of energy ($M_r$ of triolein = 884).

No. of moles of triolein in 1 g = 1/884 = $1.131 \times 10^{-3}$ mol

Fuel value of triolein = $1.131 \times 10^{-3} \times 35100 = 39.7$ kJ $g^{-1}$

- Since less energy is produced per gram,triolein is a poorer source of energy than tristearin (42.4 kJ $g^{-1}$).

[2]
[Total: 10]

**6** Aluminium oxide is frequently used in organic reactions and is also a common component in cosmetics. It is primarily used in the production of aluminium.

**(a)** Aluminium oxide reacts with aqueous sodium hydroxide to give a homogeneous solution. Similarly, aluminium reacts with aqueous sodium hydroxide to give the same homogeneous solution and a gas that pops with a lighted splint.

**(i)** Write a balanced equation for the reaction of a piece of aluminium foil when it is placed into aqueous sodium hydroxide.

$2Al(s) + 2NaOH(aq) + 6H_2O(l) \rightarrow 2Na[Al(OH)_4](aq) + 3H_2(g)$

**(ii)** In reaction **(a)(i)**, a white solid layer was first seen on the aluminium foil before the homogeneous solution was formed. Identify the solid and write an equation to explain how the homogeneous solution was formed from the solid. [2]

Solid: Aluminium hydroxide

$Al(OH)_3(s) + OH^-(aq) \rightarrow [Al(OH)_4]^-(aq)$

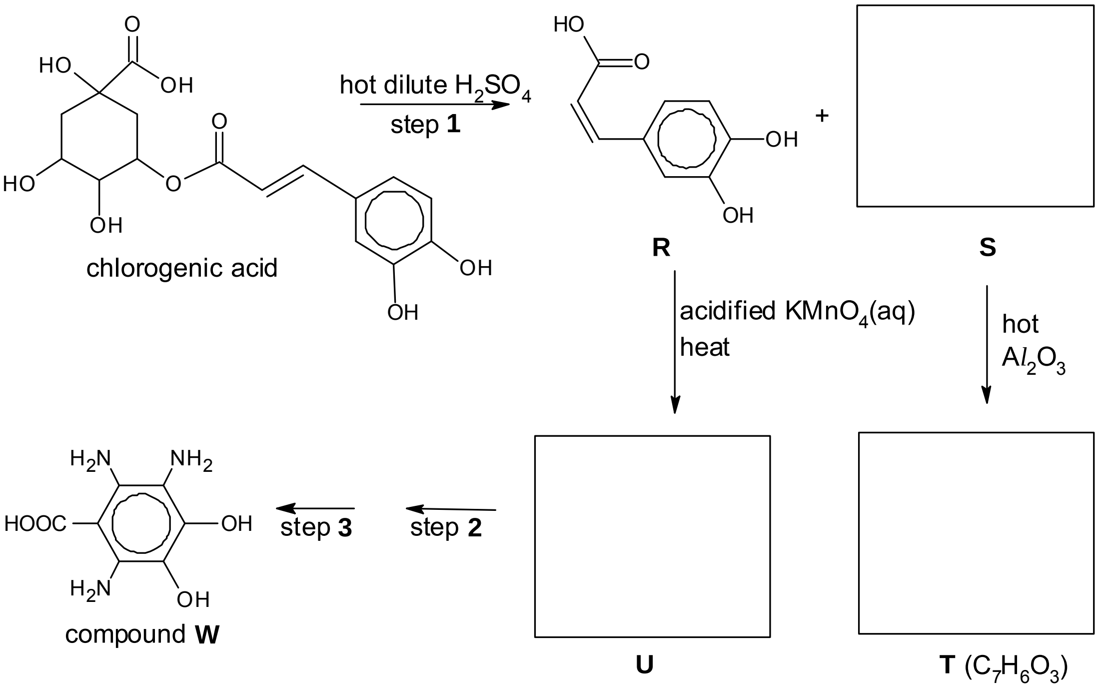
or

$Al(OH)_3(s) + NaOH(aq) \rightarrow Na[Al(OH)_4](aq)$

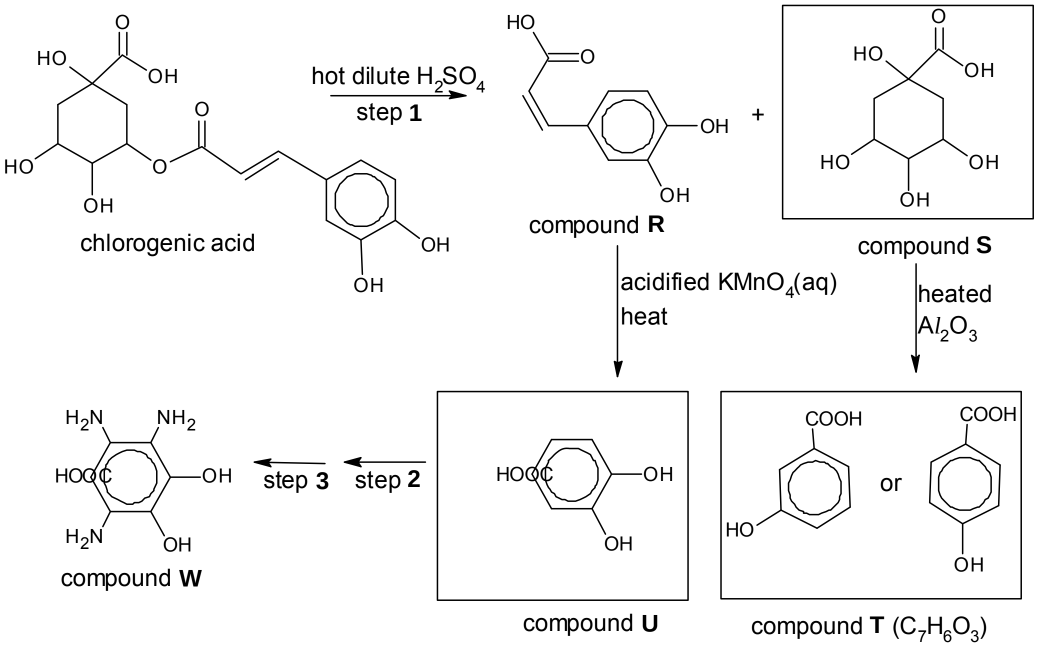
**(b)** Polyphenols are often reducing agents known as antioxidants.

An example of a polyphenol is chlorogenic acid.

The structure of chlorogenic acid and its reaction scheme is shown below. In the reaction scheme, compound **T**, $C_7H_6O_3$, is formed from compound **S** and heated $Al_2O_3$. Compound **T** reacts with neutral aqueous iron(III) chloride to form a violet solution.



**(i)** Draw the structures of organic compounds **S**, **T** and **U** in the boxes provided in the scheme above. [3]



**(ii)** Compound **U** can be converted to compound **W** in two steps.

Suggest reagents and conditions for steps **2** and **3**.

Step 2: ……………………………………………………….............. [1]

Step 3: ……………………………………………………….............. [1]

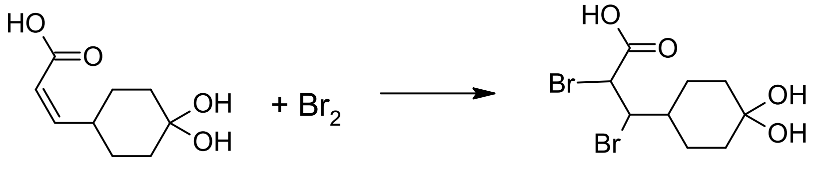
| | |
|---|---|
| Step **2**: | dilute $HNO_3$ / $HNO_3$(aq) / $HNO_3$(*l*) / concentrated $HNO_3$ |
| Step **3**: | Sn, concentrated HC*l*, heat,<br>followed by controlled addition of NaOH(aq) |

**(iii)** If hot dilute sodium hydroxide was used to react with chlorogenic acid, state the number of moles of NaOH that would be required to react with one mole of chlorogenic acid. [1]

Number of mol of NaOH: 4

**(iv)** Compound **X** shown below is an analog of compound **R** in the scheme. When compound **X** is added to bromine in $CCl_4$ in the dark, there is a rapid reaction 2, that decolourises the bromine.

reaction 2:



**X**

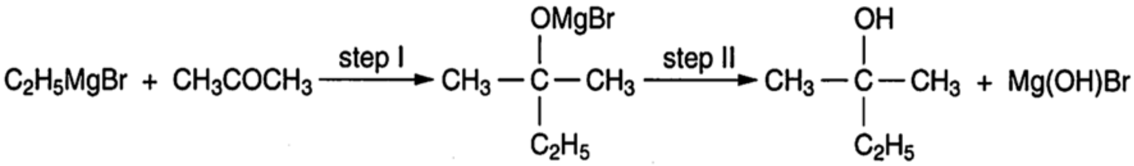
The product of this reaction 2, exists as a mixture of four stereoisomers. State the type of isomerism exhibited and draw all the stereoisomers.

Enantiomerism

[3]

**(c)** In a Grignard reaction, the Grignard reagent, RMgBr (alkyl or aryl magnesium halide), may be added to a carbonyl compound for the formation of an alcohol.

A typical example of the use of a Grignard reagent is the two-step reaction of $C_2H_5MgBr$ with propanone, $CH_3COCH_3$, to form 2-methylbutan-2-ol.

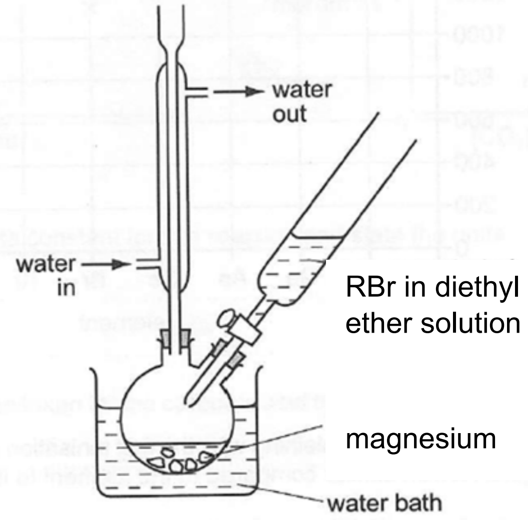


$$C_2H_5MgBr + CH_3COCH_3 \xrightarrow{\text{step I}} CH_3-\underset{C_2H_5}{\overset{OMgBr}{C}}-CH_3 \xrightarrow{\text{step II}} CH_3-\underset{C_2H_5}{\overset{OH}{C}}-CH_3 + Mg(OH)Br$$

**(i)** Draw the structural formula of the Grignard reagent that will react with propanone to form 2–methylhexan–2–ol in a similar two–step reaction. [1]

$CH_3CH_2CH_2CH_2MgBr$

**(ii)** To prepare 2–methylhexan–2–ol, the following set-up and procedure was used.



**Preparation of the Grignard reagent:**

1. Several small pieces of Mg was placed in a round-bottomed flask.
2. 9.6 g of an appropriate bromoalkane, RBr, was dissolved in anhydrous diethyl ether. It is important to exclude water as Grignard reagent undergoes acid-base reaction with water rapidly to form an alkane, destroying the Grignard reagent.
3. To initiate the reaction, add just enough RBr/ ether solution from the dropping funnel to cover the magnesium. Start stirring with a magnetic stir bar and use a water bath to heat the reaction flask as the RBr/ ether solution is slowly added dropwise into the metal.
4. The mixture was heated under reflux for about 15 minutes and cooled in an ice-bath.

**Reaction of Grignard reagent with propanone:**

5. Add 1.2 g of anhydrous propanone in the dropping funnel and add propanone dropwise to the Grignard reagent.
6. Allow the reaction mixture to stand at room temperature for 30 minutes.
7. The mixture was then slowly poured with vigorous stirring into an ice-cold substance **Z** in a beaker. Almost immediately, a solid precipitate is seen.
8. Filter the mixture and collect the ethereal solution in a clean and dry conical flask.
9. Add anhydrous magnesium sulfate to the ethereal solution, cork the flask tightly and leave the mixture to stand for a while.
10. Filter and collect the filtrate in a round-bottom flask which is then placed on a rotary dryer to evaporate all the solvent diethyl ether away.

**I.** Assuming that 1.9 g of 2–methylhexan–2–ol was prepared using the procedure, calculate the percentage yield for this synthesis. [2]

n(RBr) = 9.6 / 136.9 = 0.07012 mol (4 s.f)
n(propanone) = 1.2 / 58 = 0.02069 mol (4 s.f) (limiting reagent)
Recognising propanone is limiting reagent = no. of mol of 2–methylhexan–2–ol
n(2–methylhexan–2–ol = 0.02069 x 116 = 2.400g
% yield = 1.9/2.400 x 100 = 79.2%

**II.** During the preparation of the Grignard reagent, anhydrous diethyl ether was used as the solvent in step 2, as the Grignard reagent can be destroyed in the presence of water.

Write an equation to show the reaction of the Grignard reagent with water.
RMgBr + HO → RH + MgBr(OH)

**III.** Identify substance **Z** in step 7, in the beaker.

Water

**IV.** Suggest what is removed when **anhydrous** magnesium sulfate added to the ethereal solution in step 9.

To remove water from the ethereal solution.

[Total: 18]

**End of paper**

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE NAME

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# CHEMISTRY 9729/03

Paper 3 Free Response **19 September 2018**

**2 hours**

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet
Cover Page

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**READ THESE INSTRUCTIONS FIRST**

Write your name, index number and CT group on all work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough workings.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

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.

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This document consists of **15** printed pages.

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## Section A

Answer all questions in this section.

**1** **(a)** Steam reforming is an important industrial method for producing hydrogen and carbon monoxide, from hydrocarbon fuels. This is achieved in a processing device called a reformer which reacts steam at high temperature with the fuel, such as methane gas.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \quad \Delta H = +210 \text{ kJ mol}^{-1}$$

**(i)** Write an expression of $K_p$ for the reaction, indicating its units. [2]

**(ii)** At temperature ***T***, a mixture of gaseous methane, steam and carbon monoxide were introduced into an evacuated reactor.

The table below shows the initial pressures of the gases before they were added to the reactor.

| **Gas** | **Initial pressure / atm** |
|---|---|
| methane, $CH_4$ | 1.50 |
| steam, $H_2O$ | 2.50 |
| carbon monoxide, CO | 0.70 |

Given that the percentage dissociation of methane is 20% at equilibrium, find the $K_p$ for the reaction. [2]

**(iii)** A chemist decided to raise the temperature of the reactor. He suggested that this would result in a lower yield of the product.

Do you agree with the chemist? Explain your answer. [2]

In order to produce more hydrogen gas, the carbon monoxide gas that is produced from the steam reforming reaction can further react with steam. This is known as the "water-gas shift" reaction.

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g) \qquad \Delta H_1$$

**(iv)** Given that the reaction conditions were set at 500°C and 1.5 atm, determine the maximum volume of hydrogen gas that can be produced from 5kg of carbon monoxide gas.

State the assumption made in your calculation. [3]

**(v)** Given the following,

| | |
|---|---|
| enthalpy change of formation of $CO(g)$ / kJ mol$^{-1}$ | -99 |
| enthalpy change of formation of $H_2O(g)$ / kJ mol$^{-1}$ | -245 |
| enthalpy change of formation of $CO_2(g)$ / kJ mol$^{-1}$ | -394 |

With reference to the above data, calculate the enthalpy change of reaction of the "water-gas shift" reaction, $\Delta H_1$.

[1]

**(b)** The hydrogen gas obtained from the steam reforming process in part **(a)** can be reacted with nitrogen gas to produce ammonia gas.

This reaction is known as the Haber-Bosch Process, using iron as a catalyst.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

**(i)** Predict and explain the sign of $\Delta S$ for the Haber-Bosch reaction. [1]

**(ii)** Using your answer in **(b)(i)**, calculate the maximum temperature for the Haber-Bosch reaction to be spontaneous.

It is known that the numerical value of $\Delta S$ is 198 J K$^{-1}$ mol$^{-1}$, and that $\Delta H$ = -92.0 kJ mol$^{-1}$. [2]

**(c)** The hydrogen gas obtained from steam reforming, and the ammonia gas obtained from the Haber-Bosch reaction, are the key reagents required for the reductive amination reaction. Many amines in the pharmaceutical drugs are synthesised through this reaction.

The diagram, **Fig. 1.1**, shows the 3 stages involved in reductive amination.

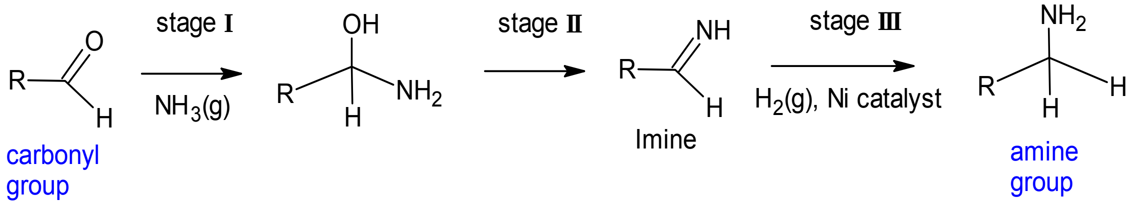


**Fig. 1.1**

During the reaction, a carbonyl group is converted into an amine group via an intermediate imine.

**(i)** State the types of reaction occurring in stage **I** and stage **II**. [2]

The reaction scheme below, **Fig.1.2**, shows the production of α-methylphenethylamine, which involves reductive amination in step **4**.

Step **4** in **Fig. 1.2** comprises of the 3 stages of reductive amination in Fig. 1.1.

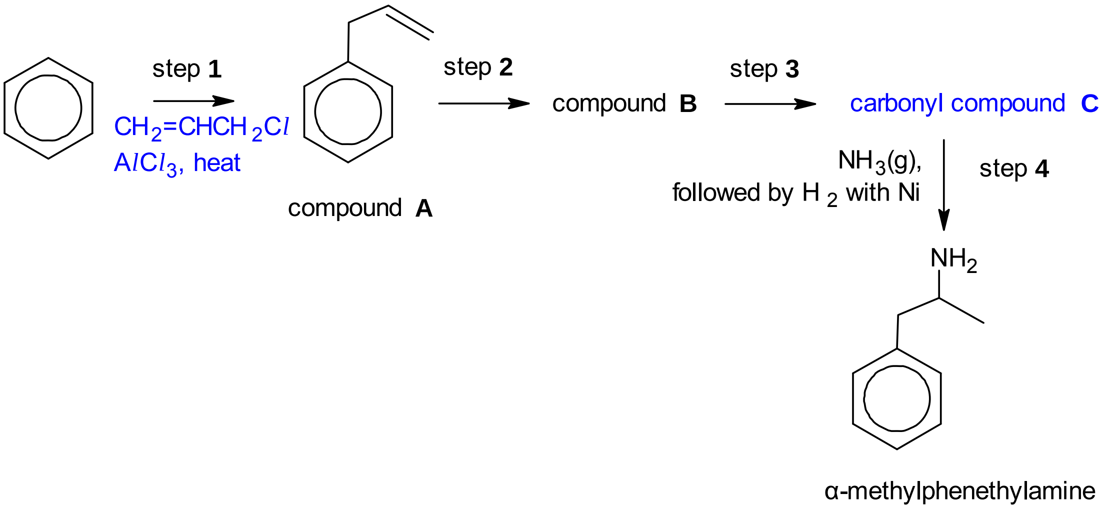


**Fig.1.2**

**(ii)** In step **1**, benzene undergoes a reaction with 3-chloroprop-1-ene with the aid of anhydrous aluminium chloride catalyst. Name and describe the mechanism for step **1**, showing clearly any relevant charges, dipoles or lone pairs of electrons that are important. [4]

**(iii)** Deduce and draw the structure for carbonyl compound **C**, and suggest the structure of compound **B**. [2]

[Total: 21]

**2** This question is on halogen-containing compounds.

**(a)** The following experiments are carried out starting from solid aluminium chloride.

$$AlCl_3(s) \xrightarrow{\text{water}} \text{acidic solution} \xrightarrow{Na_2CO_3(aq)} \text{white precipitate } \mathbf{D} + \text{effervescence}$$

**(i)** Explain with the aid of balanced equations, why $AlCl_3(s)$ dissolves to form an acidic solution. Suggest the pH of the acidic solution. [3]

**(ii)** Identify precipitate **D**. [1]

**(b)** When aqueous $AgNO_3$ is added to separate test-tubes containing aqueous $KCl$ and $KI$, the various $AgX$ ($X = Cl, I$) precipitates were observed.

With the aid of relevant equations, explain why a precipitate of $AgCl$ is soluble in excess aqueous $NH_3$ but a precipitate of $AgI$ is insoluble in excess aqueous $NH_3$. [3]

**(c)** The standard redox potential of chlorate (V) ions is given below.

$$ClO_3^- + 6H^+ + 6e^- \rightleftharpoons Cl^- + 3H_2O \quad E^\ominus = 1.45\text{ V}$$

Predict what you expect to observe, when acidified potassium chlorate (V) is added separately to each of the following reagents.

State clearly if no reaction occurs. Write a balanced equation for any reaction that occurs. Explain your answer using $E^\ominus$ values from the *Data Booklet.*

**(i)** $FeSO_4$ (aq)

**(ii)** Acidified $KMnO_4$ (aq)

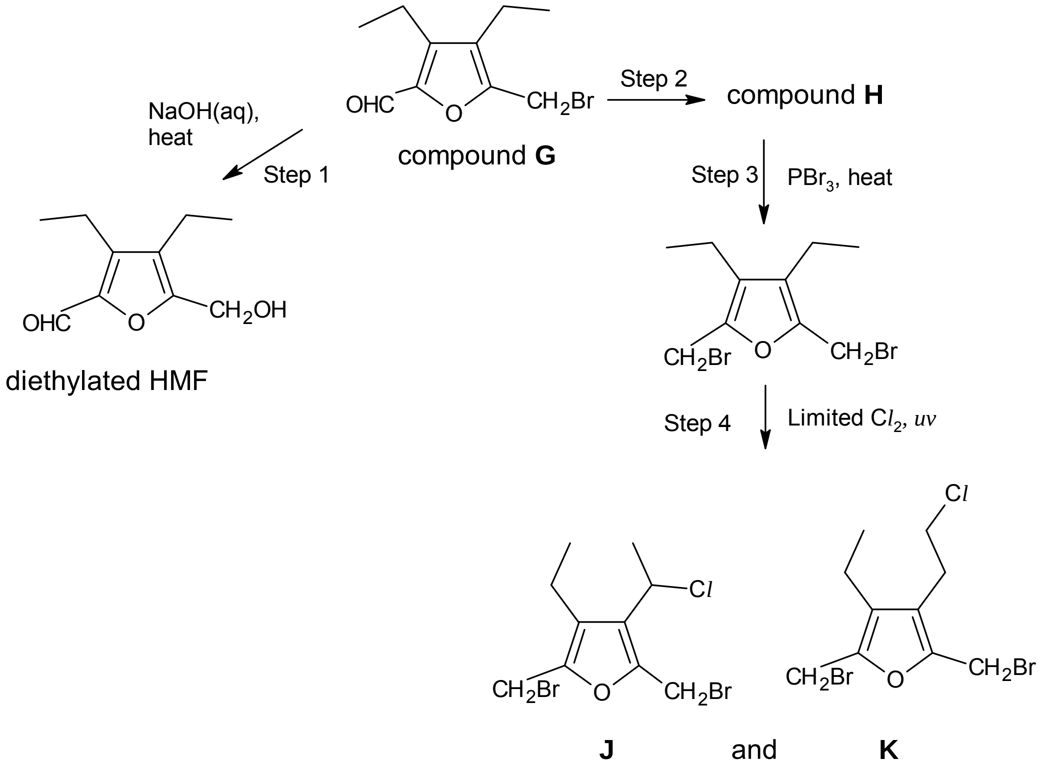
[3]

**(d)** $PCl_5$ reacts with hydrazine, $N_2H_4$, to give compound **E**, which has the following composition by mass: P, 20.5%; N, 9.2%; Cl, 70.3%. The molecule of **E** contains an N-N single bond.

Calculate the empirical formula of **E**, and suggest its molecular formula and the structure of its molecule, assuming its constituent atoms show their usual valencies.

[2]

**(e)** Diethylated HMF is used to synthesize a variety of pharmaceuticals. The flow-scheme below shows the reactions involving diethylated HMF and compound **G**, its precursor. Assume the C-O-C ether group is inert.



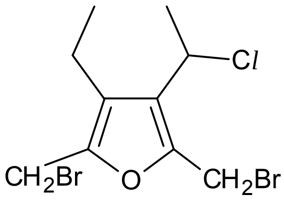
**(i)** When the reaction in step **1** was investigated kinetically, it was found that its rate was independent of [$OH^-$], but was first order with respect to [compound **G**].

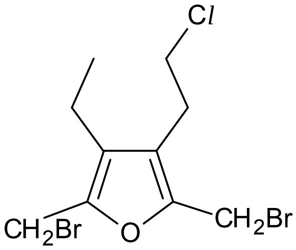
Name and describe a mechanism for this reaction, showing curly arrows in your answer. [3]

You may represent compound **G** as R-$CH_2Br$.

**(ii)** Draw the structure of compound **H**. [1]

**(iii)** When the mono-chlorination is carried out in step **4**, two possible monochloroalkanes **J** and **K** can be formed.





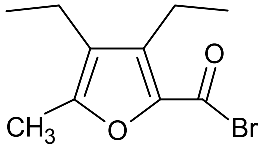
**J** and **K**

Predict the relative proportions of **J** and **K** formed. [1]

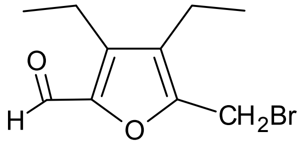
**(iv)** When the monochlorinated products of step **4** were analysed, it is found that the mole ratio of **J: K** formed was about 97: 3.

Suggest a reason for the difference between this ratio and the one you gave in (**iii** ). [1]

**(v)** Compounds **M** and **G** are both bromine-containing compounds that are isomers of each other.



Compound **M**



Compound **G**

Compare the reactivities of **M** and **G** with water. Explain your answer. [2]

[Total:20]

**3** **(a)** **(i)** Use the following data to construct an energy level diagram and hence calculate the enthalpy change for the hydrogenation of ethene gas to ethane gas.

| | $\Delta H$ / kJ mol$^{-1}$ |
|---|---|
| Enthalpy change of combustion of $CH_3CH_3(l)$ | -1545 |
| Enthalpy change of condensation of $CH_3CH_3(g)$ | -15 |
| Enthalpy change of combustion of $H_2(g)$ | −286 |
| Enthalpy change of combustion of $CH_2{=}CH_2(g)$ | −1411 |

[4]

**(ii)** Define the term bond energy. [1]

**(iii)** Using appropriate bond energy values from the *Data Booklet* alone, calculate another value for the enthalpy change of the reaction in **(a)(i)**.

[2]

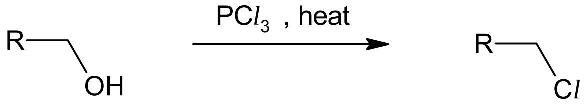
**(iv)** Suggest a reason for the discrepancy between the enthalpy change for the hydrogenation of ethene gas to ethane gas calculated in **(a)(i)** and **(a)(iii)**. [1]

**(b)** Hot sulfuric acid, $H_2SO_4$ is added to ethanol, an alcohol, to produce ethene.

Draw a 'dot-and-cross' diagram showing the electrons (outer shell only) in a $H_2SO_4$ molecule.

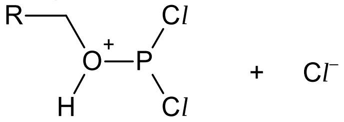
Use the VSEPR (valence shell electron pair repulsion) theory to predict the bond angle around sulfur in $H_2SO_4$. [3]

**(c)** Phosphorous halides such as $PX_3$ can act as both Lewis acids or Lewis bases. $PCl_3$ is used to convert an alcohol to an alkyl chloride.



The mechanism above involves 2 steps:

- Step **1**: The nucleophilic alcohol attacks $PCl_3$ to form the following intermediate, along with a $Cl^-$ ion:



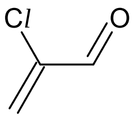
- Step **2**: (slow) $Cl^-$ ion attacks the electrophilic carbon on the intermediate, simultaneously the C–O bond breaks heterolytically.

State and explain if $PCl_3$ acts as a Lewis acid or Lewis base in step **1** of the mechanism. [1]

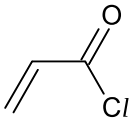
**(d)** For the following pair of compounds, describe **one** chemical test which would enable you to distinguish clearly between them.

State the observations for **each** compound.

State the type of reaction undergone for the compound that shows a positive test.



compound **N**

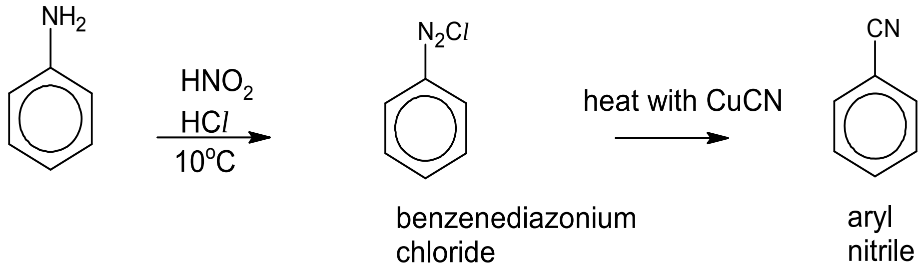


compound **O**

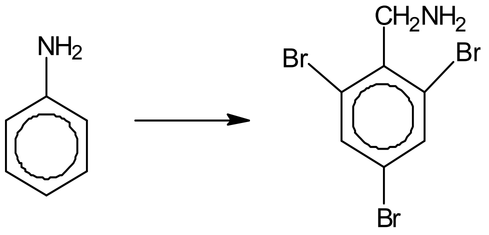
[3]

**(e)** Phenylamine reacts with nitrous acid, $HNO_2$, and hydrochloric acid at 10°C to form benzenediazonium chloride, $C_6H_5N_2Cl$.

This is an important intermediate in the synthesis of aromatic compounds. It undergoes the Sandmeyer reaction, shown below, in the presence of a copper(I) catalyst to form aryl nitriles.



Suggest a four-step reaction sequence for the following conversion. You are to make use of the Sandmeyer reaction in one of the steps.



[4]

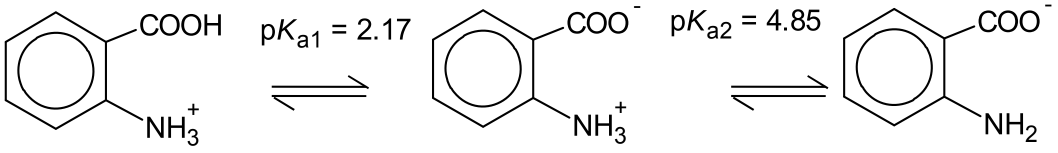
[Total:19]

## Section **B**

Answer **one** question from this section.

**4** **(a)** Vitamin L1, also known as 2-aminobenzoic acid, can be obtained from bovine liver, and its deficiency has been associated with lactation issues in females.

The diagram below shows how the protonated form of Vitamin L1 acts as a dibasic acid, which dissociates in two stages:



Protonated form
of Vitamin L1

**(i)** Calculate the pH of 10 $cm^3$ of 0.100 mol $dm^{-3}$ of the protonated form of Vitamin L1. Ignore the effect of $pK_{a2}$ on the pH of the sample. [1]

**(ii)** A sample containing 10 $cm^3$ of 0.100 mol $dm^{-3}$ of the protonated form of Vitamin L1 was titrated with 30 $cm^3$ of 0.100 mol $dm^{-3}$ of NaOH.

Sketch clearly the titration curve obtained, which should include the following key points:

- initial pH;
- points where $pK_{a1}$ and $pK_{a2}$ occur;
- isoelectric point of Vitamin L1 and its estimated value, given that: isoelectric point = $(pK_{a1} + pK_{a2}) / 2$

[4]

**(iii)** Define what is meant by a buffer. [1]

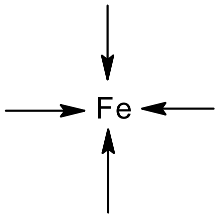
**(iv)** Draw the structures of the two chemical species present in a solution of Vitamin L1 at pH 5.00.

Hence, show by means of balanced equations, how this solution regulates the acidity on addition of $H^+$ ions and $OH^-$ ions. [3]

**(b)** Iron ions can form transition metal complexes with the basic form of the amino acid, alanine. The formula of the complex formed is $Fe(CH_3CH(NH_2)COO)_2$.

**(i)** State the oxidation state of Fe in the transition complex. [1]

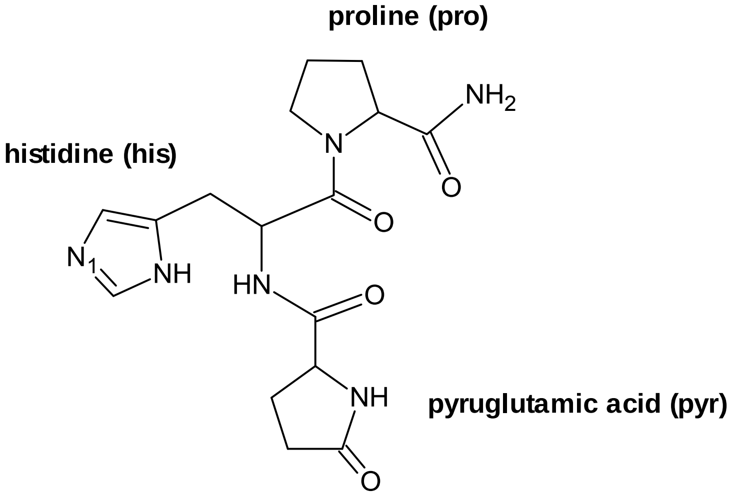
**(ii)** The diagram below shows the incomplete structure of the complex. Copy the diagram and draw the complete structure of this complex.



[1]

**(c)** Thyrotropin-releasing hormone (TRH) is a hormone that is produced by the hypothalamus in the brain. TRH has been used clinically for the treatment of the disturbance of consciousness in humans.

TRH is a tripeptide that is made of three amino acids proline, histidine and pyruglutamic acid, as shown in the diagram below.



**TRH tripeptide**

In the questions below, assume that the side chain for histidine (his) is inert.

**(i)** State the reagents and conditions for TRH to undergo hydrolysis. [1]

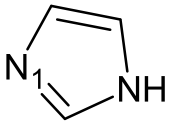
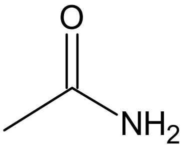
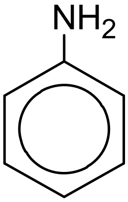
**(ii)** Draw the structures of the amino acids formed when TRH undergoes hydrolysis using the reagents and conditions stated in **(c)(i)**. [3]

**(iii)** Explain why amino acids exist as solids with high melting points. [1]

**(iv)** State the hybridisation state of nitrogen atom labeled $N_1$ in the histidine side chain of TRH. [1]

**(v)** The amino acid histidine has a cyclic imidazole side-chain.

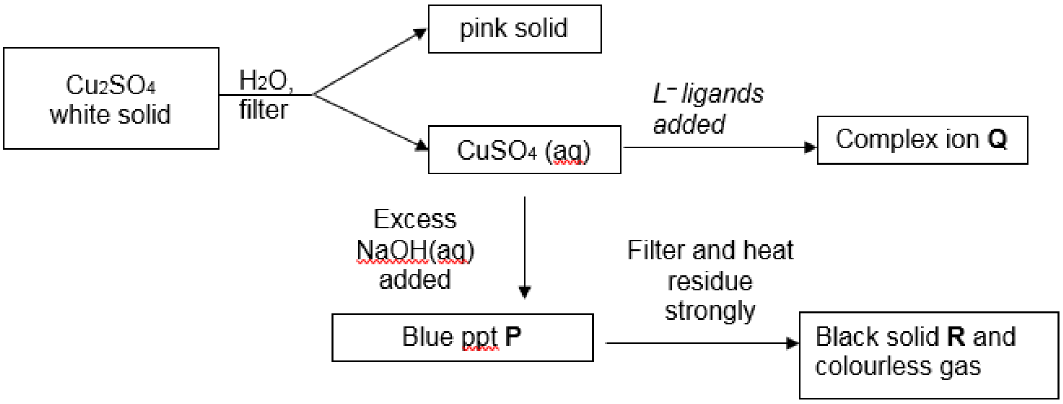
The table below compares the p$K_b$ value of $N_1$ nitrogen atom of imidazole ring, with the p$K_b$ values of ethanamide and phenylamine.

| **Compound name** | **Structure** | **p$K_b$** |
|---|---|---|
| **imidazole** |  | 8.8<br>(p$K_b$ of $N_1$) |
| **ethanamide** |  | 14.5 |
| **phenylamine** |  | 9.4 |

Using the data provided, list the 3 compounds in increasing basicity, and suggest explanations for their relative basicities. [3]

[Total: 20]

**5** **(a)** The scheme below shows the reactions of different compounds of copper.



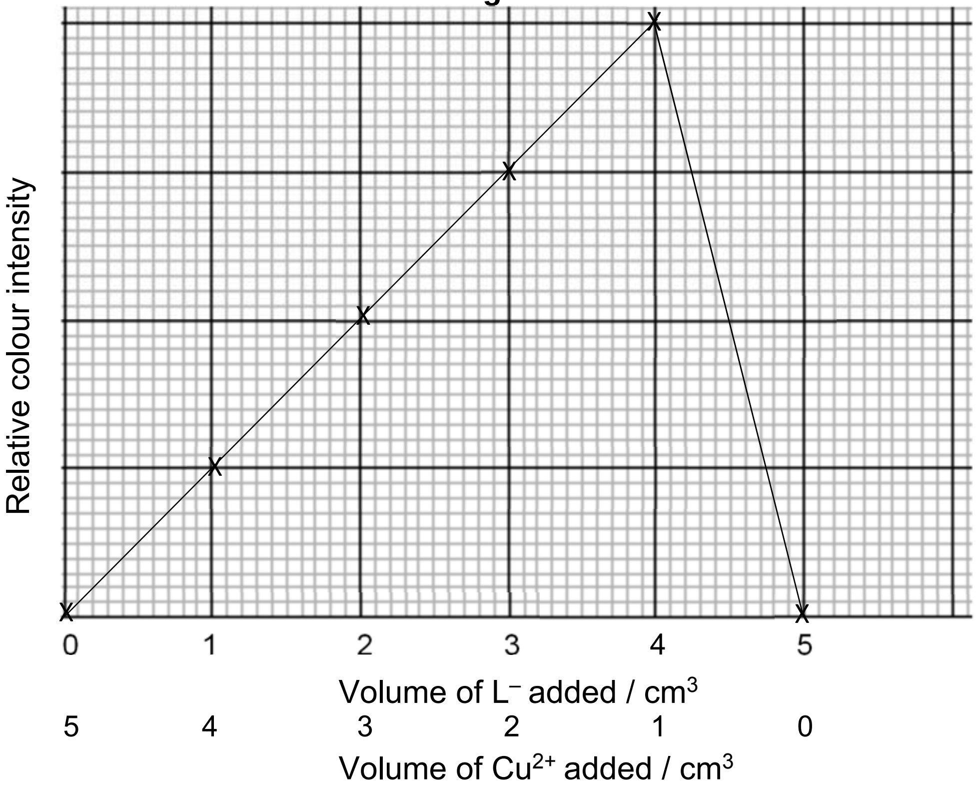
**(a)** **(i)** Suggest the formulae of blue ppt **P** and black solid **R**. [2]

**(ii)** Write an equation to show how the pink solid and $CuSO_4$ are obtained when $Cu_2SO_4$ is added to water. [1]

To determine the stoichiometry of the green complex ion **Q** formed between aqueous copper (II) sulfate and $L^-$ ligands, the colour intensities of solutions containing different proportions of the ligand, $L^-$, and $Cu^{2+}$ ion were measured.

The intensity of the green colour is directly proportional to the concentration of the complex ion. The higher the concentration of the complex, the higher is the colour intensity. In one such experiment, the results obtained for different volume mixtures of $1.0 \times 10^{-3}$ mol dm$^{-3}$ $Cu^{2+}$(aq) and $1.0 \times 10^{-3}$ mol dm$^{-3}$ $L^-$(aq) were plotted below.

**Fig. 5.1**



**(iii)** State the type of reaction that occurs when complex ion **Q** is formed from aqueous $CuSO_4$. [1]

**(iv)** Based on the plotted graph in **Fig. 5.1**, determine the mole ratio of $Cu^{2+}$(aq) to $L^-$ (aq) in the complex **Q**.

Given that complex **Q** has an octahedral shape and it retains some water molecules as ligands, suggest a formula for the complex **Q**, including its overall charge. [2]

**(b)** Explain why complexes of Cu(II) are coloured whereas complexes of Cu(I) are colourless. [4]

**(c)** Chlorine can exist in different oxidation states.

| **Half-equation** | $E^\ominus$ **/ V** |
|---|---|
| $2ClO_3^- + 12H^+ + 10e^- \rightleftharpoons Cl_2 + 6H_2O$ | +1.47 |
| $Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ | +1.36 |

A Latimer diagram shown below, summarises the standard electrode potential, $E^\ominus$ of different chlorine-containing species in acidic medium. The most highly oxidised form of the element is on the left, with successively lower oxidation states to the right. The electrode potentials are shown on the arrows.

$$\begin{tikzcd}
ClO_3^- \arrow[r, "+1.47\ \text{V}"] \arrow[rr, bend right, "E^\ominus(ClO_3^-/Cl^-)"'] & Cl_2 \arrow[r, "+1.36\ \text{V}"] & Cl^-
\end{tikzcd}$$

The standard electrode potential of converting $ClO_3^-$ to $Cl^-$, $E^\ominus(ClO_3^- /Cl^-)$ is **NOT** the summation of +1.47 V and +1.36 V.

Determine the number of electrons involved in the conversion of 1 mole of $ClO_3^-$ to 1 mole of $Cl^-$.

Hence, given that $\Delta G^\ominus$ for the conversion of $ClO_3^-$ to $Cl^-$ is -150 kJ $mol^{-1}$, calculate $E^\ominus(ClO_3^- / Cl^-)$. [2]

**(d)** *Use of the Data Booklet is relevant to this question.*

**X,** $C_5H_6O_3$, is soluble in dilute NaOH. **X** gives an orange precipitate with 2,4-dinitrophenylhydrazine reagent, and a yellow precipitate with warm alkaline aqueous iodine. **X** decolourises aqueous bromine.

When it is reacted with a methanolic solution of $NaBH_4$ it gives **Y**, $C_5H_8O_3$. Catalytic hydrogenation of **X** gives **Z**, $C_5H_{10}O_3$. When **Z** is reacted with alkaline aqueous iodine, it gives $^{-}O_2C(CH_2)_2CO_2^{-}$.

Oxidation of 1 mole of **X** with hot acidified potassium manganate(VII) gives 1 mole of $CH_3COCO_2H$ and 2 moles of $CO_2$ gas.

*Additional optional information: **X, Y** and **Z** have a proton ($^1$H) chemical shift value of 13.0 ppm. (Refer to Data Booklet Section 6: Typical proton ($^1$H) chemical shift values ($\delta$))*

Suggest structures for **X**, **Y** and **Z**. Explain your reasoning clearly. [8]

[Total: 20]

**End of paper**

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE NAME

CT GROUP 1 7

INDEX NUMBER

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## CHEMISTRY 9729/03

Paper 3 Free Response

**19 September 2018**

**2 hours**

Candidates answer on separate paper.

| | |
|---|---|
| Additional Materials: | Answer Paper<br>Data Booklet<br>Cover Page |

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**READ THESE INSTRUCTIONS FIRST**

Write your name, index number and CT group on all work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough workings.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

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.

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This document consists of **15** printed pages.

## Section A

Answer all questions in this section.

**1** **(a)** Steam reforming is an important industrial method for producing hydrogen and carbon monoxide, from hydrocarbon fuels. This is achieved in a processing device called a reformer which reacts steam at high temperature with the fuel, such as methane gas.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \quad \Delta H = +210 \text{ kJ mol}^{-1}$$

**(i)** Write an expression of $K_p$ for the reaction, indicating its units. [2]

$$K_p = \frac{(P_{CO})(P_{H_2})^3}{(P_{CH_4})(P_{H_2O})} \text{ atm}^2$$

**(ii)** At temperature ***T***, a mixture of gaseous methane, steam and carbon monoxide were introduced into an evacuated reactor.

The table below shows the initial pressures of the gases before they were added to the reactor.

| Gas | Initial pressure / atm |
|---|---|
| methane, $CH_4$ | 1.50 |
| steam, $H_2O$ | 2.50 |
| carbon monoxide, CO | 0.70 |

Given that the percentage dissociation of methane is 20% at equilibrium, find the $K_p$ for the reaction. [2]

| | $CH_4(g)$ | $+ H_2O(g) \rightleftharpoons$ | $CO(g)$ | $+ 3H_2(g)$ |
|---|---|---|---|---|
| Initial P /atm | 1.50 | 2.50 | 0.70 | 0 |
| Change P /atm | -0.2(1.5)<br>= -0.3 | -0.3 | +0.3 | +0.9 |
| Eqm P /atm | 1.20 | 2.20 | 1.00 | 0.90 |

$$K_p = \frac{(P_{CO})(P_{H_2})^3}{(P_{CH_4})(P_{H_2O})}$$

$$K_p = \frac{(1.00)(0.90)^3}{(1.20)(2.20)} = 0.276 \text{ atm}^2$$

**(iii)** A chemist decided to raise the temperature of the reactor. He suggested that this would result in a lower yield of the product.

Do you agree with the chemist? Explain your answer. [2]

No. When the temperature is raised, the endothermic reaction is favoured since it absorbs energy. The position of equilibrium shifts to the right in favour of the forward reaction, yield of $H_2$ should increase.

In order to produce more hydrogen gas, the carbon monoxide gas that is produced from the steam reforming reaction can further react with steam. This is known as the "water-gas shift" reaction.

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$$

**(iv)** Given that the reaction conditions were set at 500°C and 1.5 atm, determine the maximum volume of hydrogen gas that can be produced from 5kg of carbon monoxide gas.

State the assumption made in your calculation. [3]

Amount of CO in 5kg = (5 x 1000)/28 = 178.6 mol = Amount of $H_2$ gas

Amount of $H_2$ produced = 178.6 mol

pV=nRT

$$V = \frac{nRT}{p}$$

$$V = \frac{178.6 \times 8.31 \times (500 + 273)}{1.5 \times 1.01 \times 10^{-5}}$$

= 7.55 $m^3$

Assumption: Hydrogen gas is behaving like an ideal gas

**(v)** Given the following,

| | |
|---|---|
| enthalpy change of formation of CO(g) / kJ $mol^{-1}$ | -99 |
| enthalpy change of formation of $H_2O$(g) / kJ $mol^{-1}$ | -245 |
| enthalpy change of formation of $CO_2$(g) / kJ $mol^{-1}$ | -394 |

With reference to the above data, calculate the enthalpy change of reaction of the "water-gas shift" reaction, $\Delta H_1$. [1]

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$$

$\Delta H_1 = \Delta H_f(CO_2(g)) - [\Delta H_f(CO(g)) + \Delta H_f H_2O(g))$

= (-394) – (-99 + -245) =-50 kJ $mol^{-1}$

**(b)** The hydrogen gas obtained from the steam reforming process in part **(a)** can be reacted with nitrogen gas to produce ammonia gas.

This reaction is known as the Haber-Bosch Process, using iron as a catalyst.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

**(i)** Predict and explain the sign of $\Delta S$ for the Haber-Bosch reaction. [1]

$\Delta S$ is negative as the there is a decrease in number of moles of gaseous particles (from 4 mol to 2 mol), hence less disorderliness.

**(ii)** Using your answer in **(b)(i)**, calculate the maximum temperature for the Haber-Bosch reaction to be spontaneous.

It is known that the numerical value of $\Delta S$ is 198 J $K^{-1}$ $mol^{-1}$, and that $\Delta H$ = -92.0 kJ $mol^{-1}$. [2]

$\Delta G = \Delta H - T\Delta S$
$0 = (-92.0) - T(-198/1000)$
T = 465K

**(c)** The hydrogen gas obtained from steam reforming, and the ammonia gas obtained from the Haber-Bosch reaction, are the key reagents required for the reductive amination reaction.

Many amines in the pharmaceutical drugs are synthesised through this reaction.

The diagram, **Fig. 1.1**, shows the 3 stages involved in reductive amination.

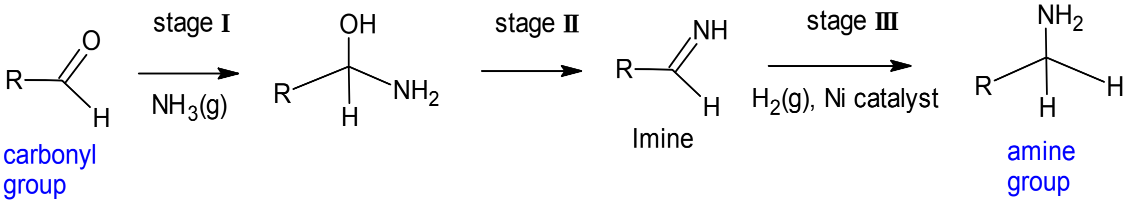


**Fig. 1.1**

During the reaction, a carbonyl group is converted into an amine group via an intermediate imine.

**(i)** State the types of reaction occurring in stage **I** and stage **II**. [2]

stage **I:** Nucleophilic addition.
stage **II:** elimination

The reaction scheme below, **Fig.1.2**, shows the production of α-methylphenethylamine, which involves reductive amination in step **4**.

Step **4** in **Fig. 1.2** comprises of the 3 stages of reductive amination in Fig. **1.1**.

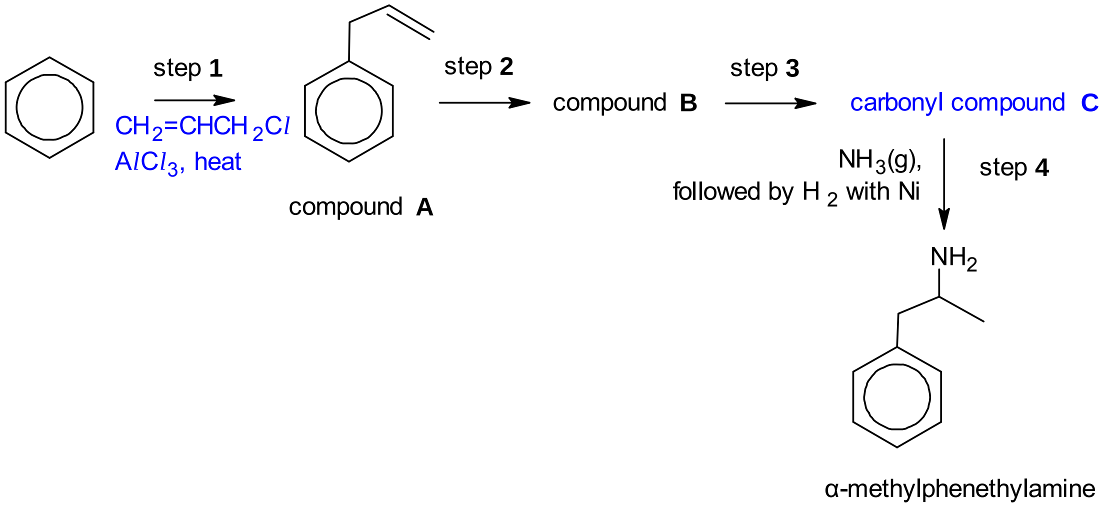


**Fig.1.2**

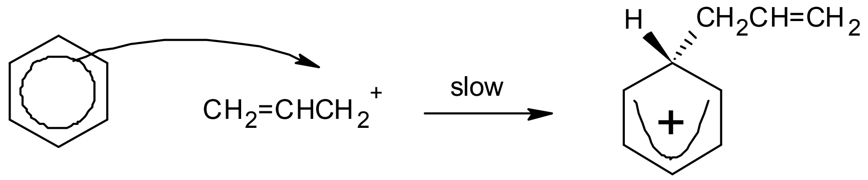
**(ii)** In step **1**, benzene undergoes a reaction with 3-chloroprop-1-ene with the aid of anhydrous aluminium chloride catalyst.

Name and describe the mechanism for step **1**, showing clearly any relevant charges, dipoles or lone pairs of electrons that are important. [4]

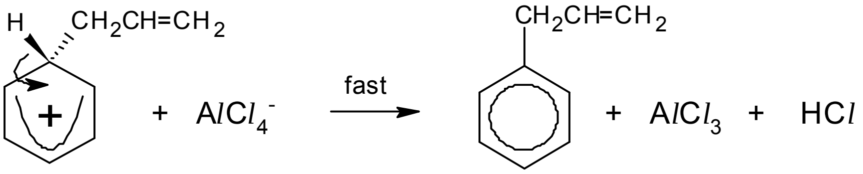
Electrophilic Substitution

**Step 1:** $CH_2{=}CHCH_2Cl + AlCl_3 \rightleftharpoons AlCl_4^- + CH_2{=}CHCH_2^+$

**Step 2:**

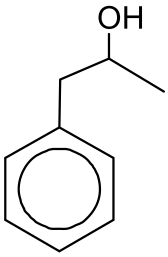


**Step 3:**

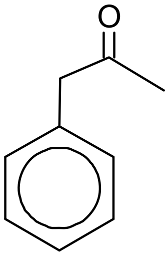


**(iii)** Deduce and draw the structure for carbonyl compound **C**, and suggest the structure of compound **B**. [2]

compounds **B**:



compounds **C**:



[Total: 21]

**2** This question is on halogen-containing compounds.

**(a)** The following experiments are carried out starting from solid aluminium chloride.

$$AlCl_3(s) \xrightarrow{\text{water}} \begin{matrix}\text{acidic}\\ \text{solution}\end{matrix} \xrightarrow{Na_2CO_3(aq)} \text{white precipitate } \mathbf{D} + \text{effervescence}$$

**(i)** Explain with the aid of balanced equations, why $AlCl_3(s)$ dissolves to form an acidic solution. Suggest the pH of the acidic solution. [3]

$AlCl_3(s)$ dissolves in water to form $[Al(H_2O)_6]^{3+}(aq)$

- $AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

A hydrolysis reaction occurs, making the solution acidic.

- $[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$
- Since $Al^{3+}$ has high charge density, it polarises and weakens the O-H bond of the water attached to it, causing the O-H bond to break to release $H^+$ (hydrolysis)
- pH=3

**(ii)** Identify precipitate **D**.
[1]

$Al(OH)_3$

**(b)** When aqueous $AgNO_3$ is added to separate test-tubes containing aqueous $KCl$ and KI, the various AgX (X = C*l*, I) precipitates were observed.

With the aid of relevant equations, explain why a precipitate of $AgCl$ is soluble in excess aqueous $NH_3$ but a precipitate of AgI is insoluble in excess aqueous $NH_3$. [3]

$Ag^+(aq) + X^-(aq) \rightleftharpoons AgX(s)$ ....(1)
$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$ ....(2)

When excess $NH_3$ is added (high $[NH_3]$), the position of equilibrium for (2) shifts to the right **to form complex $[Ag(NH_3)_2]^+$** and **$[Ag^+]$ decreases**, resulting in **eqm (1) to shift left** & a **decrease** in ionic product of AgX .
For $AgCl$, IP decreases, **ionic product becomes smaller than $K_{sp}(AgCl)$** and the position of equilibrium (1) to shift to the left and $AgCl$ dissolves completely.
For AgI, although IP decreases, ionic product is **still higher** than $K_{sp}$(AgI) (as $K_{sp}$(AgI) is very small) and thus there is no dissolution of AgI in excess aqueous ammonia.

**(c)** The standard redox potential of chlorate (V) ions is given below.

$$ClO_3^- + 6H^+ + 6e^- \rightleftharpoons Cl^- + 3H_2O \qquad E^\ominus = 1.45\text{ V}$$

Predict what you expect to observe, when acidified potassium chlorate (V) is added separately to each of the following reagents.

State clearly if no reaction occurs. Write a balanced equation for any reaction that occurs. Explain your answer using $E^\ominus$ values from the *Data Booklet.*

**(i)** $FeSO_4$ (aq)

From the eqn given and highly positive $E^\ominus = 1.45$ V, $ClO_3^-$is easily reduced.
For redox to occur, $Fe^{2+}$ must be oxidised.
$Fe^{2+} \rightleftharpoons Fe^{3+} + e$ $E^\ominus_{ox} = -0.77$ V
$E^\ominus_{cell} = +1.45 + -0.77 = +0.68V > 0$ (3 s.f) reaction is energetically feasible
Solution turns yellow (from green).

**(ii)** Acidified $KMnO_4$ (aq)
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ $E^\ominus_{red} = +1.52V$
$MnO_4^-$ and $ClO_3^-$ both can only be reduced – thus no redox possible and solution remains purple

[3]

**(d)** $PCl_5$ reacts with hydrazine, $N_2H_4$, to give compound **E**, which has the following composition by mass: P, 20.5%; N, 9.2%; C*l*, 70.3%. The molecule of **E** contains an N-N single bond.

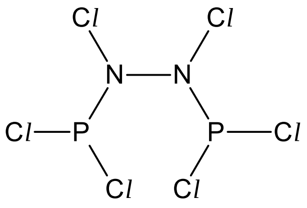
Calculate the empirical formula of **E**, and suggest its molecular formula and the structure of its molecule, assuming its constituent atoms show their usual valencies.

[2]

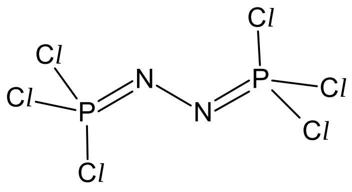
| | P | N | Cl |
|---|---|---|---|
| Mass / g | 20.5 | 9.2 | 70.3 |
| Amt / mol | 0.661 | 0.657 | 1.98 |
| Mole ratio | 1 | 1 | 3 |

Empirical formula = $PNCl_3$

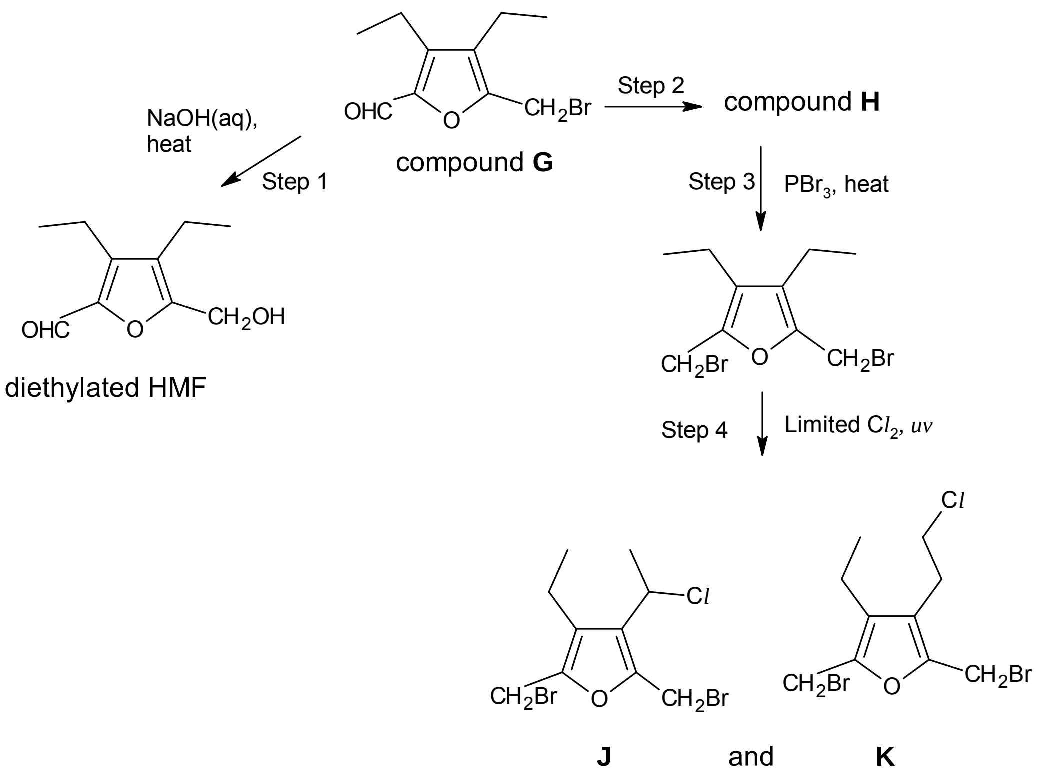
Since S contains one N-N single bond, E will contain 2 N atoms.
Molecular formula of E = $P_2N_2Cl_6$ and correct structures of E:



or



**(e)** Diethylated HMF is used to synthesize a variety of pharmaceuticals. The flow-scheme below shows the reactions involving diethylated HMF and compound **G**, its precursor. Assume the C-O-C ether group is inert.

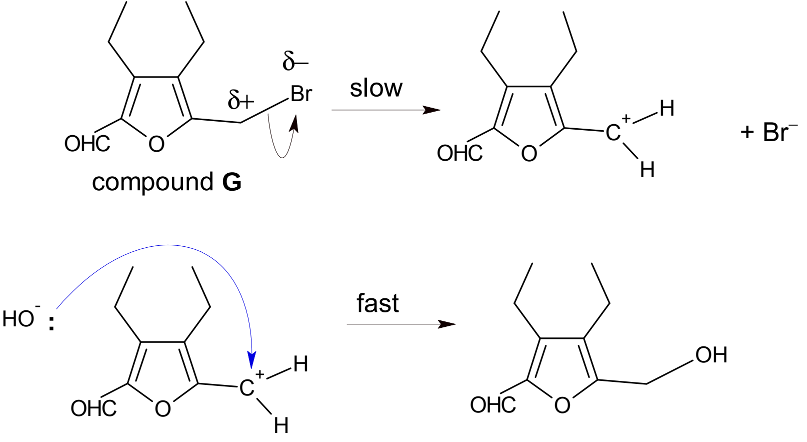


**(i)** When the reaction in step **1** was investigated kinetically, it was found that its rate was independent of [OH$^-$], but was first order with respect to [compound **G**].

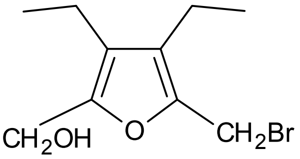
Name and describe a mechanism for this reaction, showing curly arrows in your answer. [3]

You may represent compound **G** as R-CH$_2$Br.
Nucleophilic substitution ($S_N1$)

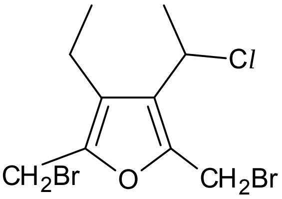
Students can represent G as R-CH$_2$Br in answer

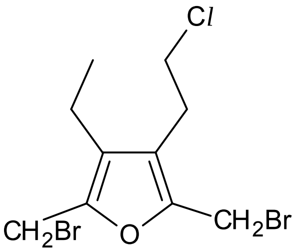


**(ii)** Draw the structure of compound **H**. [1]



**(iii)** When the mono-chlorination is carried out in step **4**, two possible monochloroalkanes **J** and **K** can be formed.





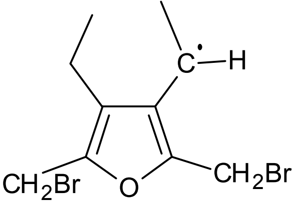
**J** and **K**

Predict the relative proportions of **J** and **K** formed. [1]

J : K
4: :6
OR 2: 3

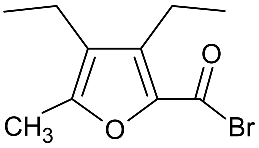
**(iv)** When the monochlorinated products of step **4** were analysed, it is found that the mole ratio of **J: K** formed was about 97: 3.

Suggest a reason for the difference between this ratio and the one you gave in (**iv**). [1]

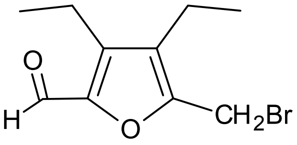


is exceptionally stable due to the overlap of p-orbital between the Carbon with unpaired electron (or resonance stabilised), and the p-orbitals of the adjacent alkene carbon atoms. This is an allylic radical. Being highly stable, it is formed in greater amount / faster and leads to major product.

**(v)** Compounds **M** and **G** are both bromine-containing compounds that are isomers of each other.



Compound **M**



Compound **G**

Compare the reactivities of **M** and **G** with water. Explain your answer. [2]

- Rate/ ease of hydrolysis: M > G

M, an acyl bromide is most reactive; it undergoes hydrolysis most readily
Reason

- The additional strongly electronegative oxygen atom in acyl bromide M further increases the partial positive charge on carbon atom (of COBr) or make it more delta $\delta+$ positive compared to carbon atom (of C-Br) in G.

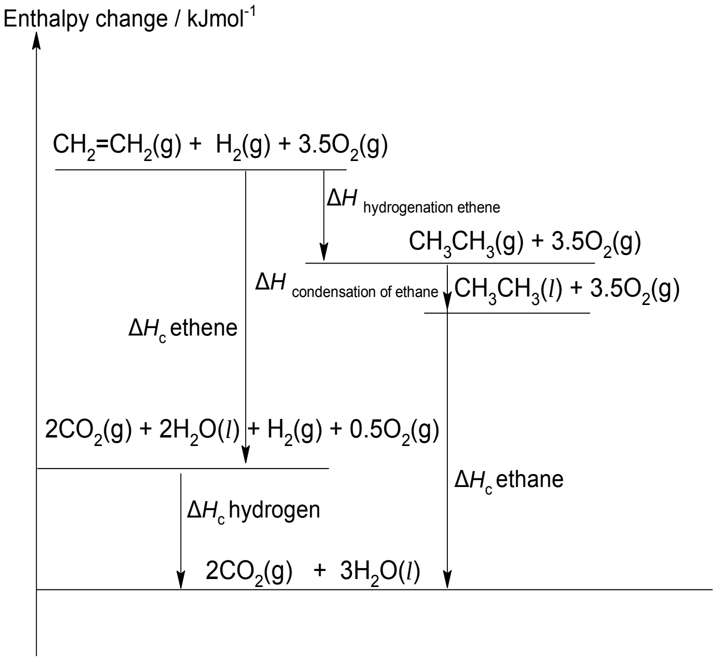
Thus the carbon atom in X is *more* readily attacked by nucleophile or X undergoes hydrolysis by water readily to give bromide ions.

[Total:20]

**3** **(a)** **(i)** Use the following data to construct an energy level diagram and hence calculate the enthalpy change for the hydrogenation of ethene gas ($CH_2{=}CH_2$) to ethane gas ($CH_3CH_3$).

| | $\Delta H$ / kJ mol$^{-1}$ |
|---|---|
| Enthalpy change of combustion of $CH_3CH_3(l)$ | -1545 |
| Enthalpy change of condensation of $CH_3CH_3(g)$ | -15 |
| Enthalpy change of combustion of $H_2(g)$ | −286 |
| Enthalpy change of combustion of $CH_2{=}CH_2(g)$ | −1411 |

[4]



By Hess' Law,

$\Delta H_{\text{hydrogenation}}$ + (– 15) + (– 1545) = (– 1411) + (– 286)

$\Delta H_{\text{hydrogenation}}$ = –137 kJ mol$^{-1}$

**(ii)** Define the term bond energy. [1]

Bond energy is the energy absorbed to break one mole of a covalent bond between two atoms in the gaseous state.

**(iii)** Using appropriate bond energy values from the *Data Booklet* alone, calculate another value for the enthalpy change of the reaction in **(a)(i)**.

$\Delta H$ = ∑B.E.(reactants) – ∑B.E.(products)

= B.E.(C=C) + 4B.E.(C-H) + B.E.(H-H) – [ 6B.E.(C-H) + B.E.(C-C) ]

= (+610) + 4(+410) – [ (+350) + 6(+410) ]= – 124 kJ mol$^{-1}$

[2]

**(iv)** Suggest a reason for the discrepancy between the enthalpy change for the hydrogenation of ethene gas to ethane gas you calculated in **(a)(i)** and **(a)(iii)**.

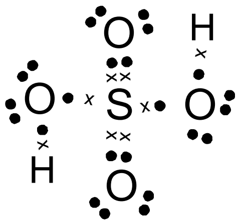
[1]

The bond energy values given in the Data Booklet are average values.

**(b)** Hot sulfuric acid, $H_2SO_4$ is added to ethanol, to produce ethene.

Draw a 'dot-and-cross' diagram showing the electrons (outer shell only) in a $H_2SO_4$ molecule.

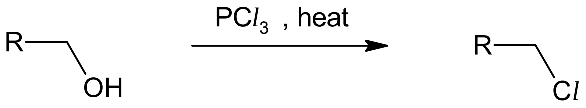
Use the VSEPR (valence shell electron pair repulsion) theory to predict the bond angle around sulfur in $H_2SO_4$. [3]



According to VSEPR, order of repulsion is given by: Lone pair – lone pair electrons > Lone pair – bond pair electrons > Bond pair – bond pair electrons

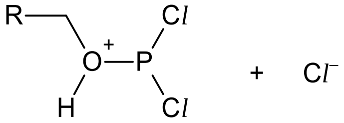
- The S atom has 4 bond pairs of electrons, no lone pair of electrons
- The bond angle is 109.5°

**(c)** Phosphorous halides such as $PX_3$ can function as both Lewis acids or Lewis bases. $PCl_3$ is used to convert an alcohol to an alkyl chloride.



The mechanism of the above reaction involves two steps:

- Step **1**: The nucleophilic alcohol attacks $PCl_3$ to form the following intermediate, along with a chloride ion:



- Step **2**: (slow step) the chloride ion attacks the electrophilic carbon on the intermediate, at the same time the C–O bond breaks heterolytically.

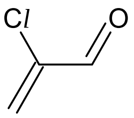
**(i)** State and explain if $PCl_3$ acts as a Lewis acid or Lewis base in step **1** of the mechanism. [1]

$PCl_3$ is a Lewis acid because it accepted lone pair of electrons.

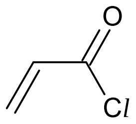
**(d)** For the following pairs of compounds, describe one chemical test which would enable you to distinguish clearly between them.

State the observations for each compound.

State the type of reaction undergone for the compound that shows a positive test.



compound **N**



compound **O**

Distinguishing test: Add Tollens' reagent, warm

Observations: Silver mirror for N, no silver mirror for O

Type of reaction: Oxidation

OR

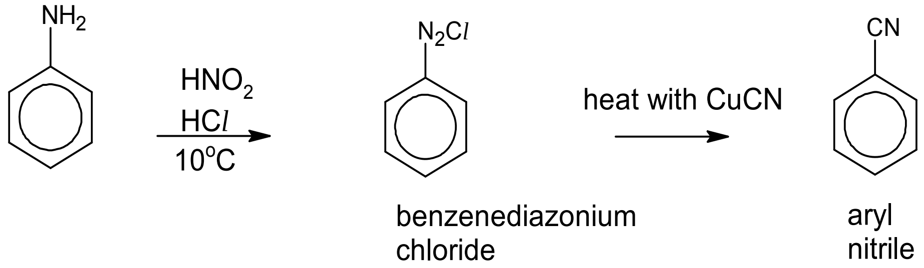
Distinguishing test: Add $AgNO_3$(aq), r.t.p

Observations: White ppt for O, no white ppt for N

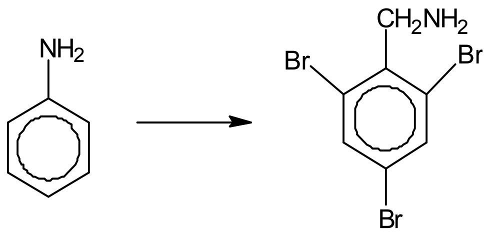
Type of reaction: Nucleophilic acyl substitution [3]

**(e)** Phenylamine reacts with nitrous acid, $HNO_2$, and hydrochloric acid at 10°C to form benzenediazonium chloride, $C_6H_5N_2Cl$.

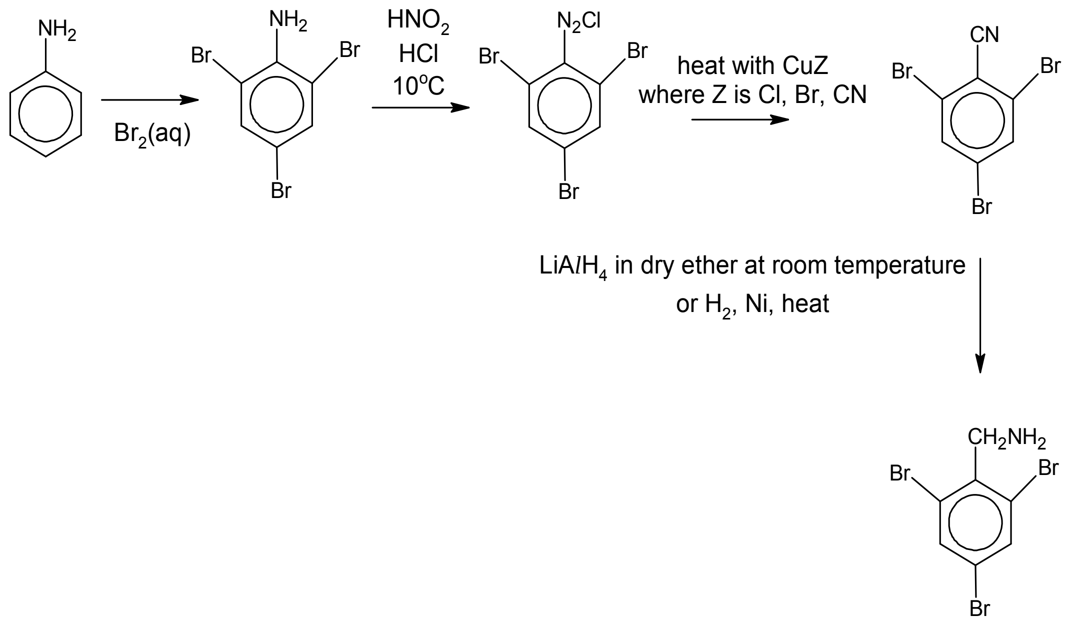
This is an important intermediate in the synthesis of aromatic compounds. It undergoes the Sandmeyer reaction, shown below, in the presence of a copper(I) catalyst to form aryl nitriles.



Suggest a four-step reaction sequence for the following conversion. You are to make use of the Sandmeyer reaction in one of the steps.



[4]


NH2
Br2(aq)
Br
HNO2
HCl
10°C
N2Cl
heat with CuZ
where Z is Cl, Br, CN
CN
LiAlH4 in dry ether at room temperature
or H2, Ni, heat
CH2NH2

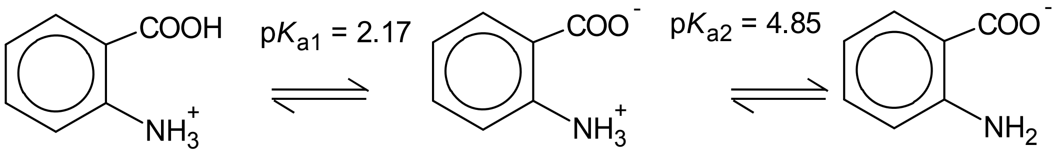
[Total:19]

## Section **B**

Answer **one** question from this section.

**4** **(a)** Vitamin L1, also known as 2-aminobenzoic acid, can be obtained from bovine liver, and its deficiency has been associated with lactation issues in females.

The diagram below shows how the protonated form of Vitamin L1 acts as a dibasic acid, which dissociates in two stages:



Protonated form
of Vitamin L1

**(i)** Calculate the pH of 10 cm$^3$ of 0.100 mol dm$^{-3}$ of the protonated form of Vitamin L1. Ignore the effect of p$K_{a2}$ on the pH of the sample. [1]

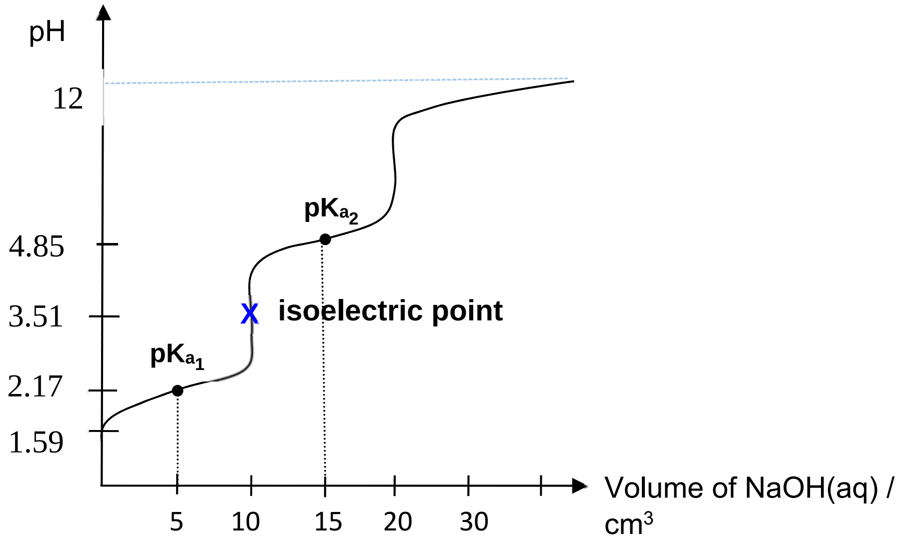
Given p$K_{a1}$ = 2.17
$K_{a1} = 10^{-2.17}$
$K_{a1} \approx [H^+]^2 / (0.100)$
$[H^+] = 0.02600$ moldm$^{-3}$
pH = 1.59

**(ii)** A sample containing 10 cm$^3$ of 0.100 mol dm$^{-3}$ of the protonated form of Vitamin L1 was titrated with 30 cm$^3$ of 0.100 mol dm$^{-3}$ of NaOH.

Sketch clearly the titration curve obtained, which should include the following key points:

- initial pH;
- points where p$K_{a1}$ and p$K_{a2}$ occur;
- isoelectric point of Vitamin L1 and its estimated value, given that: isoelectric point = (p$K_{a1}$ + p$K_{a2}$) / 2

[4]



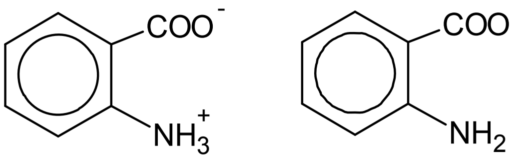
Correct shape of graph with correct axes
Correct locations of p$K_{a1}$ and p$K_{a2}$
Correct initial pH AND correct equivalence volumes
Credit for show pH tapering off at about 12-13 at about 30 cm$^3$
value of pH at isoelectric point
isoelectric point = (p$K_{a1}$ + p$K_{a2}$) / 2 = (2.17+4.85)/2 = 3.51

**(iii)** Define what is meant by a buffer. [1]

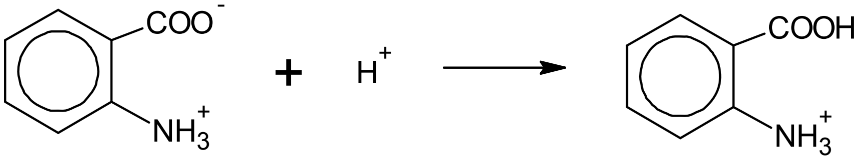
A buffer resists change to pH when small amount of acid or base is added to it and upon dilution.

**(iv)** Draw the structures of the two chemical species present in a solution of Vitamin L1 at pH 5.00.

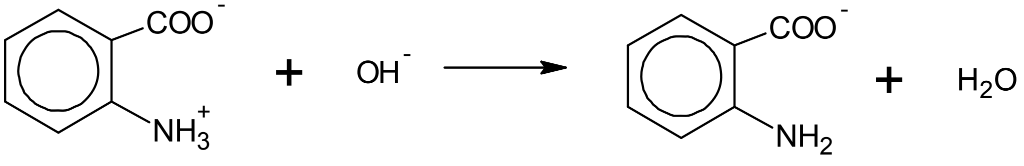
Hence, show by means of balanced equations, how this solution regulates the acidity on addition of H$^+$ ions and OH$^-$ ions. [3]



When a small amount of acid is added,



When a small amount of base is added,



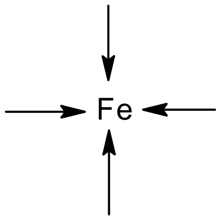
**(b)** Iron ions can form transition metal complexes with the basic form of the amino acid, alanine. The formula of the complex formed is $Fe(CH_3CH(NH_2)COO)_2$.

**(i)** State the oxidation state of Fe in the transition complex. [1]

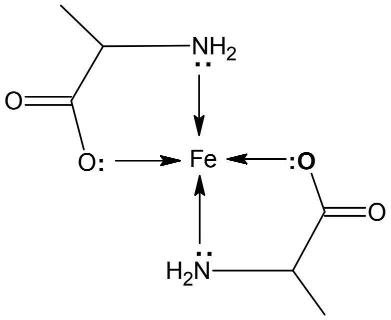
+2

Since the charge of each $CH_3CH_2(NH_2)COO^-$ is -1, iron has to be +2 for the complex to be electrically neutral as given.

**(ii)** The diagram below shows the incomplete structure of the complex. Copy the diagram and draw the complete structure of this complex.

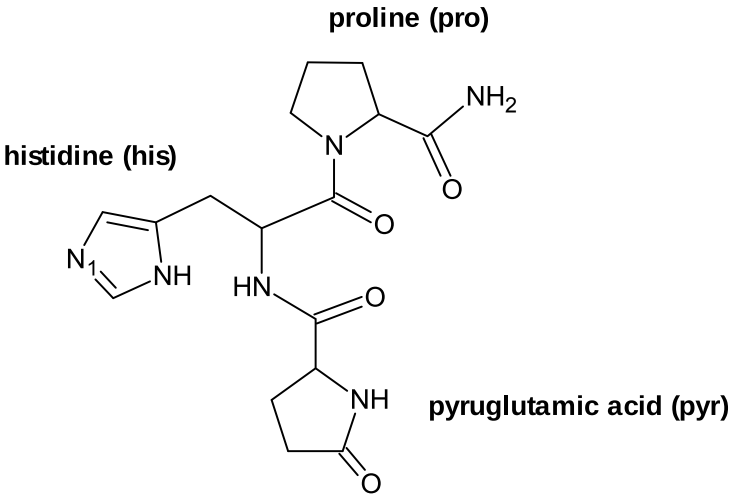


[1]



**(c)** Thyrotropin-releasing hormone (TRH) is a hormone that is produced by the hypothalamus in the brain. TRH has been used clinically for the treatment of the disturbance of consciousness in humans.

TRH is a tripeptide that is made of three amino acids proline, histidine and pyruglutamic acid, as shown in the diagram below.



**TRH tripeptide**

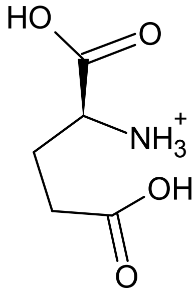
In the questions below, assume that the side chain for histidine (his) is inert.

**(i)** State the reagents and conditions for TRH to undergo hydrolysis. [1]

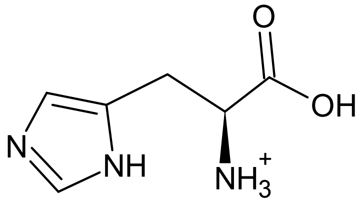
$H_2SO_4$(aq), heat
OR
NaOH(aq), heat

**(ii)** Draw the structures of the amino acids formed when TRH undergoes hydrolysis using the reagents and conditions stated in **(c)(i)**. [3]

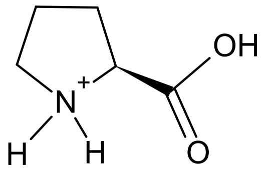
Products of acidic hydrolysis:



**pyroglutamic acid (pyr)**



**histidine (his)**



**proline (pro)**

**accept products of alkaline hydrolysis, if the candidate indicated that in (c)(i).*

**(iii)** Explain why amino acids exist as solids with high melting points. [1]

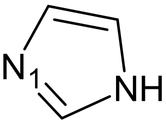
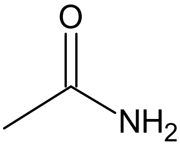
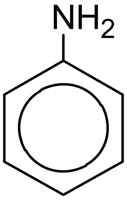
Amino acids can exist as zwitterions, with strong ionic bonds/electrostatic forces of attractions between oppositely charged ions.

**(iv)** State the hybridisation state of nitrogen atom labeled $N_1$ in TRH. [1]

nitrogen atom 1: $sp^2$

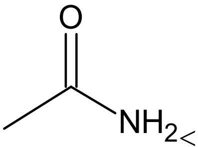
**(v)** The amino acid histidine has a cyclic imidazole side-chain.

The table below compares the p$K_b$ value of $N_1$ nitrogen atom of imidazole ring, with the p$K_b$ values of ethanamide and phenylamine.

| **Compound name** | **Structure** | **p$K_b$** |
|---|---|---|
| **imidazole** |  | 8.8<br>(p$K_b$ of $N_1$) |
| **ethanamide** |  | 14.5 |
| **phenylamine** |  | 9.4 |

Using the data provided, list the 3 compounds in increasing basicity, and suggest explanations for their relative basicities. [3]

Basicity increases from:



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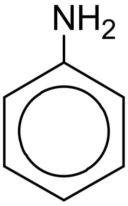

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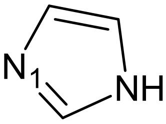
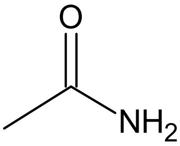
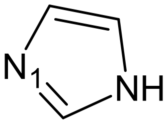
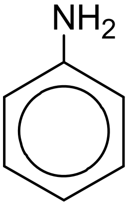




is neutral as the lone pair of electrons on N is delocalised into C=O. Hence, the lone pair of electrons on the N atom is not available for protonation.



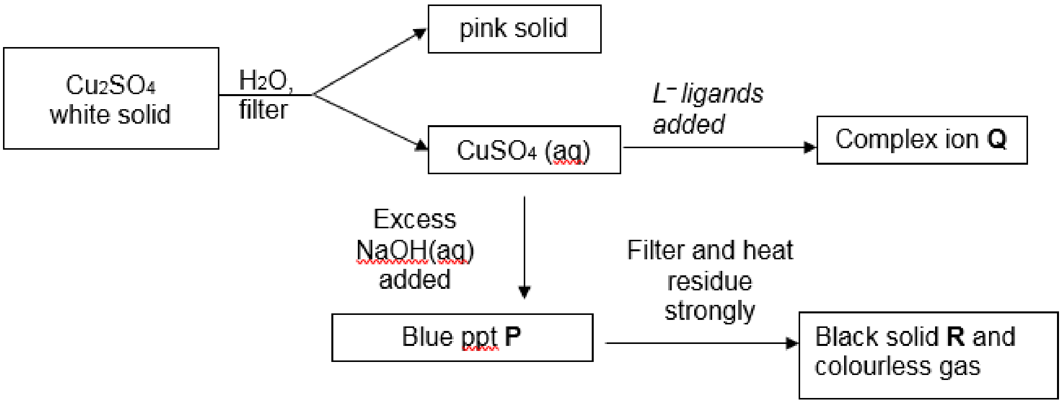
is more basic than



as the p orbital of nitrogen lies perpendicular to the plane of the C=N bond, hence, the lone pair of electrons are not delocalized and are readily available for protonation, compared to the lone pair of electrons on N atom in phenylamine which is delocalized into the benzene ring and not so readily available.

[Total: 20]

**5** **(a)** The scheme below shows the reactions of different compounds of copper.



**(a)** **(i)** Suggest the formulae of blue ppt **P** and black solid **R**. [2]

P: $Cu(OH)_2$

R: CuO

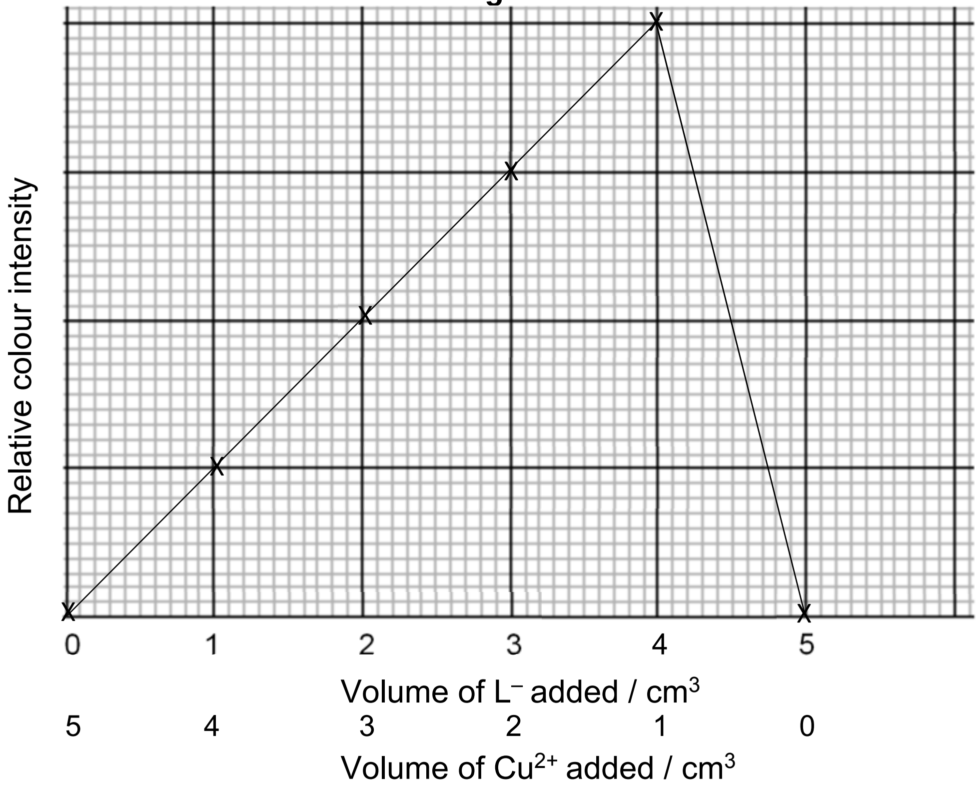
**(ii)** Write an equation to show how the pink solid and $CuSO_4$ are obtained when $Cu_2SO_4$ is added to water. [1]

$Cu_2SO_4(s) \rightarrow CuSO_4(aq) + Cu(s)$

To determine the stoichiometry of the green complex ion **Q** formed between aqueous copper (II) sulfate and $L^-$ ligands, the colour intensities of solutions containing different proportions of the ligand, $L^-$, and $Cu^{2+}$ ion were measured.

The intensity of the green colour is directly proportional to the concentration of the complex ion. The higher the concentration of the complex, the higher is the colour intensity. In one such experiment, the results obtained for different volume mixtures of $1.0 \times 10^{-3}$ mol dm$^{-3}$ $Cu^{2+}$(aq) and $1.0 \times 10^{-3}$ mol dm$^{-3}$ $L^-$(aq) were plotted below.

**Fig. 5.1**



**(iii)** State the type of reaction that occurs when complex ion **Q** is formed from aqueous $CuSO_4$. [1]

Ligand exchange

**(iv)** Based on the plotted graph in **Fig. 5.1**, determine the mole ratio of $Cu^{2+}$(aq) to $L^-$ (aq) in the complex **Q**.

Given that complex **Q** has an octahedral shape and it retains some water molecules as ligands, suggest a formula for the complex **Q**, including its overall charge. [2]

Mole ratio of $Cu^{2+}$(aq) to $L^-$ (aq) in the complex Q: 1:4

$[Cu(H_2O)_2(L)_4]^{2-}$

**(b)** Explain why complexes of Cu(II) are coloured whereas complexes of Cu(I) are colourless. [4]

Cu(I) has fully filled 3 d-orbitals ($3d^{10}$). Hence, d-to-d electron transition cannot occur, and no visible light is absorbed, which accounts for it being colourless and Cu(II) has partially filled 3d-orbitals

- In presence of ligands,
- the originally degenerate 3d orbitals split into 2 sets of different energy levels, separated
- by a small energy gap (ΔE).
- ΔE corresponds to the energy of visible light.
- An electron from the lower energy d orbital absorbs a specific wavelength of visible light and
- is promoted to a half-filled, higher energy 3d orbital. d-to-d transition can take place and
- colour observed is complementary to the colour absorbed.

**(c)** Chlorine can exist in different oxidation states.

| **Half-equation** | ***E*° / V** |
|---|---|
| $2ClO_3^- + 12H^+ + 10e^- \rightleftharpoons Cl_2 + 6H_2O$ | +1.47 |
| $Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ | +1.36 |

A Latimer diagram shown below, summarises the standard electrode potential, $E^\ominus$ of different chlorine-containing species in acidic medium. The most highly oxidised form of the element is on the left, with successively lower oxidation states to the right. The electrode potentials are shown on the arrows.

$$\begin{tikzcd} ClO_3^- \arrow[r, "+1.47\text{ V}"] \arrow[rr, bend right, "E^\ominus(ClO_3^-/Cl^-)"'] & Cl_2 \arrow[r, "+1.36\text{ V}"] & Cl^- \end{tikzcd}$$

The standard electrode potential of converting $ClO_3^-$ to $Cl^-$, $E^\ominus(ClO_3^-/Cl^-)$ is **NOT** the summation of +1.47 V and +1.36 V.

Determine the number of electrons involved in the conversion of 1 mole of $ClO_3^-$ to 1 mole of $Cl^-$.

Hence, given that $\Delta G^\ominus$ for the conversion of $ClO_3^-$ to $Cl^-$ is -150 kJ mol$^{-1}$, calculate $E^\ominus(ClO_3^-/Cl^-)$. [2]

No of electrons involved = 6 (+5 to -1)

$\Delta G^\ominus = -nFE^\ominus$

$-150\,000 = -(6)(96500)\,E^\ominus$

$E^\ominus = +0.259$ V

**(d)** *Use of the Data Booklet is relevant to this question.*

**X,** $C_5H_6O_3$, is soluble in dilute NaOH. **X** gives an orange precipitate with 2,4-dinitrophenylhydrazine reagent, and a yellow precipitate with warm alkaline aqueous iodine. **X** decolourises aqueous bromine.

When it is reacted with a methanolic solution of $NaBH_4$ it gives **Y**, $C_5H_8O_3$. Catalytic hydrogenation of **X** gives **Z**, $C_5H_{10}O_3$. When **Z** is reacted with alkaline aqueous iodine, it gives $^{-}O_2C(CH_2)_2CO_2^{-}$.

Oxidation of 1 mole of **X** with hot acidified potassium manganate(VII) gives 1 mole of $CH_3COCO_2H$ and 2 moles of $CO_2$ gas.

*Additional optional information: **X**, **Y** and **Z** have a proton ($^1H$) chemical shift value of 13.0 ppm. (Refer to Data Booklet Section 6: Typical proton ($^1H$) chemical shift values ($\delta$))*

Suggest structures for **X**, **Y** and **Z**. Explain your reasoning clearly. [8]

- **X** is a carboxylic acid which undergoes acid base with NaOH.
- **X** is a ketone or aldehyde compound as it undergoes condensation reaction with 2,4-dinitrophenylhydrazine to form an orange ppt.
- **X** undergoes oxidation with warm alkaline aqueous iodine to form a yellow ppt, $CHI_3$. **X** has $CH_3CO$– structure.
- **X** is an alkene as it undergoes electrophilic addition with $Br_2$.
- Ketone or aldehyde group in **X** is reduced by $NaBH_4$ to give **Y** as no. of H atoms increases by 2.
- Both alkene and ketone group in **X** are reduced by hydrogen to give **Z** as no. of H atoms increases by 4.
- **Z** contains $CH_3CH(OH)$– structure (not $CH_3CO$–) as it undergoes oxidation by alkaline aqueous iodine to give $^{-}O_2C(CH_2)_2CO_2^{-}$.

**X** is $CH_3COCH{=}CHCO_2H$
**Y** is $CH_3CH(OH)CH{=}CHCO_2H$
**Z** is $CH_3CH(OH)CH_2CH_2CO_2H$

[Total: 20]

**End of paper**