# RIVER VALLEY HIGH SCHOOL
## JC 2 PRELIMINARY EXAMINATION

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|---|---|---|---|---|---|---|---|---|---|
| CANDIDATE NAME | | | | | | | | | |
| CLASS | 2 | 1 | J | | | | | | |
| CENTRE NUMBER | S | | | | | INDEX NUMBER | | | |

# H2 CHEMISTRY 9729/03

Paper 3 Free Response **20 September 2022**

**2 hours**

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

**READ THESE INSTRUCTIONS FIRST**

Write your name, class and index number in the spaces at the top of this page.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

**Section A**
Answer **all** the questions.

**Section B**
Answer **one** question. **Circle** the question number of the question you attempted.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

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

| For Examiner's Use | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Question number** | **1** | **2** | **3** | **4** | **5** | **units** | **s.f.** | **Total** |
| **Marks** | /17 | /20 | /23 | /20 | /20 | | | /80 |

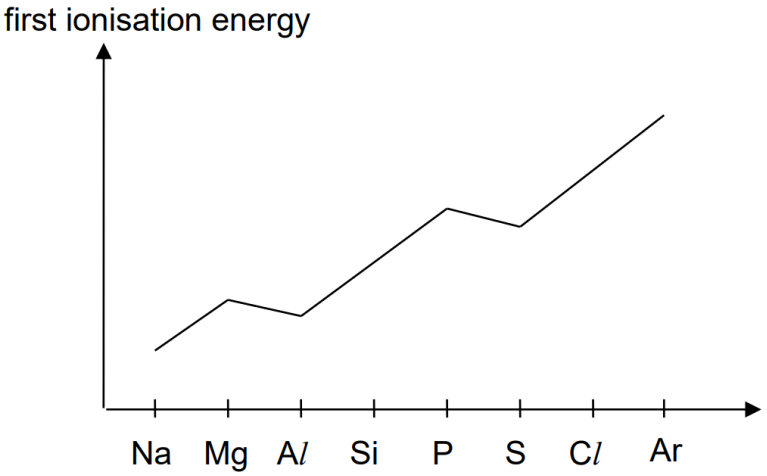
This document consists of **28** printed pages.

## Section A

Answer **all** the questions in this section.

**1** In the third period of the Periodic Table, there is considerable variation of chemical and physical properties from sodium to argon.

**(a)** The graph below shows the first ionisation energy from sodium to argon.




**(i)** Write an equation to represent the first ionisation energy of sulfur. [1]

**(ii)** Account for the difference in first ionisation energy of Mg and Al. [1]

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**(b)** Calcium carbonate decomposes when heated to about 700 °C. Copper(II) carbonate also undergoes a similar decomposition reaction when heated.

**(i)** Write a balanced equation for the thermal decomposition of copper carbonate. [1]

**(ii)** By quoting relevant values from the *Data Booklet*, state and explain if the thermal decomposition temperature of copper(II) carbonate is expected to be lower or higher than that of calcium carbonate. [2]

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**(c)** Write equations, including state symbols, for the reactions of the following compounds with water. In each case, state the pH of the resultant solution.

**(i)** $Na_2O$ [1]

**(ii)** $SiCl_4$ [1]

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**(d)** When sodium burns in oxygen, it forms a mixture of sodium oxide, $Na_2O$, and sodium peroxide, $Na_2O_2$.

**(i)** Explain the difference in the electrical conductivity of sodium and sodium oxide in their solid states. [2]

**(ii)** The peroxide anion in sodium peroxide contains an O#O bond.

Draw a 'dot-and-cross' diagram for sodium peroxide. [1]

**(iii)** When sodium peroxide is added to water, hydrogen peroxide is produced.

Explain, in terms of structure and bonding, why hydrogen peroxide is a liquid while sodium peroxide is a solid at room temperature. [2]

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**(e)** Some Pb metal and a solution of $Cr^{3+}(aq)$ were mixed and allowed to reach equilibrium.

$$Pb(s) + 2Cr^{3+}(aq) = Pb^{2+}(aq) + 2Cr^{2+}(aq)$$

The equilibrium concentrations of $Cr^{3+}(aq)$ and $Cr^{2+}(aq)$ were as follows.

$[Cr^{3+}(aq)] = 0.200 \text{ mol dm}^{-3}$

$[Cr^{2+}(aq)] = 2.96 \times 10^{-4} \text{ mol dm}^{-3}$

**(i)** Write the $K_c$ expression for this reaction. [1]

**(ii)** Calculate $K_c$ for this reaction. [2]

**(iii)** State and explain how the addition of water will affect the position of equilibrium for this reaction. [2]

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[Total: 17]

**2** This question is about the chemistry of aluminium and iron.

**(a)** Anodising is a process used to increase the thickness of the oxide layer on the surface of metal parts. Aluminium is a reactive metal that is readily oxidised by oxygen. This forms a layer of aluminium oxide, $Al_2O_3$, making it resistant to corrosion.

**(i)** Draw a labelled diagram of the electrolysis cell used to anodise an iPhone, which is made of aluminium. You should include $H_2SO_4(aq)$ as the electrolyte. [2]

**(ii)** Write chemical equations, with state symbols, to show the reactions occurring at the anode during anodising. [2]

**(iii)** The iPhone has a surface area of 96.2 $cm^2$ to be anodised. Calculate the time needed to form a 0.3 mm protective layer of $Al_2O_3$ on the iPhone if a current of 2.0 A is passed through the set-up.

(Density of $Al_2O_3$ = 3.95 g $cm^{-3}$) [3]

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

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

To speed up rate of reaction, a homogeneous catalyst is usually used.

Use appropriate equations to show the catalytic role of iron(III) ions in the reaction between $S_2O_8^{2-}$ and $I^-$. [2]

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**(c)** **(i)** When aqueous bromine is added to aqueous sodium thiosulfate, $Na_2S_2O_3$, a sulfur-containing product is formed. Upon addition of aqueous barium nitrate, a white precipitate forms which is insoluble in excess dilute nitric acid.

Identify the white precipitate. [1]

**(ii)** When aqueous bromine is replaced with iodine in the same experiment in in **(c)(i)**, no white precipitate is observed. Instead, the sulfur-containing product formed is sodium tetrathionate, $Na_2S_4O_6$.

By considering the change in oxidation state of sulfur, explain the difference between the reactions of the two halogens with $S_2O_3^{2-}$. [2]

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**(d)** Compound **P** ($C_6H_9O_2N$) does not rotate plane-polarised light and is insoluble in both aqueous hydrochloric acid and sodium hydroxide at room temperature.

When heated with aqueous sodium hydroxide, compound **P** gives three products: compound **Q**, the salt of a carboxylic acid, **R** ($C_4H_6O_4$) and ammonia gas.

1 mole of compound **R** reacts with 1 mole of aqueous sodium carbonate. On treatment with warm alkaline aqueous iodine followed by acidification, compound **Q** gives methanoic acid and a pale yellow precipitate.

The reaction of compound **P** with lithium aluminium hydride forms **Q** and **S** ($C_4H_{11}NO$). Both compounds **Q** and **S** contain a common functional group.

Deduce the structures of compounds **P**, **Q**, **R** and **S**. Explain your reasoning. [8]

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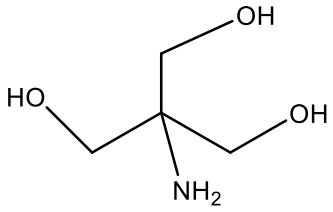
**3** **(a)** Tris(hydroxymethyl)aminomethane, TRIS, is used extensively as a component of buffer solutions for solutions of nucleic acids.




TRIS

**(i)** Name all the functional groups in TRIS. [1]

**(ii)** Explain how TRIS acts as a Lewis base in the presence of hydrochloric acid. [2]

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**(b)** To make a TRIS HC*l* buffer, 121.14 g of TRIS was dissolved in 800 $cm^3$ of deionised water. The pH was adjusted to 7.5 with an appropriate volume of concentrated hydrochloric acid, before the final volume was made up to 1 $dm^3$ with deionised water.

The protonated form of TRIS is $TRISH^+$. The value of $K_a$ for $TRISH^+$ is $8.32 \times 10^{-9}$.

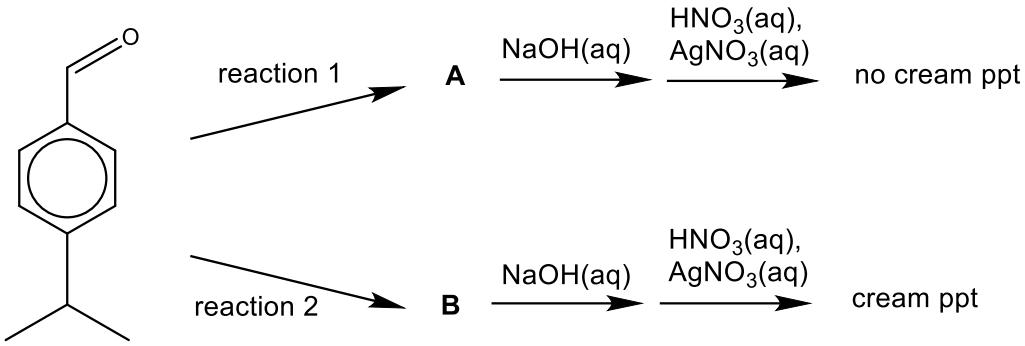
**(i)** Calculate the pH of TRIS if the final volume was made up to 1 $dm^3$ without adding concentrated hydrochloric acid. [3]

**(ii)** Calculate the ratio of $\frac{[TRIS]}{[TRISH^+]}$ at pH 7.5. [1]

**(iii)** The concentration of hydrochloric used is 11.0 mol $dm^{-3}$.

Using your answer in **(b)(ii)**, calculate the volume of hydrochloric acid required to form the buffer. [2]

**(c)** Cuminaldehyde is a component in cumin essential oil extract. It can react with halogens under different conditions to give a mixture of monohalogenated isomers, of which isomers **A** and **B** are major products.

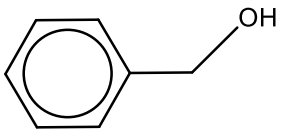



cuminaldehyde

**(i)** Suggest structures for compounds **A** and **B**. [2]

**(ii)** Explain clearly how the formation of cream precipitate confirms the functional group in compound **B**. [2]

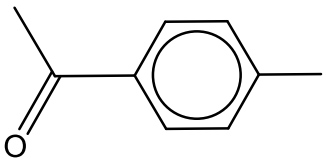
**(iii)** Cuminaldehyde can be obtained from phenylmethanol in a two-step synthesis.




phenylmethanol

Suggest the reagents and conditions for the two-step synthesis. [2]

**(iv)** Describe a simple chemical test, with appropriate observations, which would distinguish between compound **D** and cuminaldehyde.




Compound **D**

[2]

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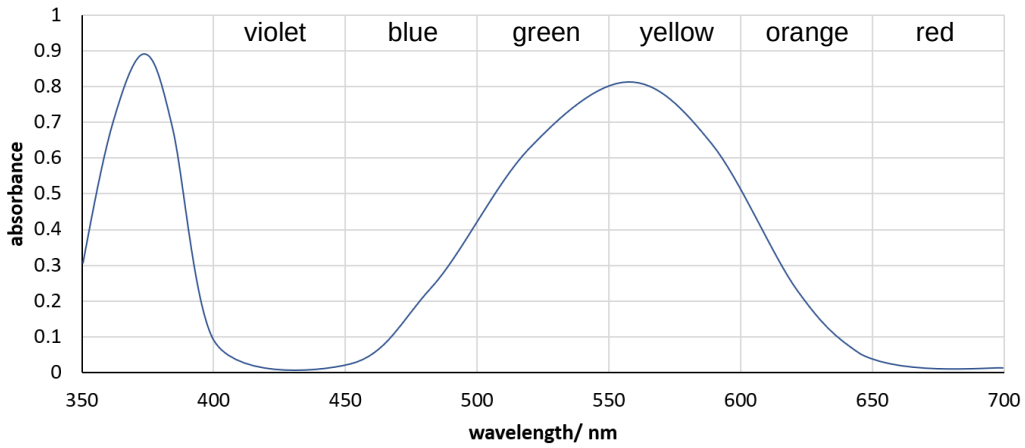
**(d)** The diagram below shows the UV-visible absorption spectrum of an aqueous transition metal complex ion, $[\mathbf{M}(H_2O)_6]^{3+}(aq)$. Absorbance on the vertical axis is a measure of the amount of light absorbed.




**(i)** Explain why transition metals form coloured complexes. [3]

**(ii)** State the expected colour of the complex ion, $[\mathbf{M}(H_2O)_6]^{3+}$. Explain your answer. [1]

**(iii)** The solution turns colourless when $[\mathbf{M}(H_2O)_6]^{3+}$ is oxidised to $[\mathbf{M}(H_2O)_6]^{4+}$. Given that **M** is a transition element from Period 4, deduce the electronic configuration of the transition metal, **M**, at ground state. [1]

**(iv)** When $F^-$ is added to $[\mathbf{M}(H_2O)_6]^{3+}$, $[\mathbf{M}F_6]^{3-}$ is formed and the solution also turned colourless. Suggest a reason for this observation. [1]

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[Total: 23]

## Section B

Answer **one** question from this section.

**4** **(a)** Acetals are a common protecting group for carbonyl compounds in organic synthesis. Acetalisation is an acid-catalysed condensation under heated conditions. An example is shown in Fig 4.1.

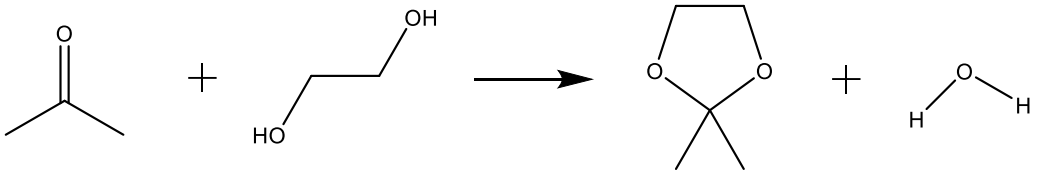



**Fig 4.1**

**(i)** The C#C bond length in propanone is 152 pm which is shorter than the C#C bond length of 154 pm in propane.

Suggest the reason and explain for the difference. [2]

**(ii)** Fig 4.2 shows part of the mechanism in the acetalisation of propanone. Copy and suggest the mechanism by drawing appropriate curly arrows and lone pairs of electrons on intermediate **Q**.

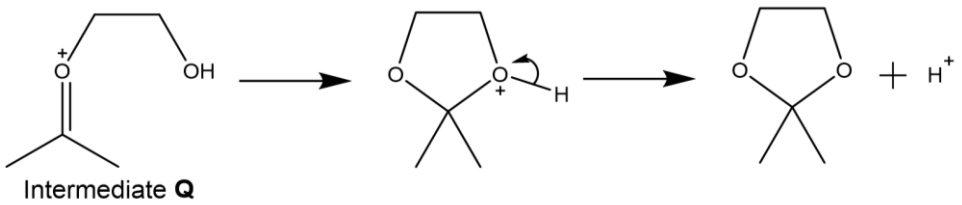
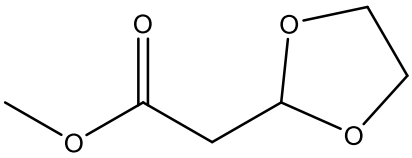



**Fig 4.2** [2]

**(iii)** Compound **R** is a cyclic acetal formed from acetalisation process depicted in Fig 4.1.

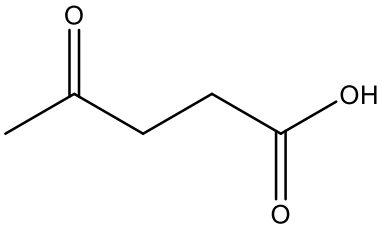



**R**

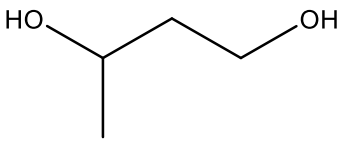
Suggest possible structures for the two reactants used in the formation of **R**. [2]

**(iv)** When 4-oxopentanoic acid and butane-1,3-diol are subject to the same reaction conditions as Fig 4.1, a mixture of 8 products are formed.

- Products **S** and **T** are structural isomers with molecular formula of $C_9H_{16}O_4$.
- **S** is acidic while **T** is neutral.
- **U** is neutral and has molecular formula of $C_{13}H_{22}O_5$.




4-oxopentanoic acid




butane-1,3-diol

Suggest possible structures for compound **S**, **T** and **U**. [3]

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**(b)** Ethene is used to produce ethane-1,2-diol. Fig 4.3 shows reactions involving ethene under different conditions.

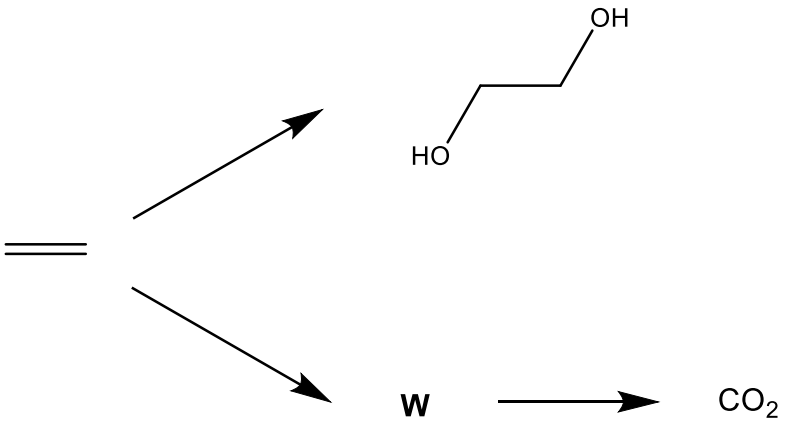


**Fig 4.3**

**(i)** State the reagent and condition to convert ethene into ethan-1,2-diol. [1]

**(ii)** Draw the displayed formula for intermediate **W**. [1]

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**(c)** Propanone undergoes acid-catalysed reaction with iodine in aqueous solution as shown in equation 1.

Equation 1 $CH_3COCH_3(aq) + I_2(aq) \xrightarrow{H^+} CH_3COCH_2I(aq) + HI(aq)$

Four experiments were carried out to investigate the order of reaction with respect to propanone, iodine and acid respectively.

| Experiment | $[CH_3COCH_3]$/ mol $dm^{-3}$ | $[I_2]$/ mol $dm^{-3}$ | $[H^+]$/ mol $dm^{-3}$ |
|---|---|---|---|
| 1 | 0.10 | 0.005 | 0.001 |
| 2 | 0.10 | 0.005 | 0.002 |

The change in concentration of iodine remaining for this reaction was measured using a photoelectric colorimeter. The reaction mixture was placed into a colorimeter. The absorbance of light at 470 nm was recorded at 15 second intervals. The absorbance measured was directly proportional to the concentration of iodine present in the sample.

The results of these experiments are shown in Fig 4.4.


**Fig 4.4**

**(i)** Explain why $CH_3COCH_3$ is used in excess in experiment 1 and 2. [1]

**(ii)** With reference to Fig 4.4, deduce the order of reaction with respect to $I_2(aq)$. Explain your reasoning. [1]

**(iii)** Hence, sketch a graph to describe the relationship between the rate of reaction and time in experiment 1. [1]

**(iv)** With reference to Fig 4.4, determine the order of reaction with respect to $H^+(aq)$. Explain your reasoning and include any calculations where necessary. [2]

**(v)** The experiment was repeated to find the initial rate of reaction at different initial concentrations of $CH_3COCH_3(aq)$, $I_2(aq)$ and $H^+(aq)$. The results of these experiments are shown in Table 4.1.

**Table 4.1**

| Expt | Initial $[CH_3COCH_3(aq)]$/ mol $dm^{-3}$ | Initial $[I_2(aq)]$/ mol $dm^{-3}$ | Initial $[H^+(aq)]$/ mol $dm^{-3}$ | Initial rate of reaction/ mol $dm^{-3}$ $s^{-1}$ |
|---|---|---|---|---|
| 3 | 0.001 | 0.003 | 0.002 | $2.45 \times 10^{-8}$ |
| 4 | 0.003 | 0.002 | 0.001 | $3.68 \times 10^{-8}$ |

Determine the order of reaction with respect to $CH_3COCH_3(aq)$. [1]

**(vi)** Outline a suitable experiment involving continuous method to determine rate constant, *k*. [3]

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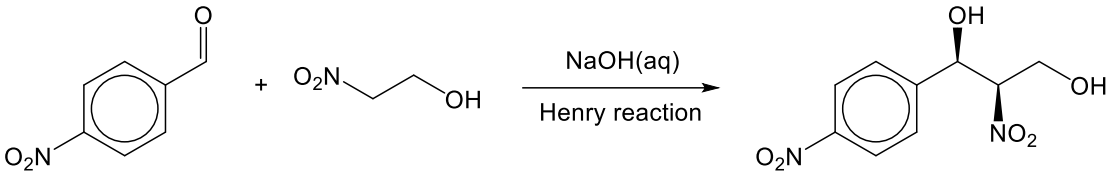
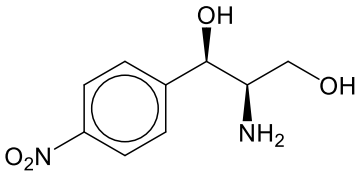
[Total: 20]

**5** Chloramphenicol is an antibiotic useful for the treatment of several bacterial infections such as conjunctivitis. Chloramphenicol can be synthesised via the Henry reaction where 4-nitrobenzaldehyde and a nitroalkane are reacted, in the presence of a base, to form β-nitro alcohols. The β-nitro alcohol then undergoes further reaction to form chloramphenicol.




4-nitrobenzaldehyde

β-nitro alcohol




chloramphenicol

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

**(ii)** Use bond energy values from the *Data Booklet* to calculate the enthalpy change of reaction for the formation of β-nitro alcohol shown above. [2]

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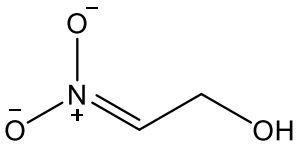
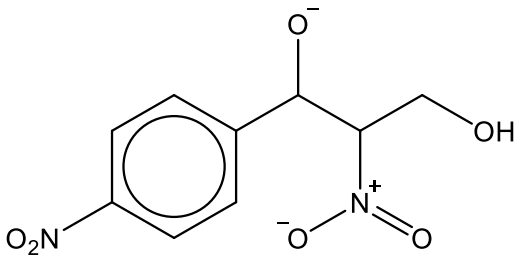
**(b)** **(i)** The mechanism for the Henry reaction is thought to involve the reaction of nitro-enolate ion with C∃O of the 4-nitrobenzaldehyde to form an alkoxide ion in a concerted step. The lone pair of electrons on the oxygen atom in nitro-enolate ion can increase the reactivity of the carbon-nitrogen double bond towards electrophilic reagents.

The structure of the nitro-enolate and alkoxide ions are given below.



nitro-enolate ion



alkoxide ion

Suggest this mechanism, showing all relevant charges, dipoles, lone pairs, and curly arrows. [2]

**(ii)** Name the type of reaction to convert β-nitro alcohol into chloramphenicol. [1]

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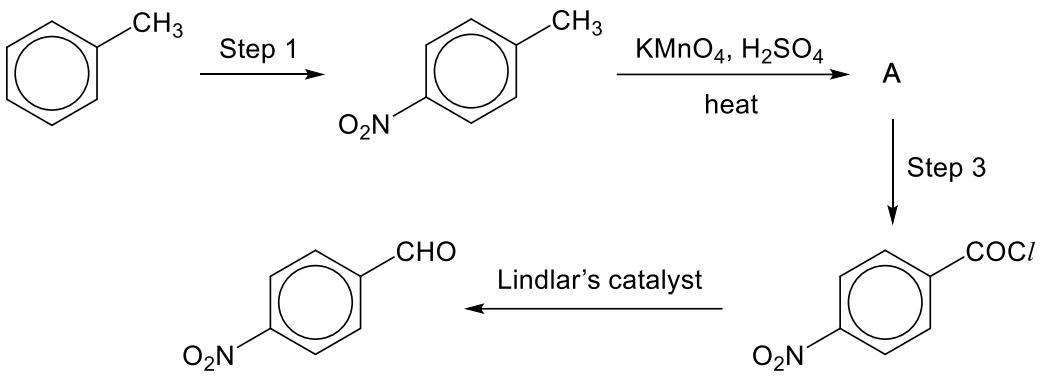
**(c)** The starting material, 4-nitrobenzaldehyde, can be synthesised from methylbenzene as shown below.




**(i)** Draw the structure for **A**. [1]

**(ii)** Suggest the reagents and conditions for Steps 1 and 3. [2]

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**(d)** The β-nitro alcohol formed in the Henry reaction is a versatile compound. It can be dehydrated to give a mixture of two alkenes **D** and **E**, with the molecular formula $C_9H_8N_2O_5$.

**(i)** Suggest the reagent and condition for the dehydration reaction. [1]

**(ii)** Draw the skeletal structures of **D** and **E**. Label the major product and explain your reasoning. [3]

**(iii)** Draw a labelled diagram to show all the valence orbitals of carbon atoms in the C∃C bond in an alkene and show how the orbitals overlap to form the C∃C bond. State the type of hybridisation involved. [2]

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**(e)** Silver nitrite, $AgNO_2$, is a sparingly soluble salt used in the synthesis of nitroalkanes.

**(i)** Write an expression for the solubility product, $K_{sp}$, of $AgNO_2$. [1]

**(ii)** Given the solubility of $AgNO_2$ in water at 0 °C is 0.155 g in 100 $cm^3$ of water, calculate the $K_{sp}$ of $AgNO_2$, stating its units. [2]

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**(f)** Acidified potassium manganate(VII) is reacted with sodium nitrite, $NaNO_2$.

Using the *Data Booklet* and the information below,

$$NO_3^- + 2H^+ + 2e^- = NO_2^- + H_2O \qquad E^\ominus = +0.42\ V$$

**(i)** Calculate the $E^\ominus_{cell}$ of the reaction. [1]

**(ii)** Hence, calculate the standard Gibbs free energy, $\Delta G^\ominus$, of the reaction. [1]

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[Total: 20]

## Additional answer space

If you use the following page to complete the answer to any question, the question number must be clearly shown.

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