BP~3

NANYANG JUNIOR COLLEGE
JC 2 Preliminary Examination
Higher 2

CHEMISTRY

9729/01

Paper 1 Multiple Choice

20 Sep 2022

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.
Write your name, CT and NRIC / FIN on the Answer Sheet in the spaces provided.

There are **thirty** questions in 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.
The use of an approved scientific calculator is expected, where appropriate.

This document consists of **22** printed pages.

[Turn Over

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

Outside the city of Wuwei in China, there is an experimental nuclear reactor that has the potential to generate much smaller amounts of radioactive wastes compared to conventional reactors.

In this reactor, isotopes of thorium-232 are irradiated with neutrons to produce isotope **Q**, which then decompose to form isotope **R**, and finally to uranium-233 in a three-step radioactive decay reaction shown below.

$$^{232}_{90}\text{Th} + ^{1}_{0}\text{n} \longrightarrow \textbf{Q} \longrightarrow \textbf{R} \longrightarrow ^{233}_{92}\text{U}$$

Which row describes:

- the identity of the element of isotope **Q**,
- the neutron number of isotope **R**?

	Q	neutron number of **R**
A	protactinium	142
B	protactinium	141
C	thorium	142
D	thorium	141

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

Which element has the highest 3rd ionisation energy?

A Cd **B** Rb **C** Sr **D** Xe

3 Gallium, atomic number 31, is a silvery blue lustrous solid. It has a low melting point of 29.8 °C, becoming silvery white in the liquid state. Analysis of the crystal structure of gallium shows the existence of only covalent Ga_2 dimers.

Unlike its melting point, gallium has a high boiling point of 2400 °C, similar to other Group 13 elements such as aluminium and indium. Ga_2 dimers are not present in liquid gallium.

Which statements explain the observed melting and boiling points of Gallium?

1 In the liquid state, gallium exist as cations surrounded by a sea of delocalised valence electrons.

2 In the solid state, there are weak instantaneous dipole-induced dipole interactions between Ga_2 dimers.

3 In the solid state, there are strong covalent bonds between Ga atoms.

A 1, 2 and 3 **B** 1 and 2 **C** 2 and 3 **D** 1 only

4 At sea level, an inflated bicycle tyre has an internal pressure of 6.8 bar and a temperature of 30 °C. The instructions on the tyre state 'Safety note: internal pressure must not exceed external pressure by 6 bar.' The atmospheric pressure is 1 bar. The tyre will burst if the difference between the internal pressure and the external pressure becomes too great.

The tyre is placed in the luggage hold of an airliner. The conditions in the luggage hold of this airliner are a temperature of 2 °C and a pressure of 0.47 bar.

Assuming the maximum volume of the tyre does not change, which statement explains what will happen to the tyre in the luggage hold?

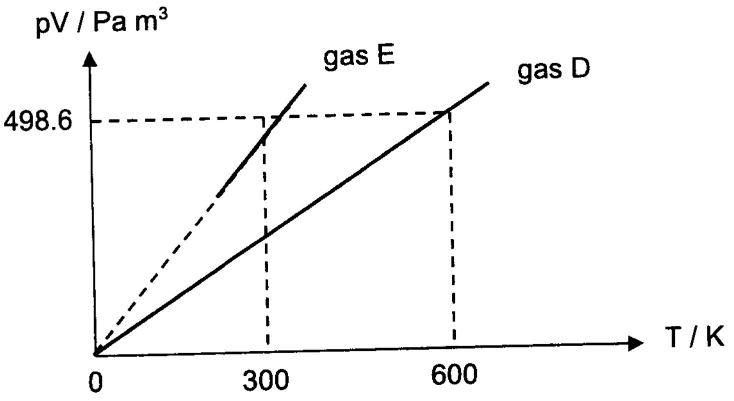
A The tyre will burst as the temperature in the luggage hold will cause the tyre to exceed its maximum allowed temperature.

B The tyre will deflate as its internal pressure will be lower than the air pressure in the luggage hold.

C The tyre will burst as its internal pressure exceeds the air pressure by the maximum allowed.

D The tyre will neither deflate nor burst as the difference between its internal pressure and the air pressure is within the maximum allowed.

5 An experiment was carried out to determine how the pressure and volume of an ideal gas D vary with different temperature. The graph below was obtained.



Which is most likely to be gas E?

A 34.02 g of silicon chloride

B 12.82 g of sulfur dioxide

C 3.100 g of phosphorus

D 0.2000 g of hydrogen

6 Which standard enthalpy change is represented by the correct equation?

A	$C(s) + O_2(g) \rightarrow CO_2(g)$	$\Delta H_f^{\ominus}(CO_2)$
B	$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$	$\Delta H_{neut}^{\ominus}$
C	$K^+(g) \rightarrow K^+(aq)$	$\Delta H_{sol}^{\ominus}(K^+)$
D	$S(g) \rightarrow S^{2-}(g) + 2e^-$	$\Delta H_{2^{nd}EA}^{\ominus}(S)$

7 Which of the following process have different signs for $\Delta G^{\ominus}$ and $\Delta S^{\ominus}$?

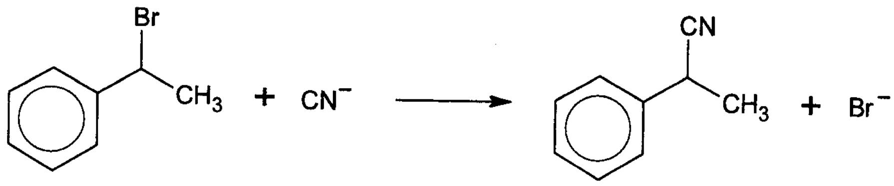
1 $SO_3(l) + H_2O(l) \rightarrow H_2SO_4(aq)$

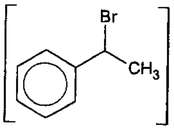
2 $Cl_2(g) + 2I^-(aq) \rightarrow I_2(aq) + 2Cl^-(aq)$

3 $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$

A 1, 2 and 3 **B** 1 and 2 only **C** 2 and 3 only **D** 1 only

8 The reaction of (1-bromoethyl)benzene with sodium cyanide, NaCN, is investigated in a series of experiments.

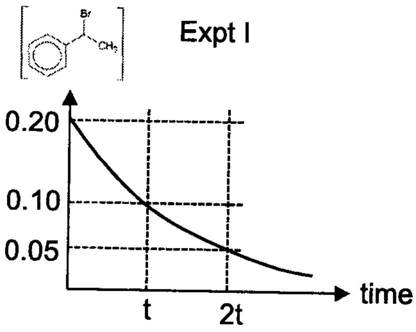


Experiment	 / mol dm^{-3}	[CN$^-$] / mol dm^{-3}
I	0.20	2.00
II	2.00	0.20
III	2.00	2.00

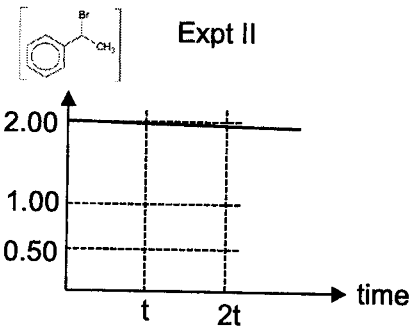
It was known that the reaction is first order with respect to (1-bromoethyl)benzene.

Which graph shows a correct experimental result and proves the reaction is zero order with respect to sodium cyanide?

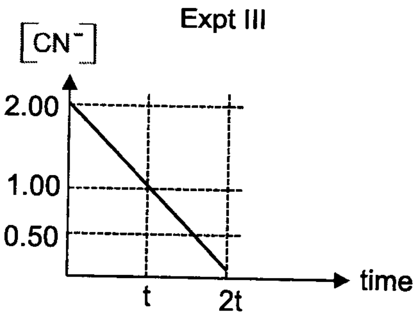
A



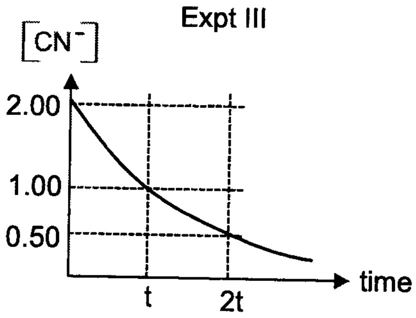
B



C



D



9 In the Haber process, nitrogen and hydrogen is passed over a hot catalyst to produce ammonia.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H < 0$$

Which row correctly describes the operating condition and the possible reason?

[POE – position of equilibrium]

	operating condition	reason
A	500 atm	high pressure to shift POE to the right
B	500 °C	high temperature to increase rate of reaction
C	60 atm	low pressure to shift POE to the right
D	60 °C	low temperature to shift POE to the right

10 The ionic product of water, K_w, is affected by temperature. The table gives the pK_w of pure water at different temperatures.

temperature / °C	pK_w
10	14.5
40	13.5

Solutions of acids and alkalis are prepared by dissolving HCl or NaOH in pure water at 10 °C and at 40 °C.

Which solution has the highest ionic concentration?

A HCl(aq) at pH 1 at 40 °C.

B HCl(aq) at pH 1 at 10 °C

C NaOH(aq) at pH 13 at 40 °C.

D NaOH(aq) at pH 13 at 10 °C.

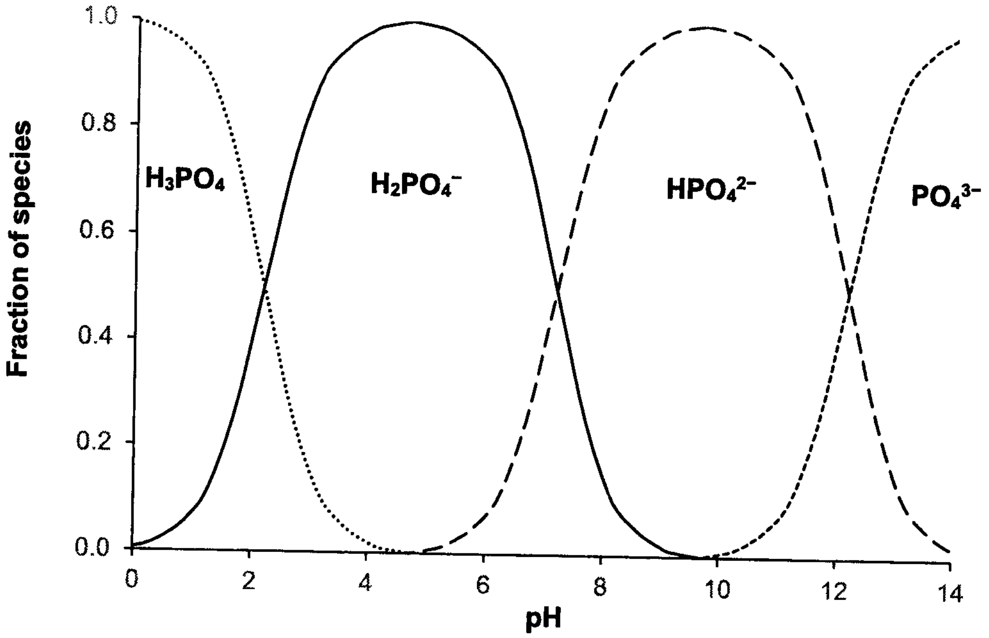
11 Phosphoric acid is a tribasic acid.

$$H_3PO_4 \overset{K_{a1}}{\rightleftharpoons} H_2PO_4^- + H^+$$

$$H_2PO_4^- \overset{K_{a2}}{\rightleftharpoons} HPO_4^{2-} + H^+$$

$$HPO_4^{2-} \overset{K_{a3}}{\rightleftharpoons} PO_4^{3-} + H^+$$

The graph shows the fraction of each species at different pH.



What is the numerical value of K_{a2}?

A 6.3×10^{-3} **B** 2.0×10^{-5} **C** 6.3×10^{-8} **D** 2.0×10^{-10}

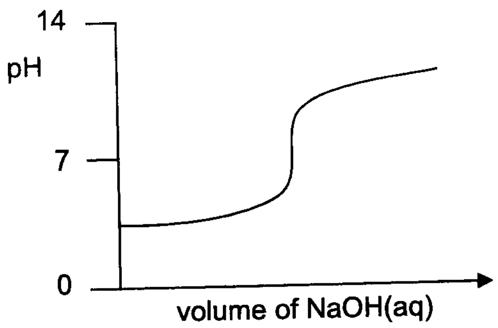
[Turn Over

12 Pyruvic acid is a weak acid that is an important intermediate in many biochemical processes.

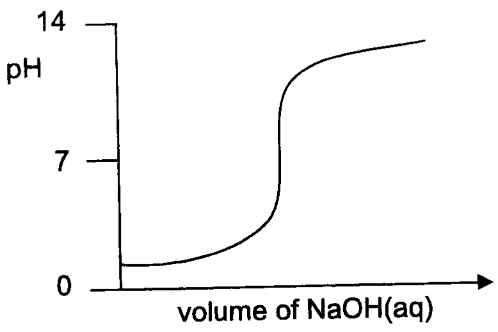
CH_3COCO_2H
pyruvic acid

Which graph best represents the change in pH that occurs when a sample of pyruvic acid is titrated against NaOH(aq)?

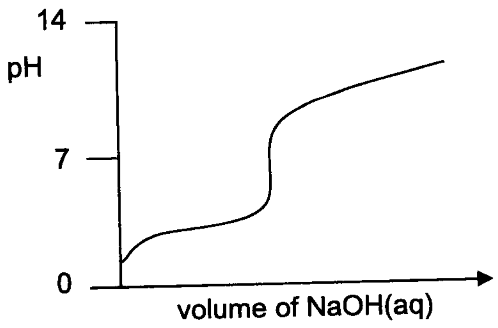
A



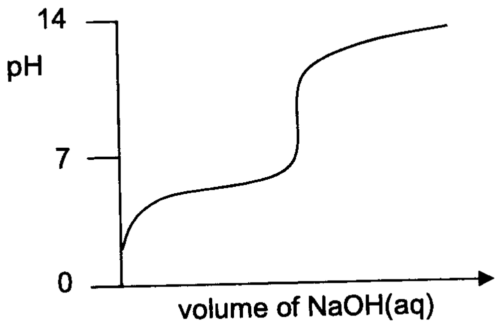
B



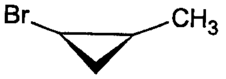
C

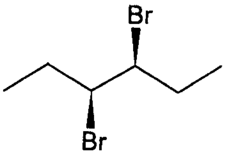


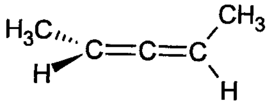
D



13 Which of the following compound will rotate plane-polarised light?

1 

2 

3 

A 1, 2 and 3 **B** 1 and 2 only **C** 2 and 3 only **D** 1 only

14 Low density polyethene, LDPE, is used in the manufacture of plastic bags due to it being lightweight and flexible.

LDPE is produced in an addition reaction. To start the reaction, reactive molecules such as *tert*-butylperoxide, $(CH_3)_3C\text{–}O\text{–}O\text{–}C(CH_3)_3$, is added to the ethene substrate.

step 1: $(CH_3)_3C\text{–}O\text{–}O\text{–}C(CH_3)_3 \rightarrow 2(CH_3)_3C\text{–}O\bullet$

The reactive species, $(CH_3)_3C\text{–}O\bullet$, combined with molecules of ethene resulting in a growing polymer chain.

step 2: $(CH_3)_3C\text{–}O\bullet + (n+1)CH_2{=}CH_2 \rightarrow (CH_3)_3C\text{–}O\text{–}(CH_2CH_2)_nCH_2CH_2\bullet$

The lengthening chain can be stopped by a disproportionation reaction.

step 3: $2(CH_3)_3C\text{–}O\text{–}(CH_2CH_2)_nCH_2CH_2\bullet$
$\rightarrow (CH_3)_3C\text{–}O\text{–}(CH_2CH_2)_nCH{=}CH_2 + (CH_3)_3C\text{–}O\text{–}(CH_2CH_2)_nCH_2CH_3$

Sometimes, chain transfer reactions take place to form branching in the polymer.

step 4: $(CH_3)_3C\text{–}O\text{–}(CH_2CH_2)_nCH_2CH_2\bullet + (CH_3)_3C\text{–}O\text{–}CH_2CH_2CH_2CH_2\text{–}$
$\rightarrow (CH_3)_3C\text{–}O\text{–}(CH_2CH_2)_nCH_2CH_3 + (CH_3)_3C\text{–}O\text{–}CH_2\dot{C}HCH_2CH_2\text{–}$

step 5: $(CH_3)_3C\text{–}O\text{–}(CH_2CH_2)_nCH_2CH_2\bullet + (CH_3)_3C\text{–}O\text{–}CH_2\dot{C}HCH_2CH_2\text{–}$
$\rightarrow (CH_3)_3C\text{–}O\text{–}(CH_2CH_2)_nCH_2CH_2CH(CH_2OC(CH_3)_3)CH_2CH_2\text{–}$

Such branching result in the formation of the low density polymers.

Which statement is **not** correct?

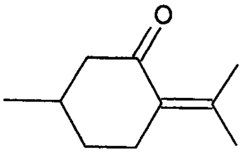
A The formation of LDPE involves free radical addition mechanism.

B The reaction in step 1 involves heterolytic fission.

C The reaction in step 2 is propagation.

D The reaction in step 5 is termination.

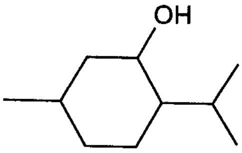
15 Pulegone is an oily liquid with a pleasant odour similar to peppermint.



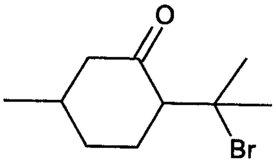
pulegone

Which product is formed from an electrophilic addition reaction with pulegone?

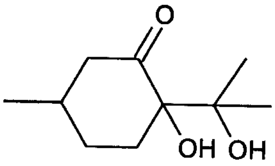
A



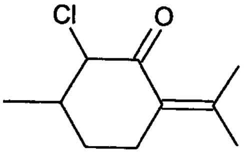
B



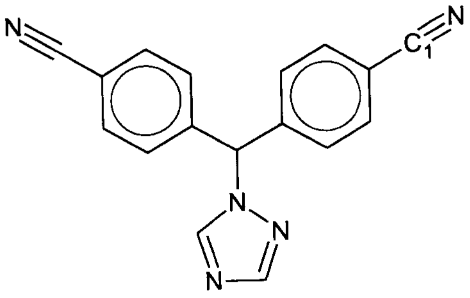
C



D



16 Letrozole is a drug used to treat some forms of breast cancer.



letrozole

Which statements about letrozole are correct?

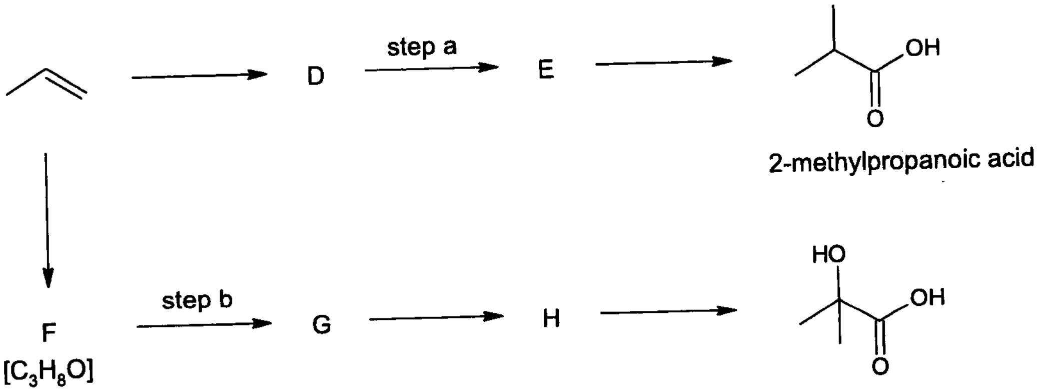
1 There are 14 carbon atoms with bond order 2.

2 Letrozole is a planar molecule.

3 The π electrons on C_1 is delocalised into the aromatic ring.

A 1, 2 and 3 **B** 1 and 3 only **C** 1 only **D** 3 only

17 Propene is the starting reagent for two synthesis pathways as shown below.



2-methylpropanoic acid

2-hydroxy-2-methylpropanoic acid

Which row shows the correct reagent and condition for step a and step b?

	step a	step b
A	NaCN, ethanol, heat	HCl(aq), $K_2Cr_2O_7$(aq), heat
B	PBr_3	$SOCl_2$
C	KCN, ethanol, heat	HCN(aq), trace NaOH(aq), 10 °C
D	CH_3Cl, ethanol, heat in sealed tube	PCl_5

18 Aliphatic halogenoalkanes can undergo bimolecular nucleophilic substitution reaction.

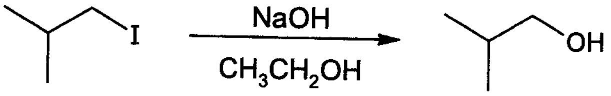
$$R{-}X + OH^- \rightarrow R{-}OH + X^-$$

Some of the factors that affect the reactivity of bimolecular nucleophilic substitution reactions are explained below.

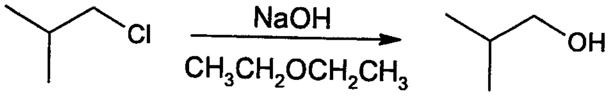
Factor affecting reactivity	Explanation
Steric effect	Bulky groups in reactant molecules blocked the approach of incoming nucleophiles, decreasing reactivity of these reactants.
Solvent effect	Protic solvents containing –OH or –NH groups form hydrogen bonds with ionic reactants, such as OH^-, dispersing the negative charge to a larger extent, decreasing the reactivity of these reactants.

Which hydrolysis reaction should have the fastest rate?

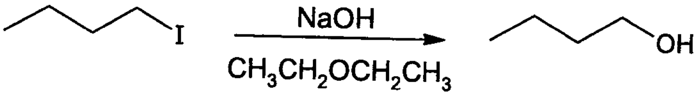
A



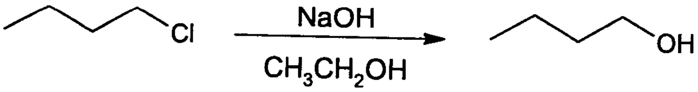
B



C



D



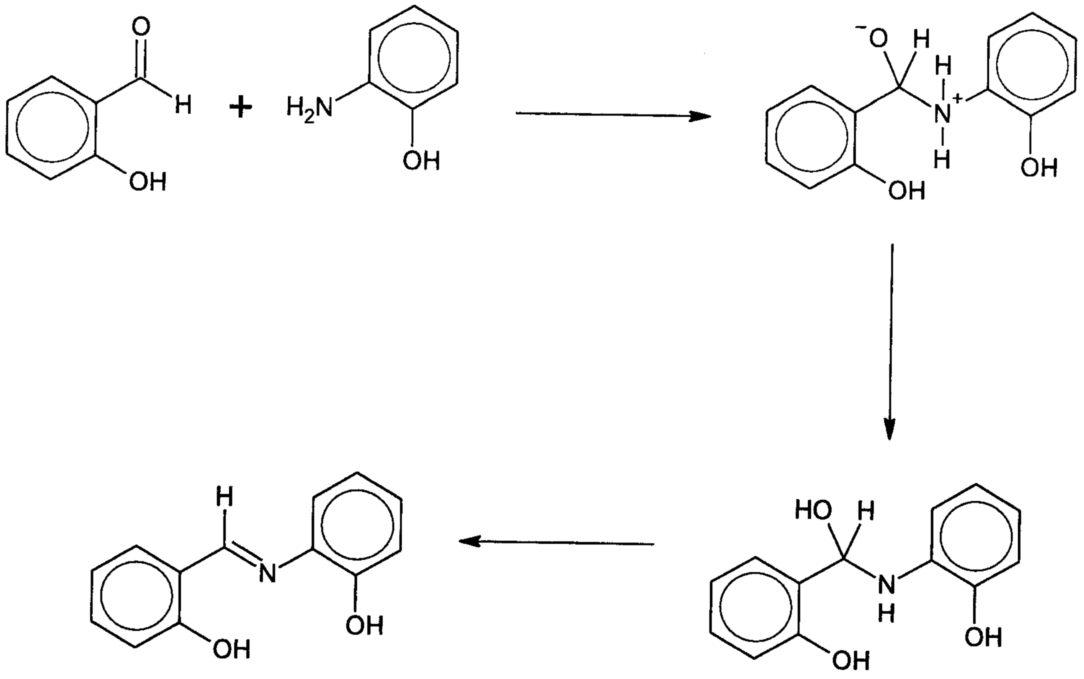
19 Four organic compounds are tested with common reagents found in the laboratory. Only one of the four is known to have an alkene functional group.

In which compound must the alkene be present?

A	$C_6H_{14}O$	• hot acidified $K_2Cr_2O_7$(aq) turns green • effervescence with sodium metal
B	$C_6H_{12}O$	• orange precipitate with 2,4-dinitrophenylhydrazine • decolourise hot acidified $KMnO_4$(aq)
C	$C_6H_{10}O$	• silver mirror with warm alkaline $Ag(NH_3)_2^+$(aq) • decolourise hot acidified $KMnO_4$(aq)
D	C_6H_6O	• decolourise orange Br_2(aq) • dissolves in NaOH(aq)

20 Schiff bases are organic compounds with an imine functional group, C=N. Recent research have shown Schiff bases to have anti-biotic properties.

The following pathway shows the formation of N-(salicylidene)-2-hydroxyphenylamine, a Schiff base with anti-bacterial properties.



N-(salicylidene)-2-hydroxyphenylamine

Which type of reaction is **not** present?

A Acid-base

B Condensation

C Elimination

D Nucleophilic substitution

21 Compound S reacts with concentrated H_2SO_4 to form a compound with molecular formula $C_7H_{10}O_3$.

Compound S also reacts with a warm solution of sodium hydroxide and copper(II)-complex to form a red precipitate and a salt with formula $Na_2C_7H_{10}O_5$.

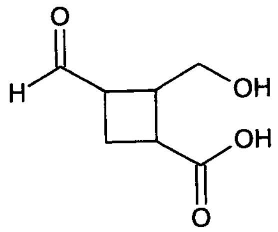
What could be the identity of S?

A $HO_2CCH(OH)C(CH_3)_2CH_2CHO$

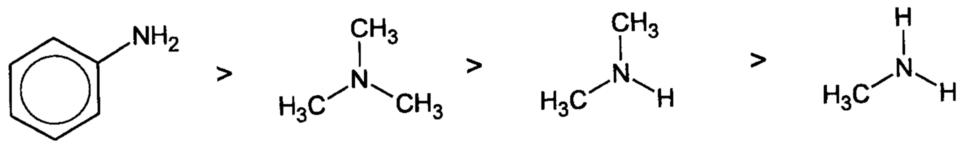
B $HO_2CCH_2C(CH_3)_2CH(OH)CHO$

C $HCOCH_2CH_2CH(OH)CH_2CH_2CHO$

D



22 Amines react with acids in the gas phase to form salts. The relative basic strength follows the order given.



most basic

least basic

Which statements can be used to explain the order of basicity?

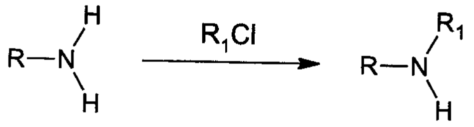
1 Phenyl groups are stronger electron-donating groups than alkyl groups.

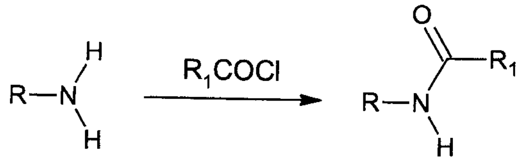
2 Alkyl groups have steric effect.

3 Negative charge on nitrogen atom is dispersed into the benzene ring.

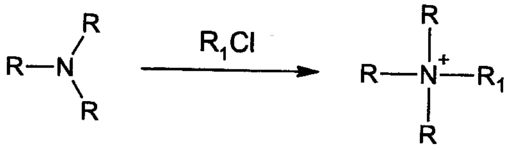
A 1, 2 and 3 **B** 1 and 3 **C** 2 and 3 **D** 1 only

23 A primary amine can undergo alkylation to form a secondary amine or it can undergo acylation to form a secondary amide.

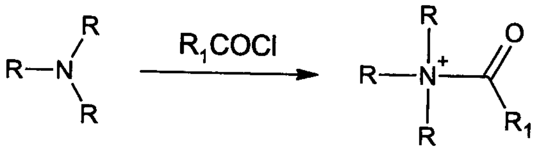




However, a tertiary amine can only undergo alkylation to form a quarternary amine salt. It does not undergo acylation to form the equivalent amide.



quarternary amine salt



no equivalent
quarternary amide salt

Which statement explains why a tertiary amine does **not** undergo acylation?

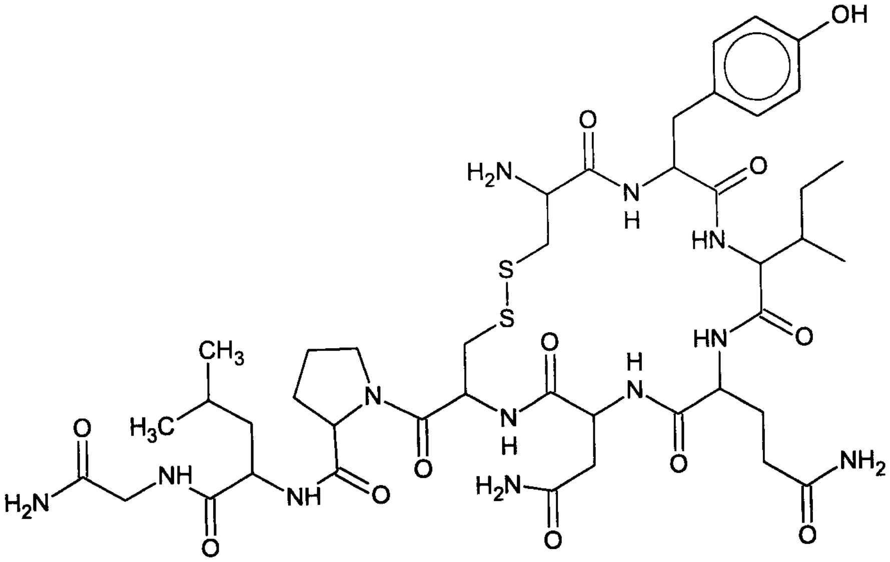
A The acyl group is an electron-withdrawing group unlike an alkyl group.

B An acyl chloride is a weaker electrophile than an alkyl chloride.

C The tertiary amine is a stronger nucleophile than a primary amine.

D There is no N–H bond on a tertiary amine unlike in a primary amine.

24 Oxytocin is a small protein that is involved in childbirth, breastfeeding and maternal behavior. The structure of oxytocin is given below. Two of the amino acids are cysteine, with $-CH_2SH$ side chain. These side chains are joined by a –S–S– bond in oxytocin.



Which two statements about oxytocin are correct?

1 Oxytocin is a nonapeptide.

2 There are eight chiral carbons in oxytocin.

3 In addition to cysteine, three other amino acids have side-chains that can react with hot NaOH(aq).

4 The N-terminal of oxytocin is glycine whose R group is –H.

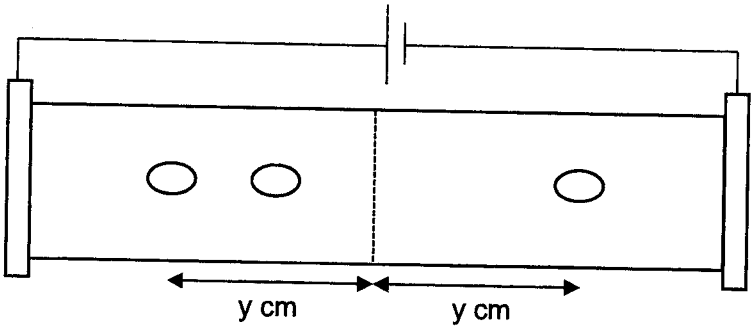
A 1 and 3 **B** 2 and 3 **C** 2 and 4 **D** 1 and 4

25 Electrophoresis is used in the separation and identification of amino acids from peptides hydrolysis.

The distance travelled by each amino acid is given by the relationship:

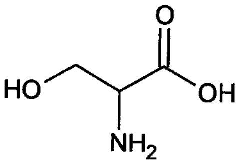
$$\text{distance} \propto \frac{\text{charge}}{\text{molecular mass}}$$

A mixture known to contain three amino acids was separated in a solution buffered at pH 6. The result of the electrophoresis is shown.



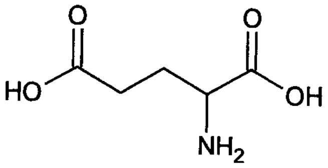
Which amino acid is **not** present?

A



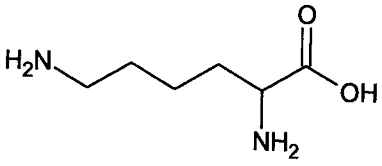
M_r = 105
pI = 5.7

B



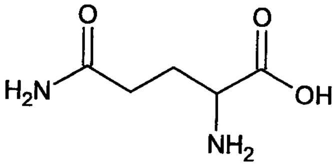
M_r = 147
pI = 3.1

C



M_r = 146
pI = 9.5

D



M_r = 146
pI = 5.7

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

An excess of aluminium powder is added into an acidified solution containing 1 mol dm^{-3} uranium(VI) ions.

Electrode reaction	$E^\ominus$ / V
$UO_2^{2+} + e^- \rightleftharpoons UO_2^+$	+0.16
$UO_2^+ + 4H^+ + e^- \rightleftharpoons U^{4+} + 2H_2O$	+0.27
$U^{4+} + e^- \rightleftharpoons U^{3+}$	−0.52
$U^{3+} + 3e^- \rightleftharpoons U$	−1.66

Assuming all feasible reactions occur quickly, how many moles of aluminium is required to react completely with one mole of uranium(VI) ions?

A 2.00 **B** 1.67 **C** 1.00 **D** 0.67

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

The standard electrode potential, $E^\ominus$, of a half-cell is the maximum potential difference between the electrode of the half-cell and the hydrogen electrode, measured under standard conditions.

Which of the following is one of the conditions necessary to measure the $E^\ominus(MnO_2/Mn^{2+})$ half-cell?

1 298 K

2 100 kPa atmospheric pressure

3 4 mol dm^{-3} $H^+(aq)$

A 1, 2 and 3 **B** 1 and 2 **C** 2 and 3 **D** 1 only

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

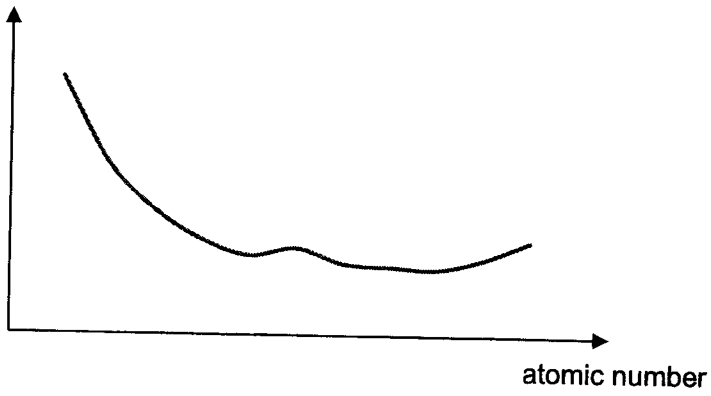
An electrolysis cell is set up with an anode made of an alloy of Cu and Ni and a cathode made of pure Cu. The electrolyte is 1.0 dm^3 of a solution which contains 1.000 mol of $NiSO_4$ and 1.000 mol of $CuSO_4$.

A current of 2.4 A is passed through the cell. After 4.2 hours, the amount of $NiSO_4$ in the electrolyte has increased to 1.047 mol.

What is the decrease in mass of the anode?

A 11.0 **B** 11.7 g **C** 11.9 **D** 23.7

29 The graph below shows a physical property of some consecutive Period 4 elements from K to Zn.



What is the y-axis?

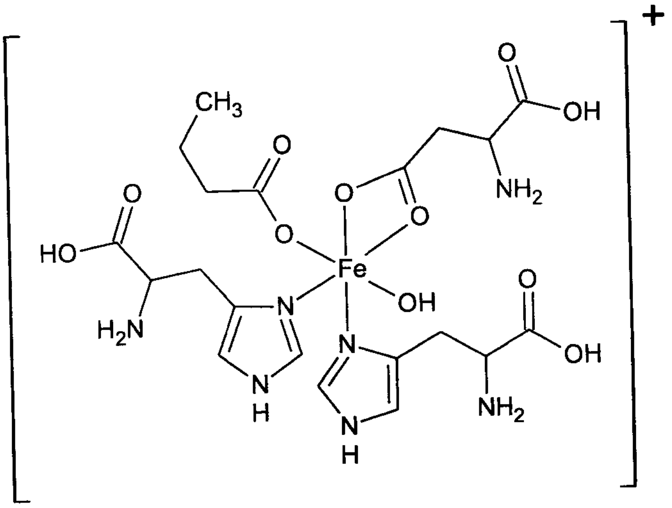
A Atomic radius

B Electrical conductivity

C First ionisation energy

D Melting point

30 Complexes containing Fe are involved in many biochemical reactions. One such complex involved in cellular respiration is shown below.



Two students, J and K, sitting for the A-Levels H2Chemistry examinations in November saw this structure and each made a comment.

student J	The electronic configuration of iron in this complex is definitely [Ar] $3d^4$.
student K	There are definitely five ligands in this complex.

Which students are correct?

A neither J nor K

B J only

C K only

D both J and K

H

NANYANG JUNIOR COLLEGE
JC 2 PRELIMARY EXAMINATION
Higher 2

CANDIDATE NAME

CLASS

TUTOR'S NAME

CHEMISTRY

9729/02

Paper 2 Structured

12 September 2022

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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

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

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	**/15**
2	**/10**
3	**/6**
4	**/24**
5	**/8**
6	**/12**
Total	**/75**

This document consists of **20** printed pages.

[Turn over

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

1(a) **X** and **Y** are oxides of elements in the third period of the Periodic Table. The oxidation number of the Period 3 element in **X** and **Y** is +3 and +5 respectively.

X reacts with both aqueous sodium hydroxide and aqueous hydrochloric acid.

Y reacts with aqueous sodium hydroxide, but not with aqueous hydrochloric acid.

(i) Identify the formulae of **X** and **Y**.

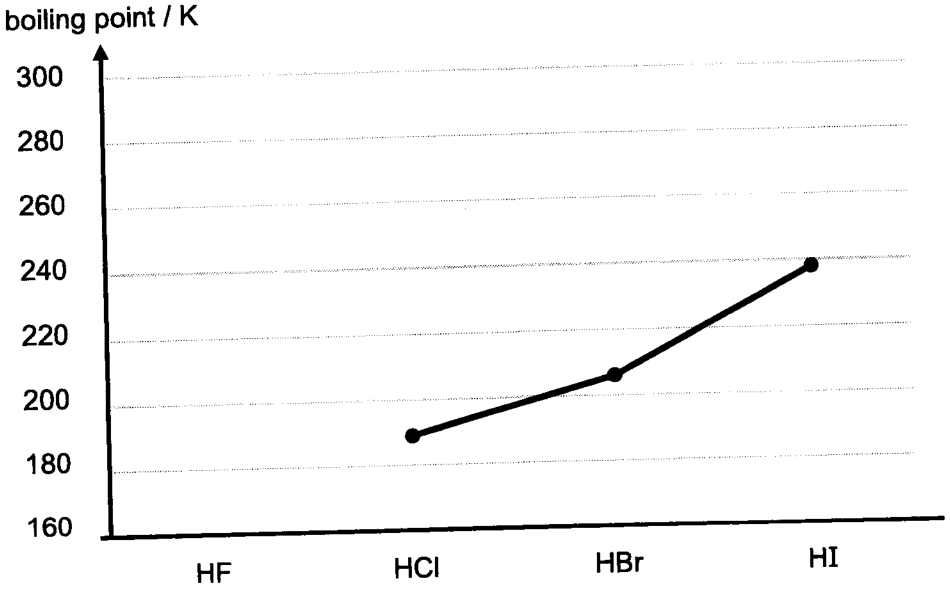
X .... **Y** ....[1]

(ii) Write equations for the reactions of **X** and **Y** with aqueous sodium hydroxide.

X: ....

Y: ....[2]

(b) The graph below shows the boiling points of HCl, HBr and HI.



(i) Explain the trend of the boiling points of HCl, HBr and HI.

....

....

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....

....[2]

(ii) Complete the sketch on page 2 to predict the boiling point of HF. Explain your answer.

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.... [2]

(c) Zinc nitrate decomposes at 300 °C whereas barium nitrate decomposes at 600 °C.

A 20.0 g sample containing a mixture of zinc nitrate and barium nitrate was heated at 350 °C until no further change occurred. A brown gas and another gas that relights glowing splint were evolved. The remaining white solid weighed 11.3 g.

(i) Draw the dot-and-cross diagram for zinc nitrate.

[2]

(ii) Use data from the *Data Booklet*, explain why zinc nitrate decomposes at a much lower temperature than barium nitrate.

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.... [3]

(iii) Write an equation for the reaction that occurred when the sample is heated at 350 °C.

....[1]

(iv) Calculate the percentage composition by mass of zinc nitrate in the sample.

[2]

[Total: 15]

2(a) Oxalic acid, HO_2CCO_2H, is a weak diprotic acid.

$$HO_2CCO_2H \rightleftharpoons HO_2CCO_2^- + H^+ \qquad pK_{a1} = 1.27$$
$$HO_2CCO_2^- \rightleftharpoons {}^-O_2CCO_2^- + H^+ \qquad pK_{a2} = 4.28$$

(i) 10 cm^3 of 0.100 mol dm^{-3} HO_2CCO_2H was mixed with 10 cm^3 of 0.150 mol dm^{-3} HO_2CCO_2Na.

Write an equation to show how this solution is able to maintain pH upon addition of alkali.

.... [1]

(ii) 14.0 cm^3 of 0.100 mol dm^{-3} KOH was added to the solution in **(a)(i)**.

Calculate the pH of the resultant solution after adding KOH(aq).

[3]

(b) Rare earth ions in the oxidation state of +3, such as cerium(III) ions, Ce^{3+}, are used in the production of luminescent materials.

Solutions containing Ce^{3+} ions may sometimes be contaminated by other cations such as Ca^{2+}. The recovery of Ce^{3+} ions from such solutions can be achieved through selective precipitation using oxalic acid as the precipitating agent. After adding oxalic acid to a solution containing Ce^{3+} ions contaminated with Ca^{2+} ions, the pH of the solution is adjusted through the addition of a strong mineral acid. The purpose is to control the concentration of the oxalate anion, $C_2O_4^{2-}$ in the solution and hence ensure that maximum amount of Ce^{3+} ion is precipitated to achieve an effective separation from the contaminant cation.

Table 2.1 contains the values of the logarithm to the base 10 of the equilibrium constant, *K*, for some of the equilibrium reactions.

Table 2.1

Equilibrium equations	lg *K*
$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \rightleftharpoons CaC_2O_4(s)$	8.63
$2Ce^{3+}(aq) + 3C_2O_4^{2-}(aq) \rightleftharpoons Ce_2(C_2O_4)_3(s)$	30.18
$HO_2CCO_2H(aq) \rightleftharpoons 2H^+(aq) + C_2O_4^{2-}(aq)$	–5.06

The numerical values for the solubility product of CaC_2O_4 and $Ce_2(C_2O_4)_3$ are 2.34×10^{-9} and 6.60×10^{-31} respectively.

(i) **Using data from Table 2.1, prove that the numerical value of K_{sp} of CaC_2O_4 is 2.34×10^{-9}.**

[1]

(ii) Solution A contains 0.010 mol dm^{-3} of Ca^{2+}, 0.010 mol dm^{-3} of Ce^{3+} and 1.0 mol dm^{-3} of oxalic acid. Calculate the minimum concentration of $C_2O_4^{2-}$ needed for the precipitation of Ca^{2+} and Ce^{3+} respectively.

[2]

(iii) Using your answers in **(b)(ii)** and data from Table 2.1, calculate the pH of solution A that is required to precipitate the maximum amount of Ce^{3+}.

[3]

[Total: 10]

3 The ideal gas law treats the molecules of a gas as point particles with perfectly elastic collisions. However, many gas molecules do not follow the ideal gas law. Instead of the ideal gas equation, Johannes D. van der Waals suggested a modification to take into account molecular size and molecular interactions. The equation is usually referred to as the van der Waals' equation and it is shown as follows:

$$[p + \mathbf{a}(\frac{n}{V})^2](\frac{V}{n} - \mathbf{b}) = RT$$

Constants **a** and **b** are called van der Waals' constants. They have positive values and are characteristic of the individual gas. If a gas behaves ideally, both **a** and **b** are zero, and the van der Waals' equation approaches the ideal gas equation $pV = nRT$.

Constant **a** provides a correction for the intermolecular forces. Constant **b** adjusts for the volume occupied by the gas particles and is a correction for finite molecular size and its value is the volume of one mole of the atoms or molecules.

The van der Waals' constants of some gases are shown in Table 3.1.

Table 3.1

Gas	**a** (dm^6 atm mol^{-2})	**b** (dm^3 mol^{-1})
N_2	1.37	0.0387
NH_3	4.17	0.0371
N_2H_4	8.46	0.0462

(a) In an experiment, 34 g of NH_3 occupies a 7 dm^3 bottle at 77 °C.

(i) Calculate the pressure of NH_3 in this bottle, in atm, using the ideal gas equation.

[1]

(ii) Calculate a value of the ideal gas constant, R, with units dm^3 atm K^{-1} mol^{-1} at s.t.p.

[1]

[Turn Over

(iii) Using the van der Waals' equation and the value calculated in **a(ii)**, calculate the pressure of NH_3, in atm, in the same bottle.

[1]

(iv) Give a possible reason why the pressure calculated in **(iii)** is more accurate.

....

....

.... [1]

Liquefaction of gases is the condensation of gases into a liquid form. In general, gases with large van der Waals' **a** constants are relatively easier to liquefy.

(b) Explain, in terms of structure and bonding, why this is so by making reference to the gases found in Table 3.1.

....

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.... [2]

[Total: 6]

4(a) The Haber–Bosch process remains the primary industrial route to synthesise ammonia. It involves the breaking of the triple bond in molecular nitrogen at high pressures and temperatures and the hydrogen gas it requires to turn nitrogen to ammonia comes mainly from natural gas.

equation 1 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

This process however is responsible for up to 3% of global CO_2 emissions.

The electrochemical lithium cycling process to make ammonia is a more sustainable approach. It is reported to have achieved an efficiency of 88.5% in lab-scale tests. The process uses electricity, which can have a renewable source, such as wind or solar energy.

In the first stage, the electrolysis of molten lithium hydroxide produces molten lithium metal at the cathode. Oxygen and steam are formed at the anode.

equation 2 $2LiOH(l) \rightarrow 2Li(s) + \frac{1}{2}O_2(g) + H_2O(g)$

(i) Using data from the *Data Booklet*, explain why an aqueous solution of LiOH cannot be used to produce lithium metal by electrolysis.

....

....

.... [1]

The next stage in the process involves gently heating the lithium metal in a stream of nitrogen to produce lithium nitride.

equation 3 $6Li(s) + N_2(g) \rightarrow 2Li_3N(s)$

(ii) Define, with the aid of an equation, lattice energy of lithium nitride.

....

....

.... [2]

(iii) Using the data in Table 4.1 and data from the *Data Booklet*, draw a Born-Haber cycle to calculate a value for the third electron affinity of nitrogen. Show your working clearly.

Table 4.1

	value / kJ mol^{-1}
sum of 1st and 2nd electron affinity of N	+680
lattice energy of Li_3N	–4830
enthalpy change of sublimation of Li: $Li(s) \rightarrow Li(g)$	+161
enthalpy change of reaction for the following reaction: $6Li(s) + N_2(g) \rightarrow 2Li_3N(s)$	–330

[3]

The last stage in the process involves reacting lithium nitride with water. A solution containing ammonia and lithium hydroxide is produced.

equation 4 $Li_3N(s) + 3H_2O(l) \rightarrow 3LiOH(aq) + NH_3(g)$

The ammonia produced can be removed by heating the solution. Evaporation of the remaining water gives solid lithium hydroxide, which can be recycled in the electrolytic cell.

(iv) The following equation represents the overall equation for electrochemical lithium cycling process.

$$\_\_\_N_2 + \_\_\_H_2O \rightarrow \_\_\_O_2 + \_\_\_NH_3$$

Complete the balancing of the above equation. Show your working clearly.

[1]

The standard Gibbs free energy changes of formation, $\Delta G_f^\ominus$, of several compounds are listed in Table 4.2.

Table 4.2

compound	$\Delta G_f^\ominus$ / kJ mol^{-1}
$LiOH(s)$	–439
$Li_3N(s)$	–137
$H_2O(l)$	–237
$NH_3(g)$	–17

(v) Using your equation in **a(iv)**, calculate the standard Gibbs free energy change, $\Delta G^\ominus$, when 2 mol of ammonia are produced.

[1]

(vi) Calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for the Haber-Bosch process shown in equation 1. By considering the stability of the reactants and products, explain why this value is different from that calculated in **a(v)**.

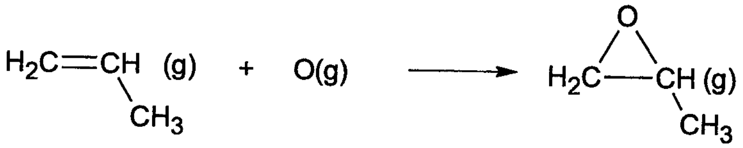
....

....

.... [2]

(b) An epoxide is a cyclic ether (C–O–C) that is highly reactive. Like all compounds containing a 3-membered ring, the bonds in 1,2-epoxypropane are weaker. This can be illustrated by the following calculation, in which you can assume that the C–H bond energy is the same in propane and 1,2-epoxypropane.

The $\Delta H^{\ominus}$ for the reaction between propene molecules and oxygen atoms has been calculated to be –363 kJ mol^{-1}.



(i) Use the data from the *Data Booklet* to calculate a theoretical value for the sum of the C–C and 2 × C–O bond energies in 1,2-epoxypropane.

[1]

(ii) Use the $\Delta H^{\ominus}$ value for the reaction between propene and oxygen atoms given above to calculate the actual value for the sum of the C–C and 2 × C–O bond energies in 1,2-epoxypropane. Suggest an explanation for the difference between the theoretical and actual values.

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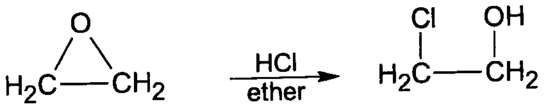
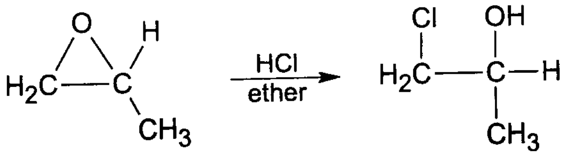
.... [2]

(c) The bonds in epoxides can be broken by reacting with anhydrous hydrogen halide. For example, when anhydrous HCl is used in ether solvent, the epoxide forms a halohydrin.



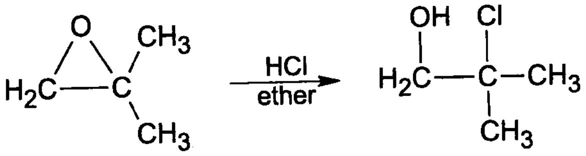
The ring–opening reaction of epoxides can proceed by either S_N1 or S_N2 mechanism, depending on the nature of the epoxide and the reaction conditions. If the epoxide is asymmetric, the structure of the product will vary according to which mechanism predominates. For example, 1,2-epoxypropane and 2-methyl-1,2-epoxypropane reacts with HCl via different mechanisms to give the following major products.

Reaction 1



1,2-epoxypropane

Reaction 2



2-methyl-1,2-epoxypropane

(i) Explain why the reaction proceeds via the given predominant mechanism and not the other.

Type of mechanism for reaction 1: S_N2

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Type of mechanism for reaction 2: S_N1

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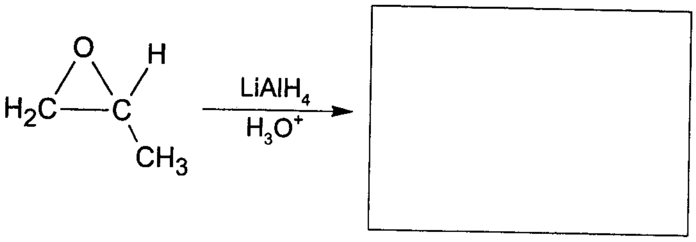
.... [3]

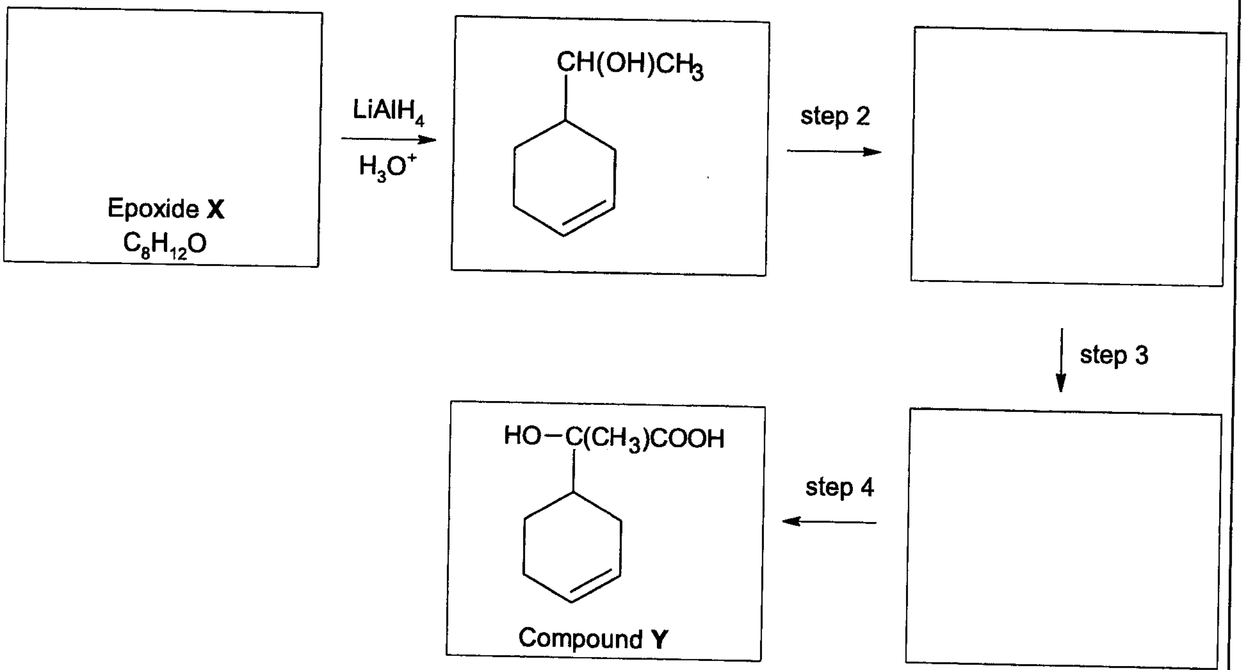
Basic nucleophiles such as hydride ions, H^- can also be used for the ring-opening of epoxides. S_N2 mechanism usually predominates with these reagents.

(ii) Draw the structural formula of the major product formed when 1,2-epoxypropane reacts with $LiAlH_4$.



[1]

(iii) Compound **Y** can be formed via a four-step synthesis with epoxide **X** as the starting material. Draw the structures of the reaction intermediates and state the reagents and conditions for each step.



step 2: ....

step 3: ....

step 4: .... [6]

(iv) A small amount of a sweet-smelling side product, $C_{18}H_{24}O_4$, is formed in step 4. Draw the structure of this side product.

[1]

[Total: 24]

5(a) **(i)** Complete the electronic configurations for copper atom and its copper(II) ion.

Cu $1s^2$ ....

Cu^{2+} $1s^2$ .... [1]

(ii) The copper used for electrical wiring must be very pure. An impure copper bar containing silver and zinc impurities is purified by electrolysis. Describe the electrode reactions that take place and explain in detail how each of the two impurity metals is removed.

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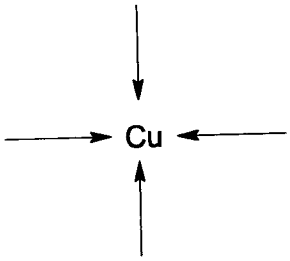
.... [3]

(b) Copper(II) ions will form a complex with the basic form of the amino acid glycine as the ligand. The formula of this complex may be written as $Cu(CH_2(NH_2)CO_2)_2$.

Complete the diagram to suggest the structure for this complex.



[1]

(c) Describe and explain what you would see when NH_3(aq) is added slowly to a solution of copper(II) nitrate, until the NH_3(aq) is in an excess. Write equations for any reactions that occur.

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.... [3]

[Total: 8]

6 Compound **W** has the molecular formula C_7H_7OCl. It is an aromatic compound which contains two functional groups.

Data about the reactions of **W** are given in the table.

reaction	reagent	result
1	$AgNO_3$(aq), warm	white solid formed which is soluble in an excess of NH_3(aq)
2	Br_2(aq) in an excess	white solid formed which has $M_r = 379.2$
3	MnO_4^-/ OH^- heat under reflux then acidify	MnO_4^- is decolourised; one organic product formed with $M_r = 138$
4	Na	colourless gas evolved; white solid formed which is soluble in H_2O
5	NaOH(aq) at room temperature	colourless solution formed

In this question, when identifying functional groups, your answers should be unambiguous.

(a) **(i)** Name the functional group that reaction **1** shows to be present in **W**.

.... [1]

(ii) Based only on reaction **4**, give the names of two different functional groups that could be present in **W**.

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

(iii) Which of the functional groups you have named in **(ii)** is confirmed by reaction **5**? Explain your answer.

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.... [2]

(b) **(i)** Deduce the molecular formula of the white solid formed in reaction **2**.

[1]

(ii) Explain clearly how the formation of this compound shows that compound **W** is an aromatic compound rather than an aliphatic compound.

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.... [2]

(iii) Which other reaction confirms that **W** is aromatic? Explain your answer.

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....

.... [1]

(c) You now have enough information to determine the structural formula of **W**.

(i) Draw the fully displayed structure of **W**.

[2]

(ii) Explain clearly why you have placed **each** of the two functional groups in their particular positions.

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.... [2]

[Total:12]

[End of Paper]

H

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME	

CLASS		TUTOR'S NAME	

CHEMISTRY

Paper 3 Free Response

9729/03

15 September 2022

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Answer **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** questions.

Section B
Answer **one** question. Circle the question you attempted in the box below.

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

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	**/25**
2	**/15**
3	**/20**
4 or 5	**/20**
Total	**/80**

This document consists of **32** printed pages.

[Turn over

Section A

Answer **all** questions in this section.

1 This question is about alkene and diene. Diene is an unsaturated compound containing two double bonds between carbon atoms.

(a) Table 1.1 shows the structures of hexa-1,2-diene, hexa-1,3-diene and hexa-1,5-diene.

Table 1.1

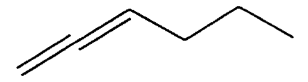	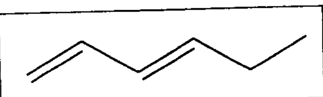	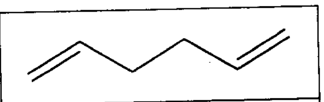
hexa-1,2-diene	hexa-1,3-diene	hexa-1,5-diene

Table 1.2 shows the enthalpy change of combustion of some organic compounds.

Table 1.2

substance	**ΔH_c / kJ mol^{-1}**	**$\Delta H_{hydrogenation}$ / kJ mol^{-1}**
Liquid hexa-1,2-diene	–3867	ΔH_1
Liquid hexa-1,3-diene	–3816	–225
Liquid hexa-1,5-diene	–3843	–252
Liquid hexane	–4163	NA
Hydrogen gas	–286	NA

(i) Use data in Table 1.2 to draw an energy level diagram to calculate the enthalpy change of hydrogenation of hexa-1,2-diene, ΔH_1. [2]

(ii) Suggest which isomer, hexa-1,3-diene or hexa-1,5-diene, is more stable using data in Table 1.2. Explain your answer by considering the type of orbitals present in the carbon atoms of the isomer. [2]

(iii) Choose a suitable isomer of hexadiene from Table 1.1 and devise a three-step synthetic route to synthesise buta-1,3-diene. [5]

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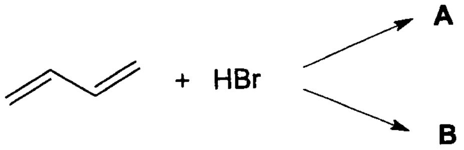
(b) When buta-1,3-diene undergoes electrophilic addition reaction with 1 mol of HBr, a mixture of two products, **A** and **B** is formed. Both **A** and **B** have molecular formula of C_4H_7Br.



A exhibits cis-trans isomerism while **B** contains a chiral centre.

(i) Draw the structures of **A** and **B**. [2]

(ii) By referring to your structure in **(b)(i)**, explain how cis-trans isomerism arises in **A**. [2]

Kinetic and thermodynamic factors decide the type of addition product that is obtained. **A** is known as the kinetic product as it is formed faster while **B** is known as the thermodynamic product as it is formed more slowly and is also more thermodynamically stable than the kinetic product.

(iii) In a **single** set of axis, sketch and label two reaction pathway diagrams for the second step of the mechanism to form **A** and **B** respectively. The carbocation intermediates used to form **A** and **B** occupy the same energy level. Use E_{a1} and E_{a2} to label the activation energies and ΔH_1 and ΔH_2 to label the enthalpy changes to form **A** and **B** respectively. [2]

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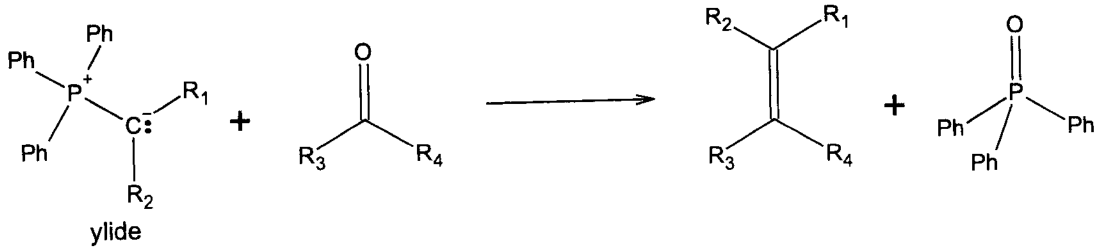
(c) The Wittig reaction is an organic chemistry synthesis technique that involves the conversion of carbonyl compounds into alkenes using an ylide as the reagent and via a nucleophilic addition pathway.



where Ph is phenyl and R_1, R_2, R_3, and R_4 is either H atom or alkyl group

Fig 1.1: The Wittig reaction

Ylides can be synthesised from triphenyl phosphine and an alkyl halide. The first step is to react the triphenyl phosphine and alkyl halide via a nucleophilic substitution reaction. This step is an elementary reaction. The second step is to add a very strong base such as butyl lithium, $CH_3CH_2CH_2CH_2^-Li^+$ to deprotonate the intermediate product formed in step 1.

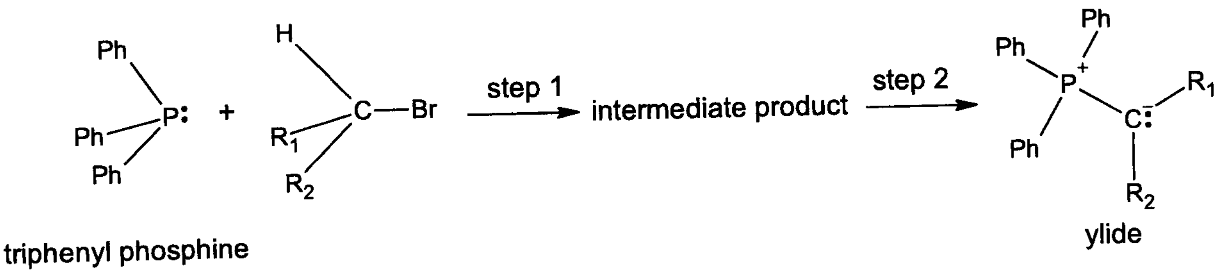


Figure 1.2: Synthesis of ylide

(i) Draw the full structural formula of the intermediate product for the reaction shown in Fig. 1.2 when R_1 is hydrogen atom and R_2 is methyl group. [1]

(ii) Predict the organic products **L** and **M** of the reactions shown in Fig. 1.3. [2]

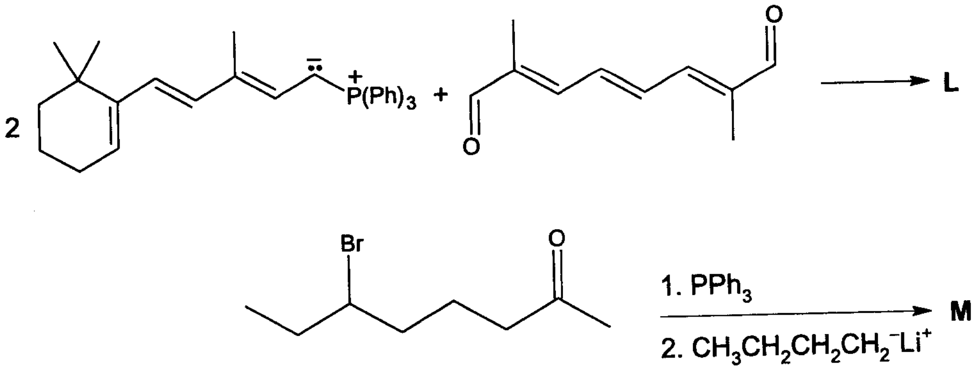


Fig. 1.3

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(d) Coumarin, $C_9H_6O_2$, is a colourless crystalline solid with a sweet odour resembling the scent of vanilla. It is formed when compound **T**, $C_9H_7O_3Br$ is treated with triphenyl phosphine followed by a strong base.

Both coumarin and **T** are neutral.

When heated with aqueous sulfuric acid, **T** gives **U**, $C_7H_6O_2$ and **V**, $C_2H_3O_2Br$.

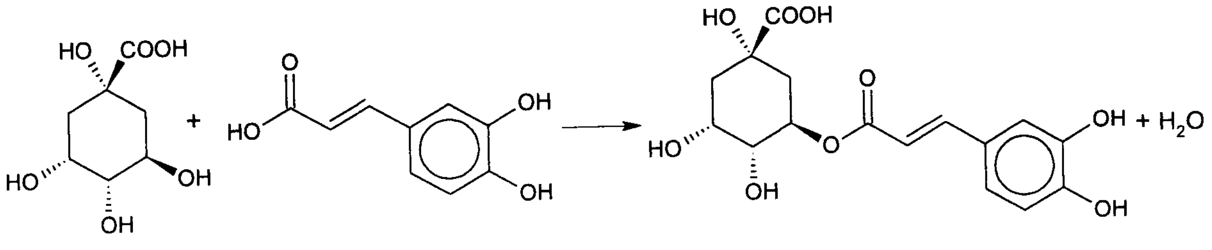
U reacts with 2 moles of aqueous bromine to give a white ppt and forms a silver mirror with Tollens' reagent.

Both **T** and **U** do not rotate plane-polarised light.
Both **U** and **V** "pop" with a lighted splint when treated with Na metal.

Deduce the structures of compounds **T**, **U**, **V** and coumarin, explaining the observations described. [7]

[Total: 25]

2 Green coffee beans contain chlorogenic acid. It is an ester formed from quinic acid and caffeic acid.

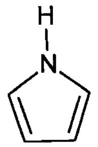


quinic acid caffeic acid chlorogenic acid

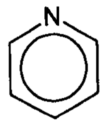
(a) Describe a simple chemical test to distinguish quinic acid and caffeic acid. State what you would observe for **each** compound. [2]

(b) During roasting, chlorogenic acid readily decomposes to quinic acid and caffeic acid. Quinic acid creates bitterness and astringency thus the very dark roasts taste bitter.

After roasting, there are more than 1000 volatile compounds found in coffee. However, there are only 20 – 30 volatile compounds that contributed to the perceived aroma. These include aldehydes, ketones, carboxylic acids, esters, pyrroles, and pyridines.



pyrrole

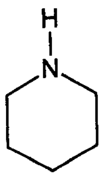


pyridine

(i) Given that both pyrrole and pyridine are aromatic and the nitrogen atoms in pyrrole and pyridine are sp^2 hybridised, explain why pyrrole is a weaker base than pyridine.

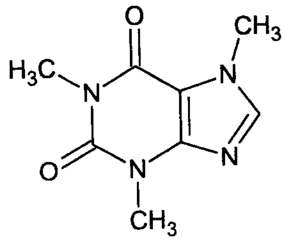
You may draw a labelled diagram to illustrate all the orbitals on nitrogen atom in pyrrole. Identify the orbital which the lone pair of electrons on nitrogen atom resides. [3]

(ii) State the type of hybridisation of nitrogen atom in piperidine. Hence, explain the relative basicity of piperidine and pyridine. [2]



piperidine

(c) Caffeine is a natural stimulant found in coffee and tea. It is soluble in water.



caffeine (M_r = 194.0)

(i) Draw a labelled diagram to show how a water molecule can be attached to a caffeine molecule. [2]

(ii) Draw the structural formula of the organic products when caffeine is heated with aqueous sodium hydroxide. [3]

(iii) Decaffeinated coffee and tea are made by extracting the caffeine from solid coffee or tea using a solvent.

Suggest a reason, which of the following industrial solvents would be most suitable. [1]

- benzene
- cyclohexane
- liquid carbon dioxide

(iv) Caffeine can also be added to cola drinks. A can of cola contains 50 mg of extracted caffeine in a volume of 330 cm^3. Calculate the concentration of caffeine in mol dm^{-3}. [2]

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[Total: 15]

3 Hydrogen peroxide decomposes according to the equation below.

$$2H_2O_2(aq) \rightarrow O_2(g) + H_2O(l)$$

There are several ways to monitor the decomposition reaction of hydrogen peroxide by a catalyst.

(a) The decomposition of hydrogen peroxide has been shown to have first order kinetics. It was found that 10 % of hydrogen peroxide was left after 9 hours.

(i) Determine the half-life of hydrogen peroxide. [1]

(ii) Hence, determine the rate constant, *k*, of the reaction. [1]

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(b) **(i)** Sketch the graph of rate against [H_2O_2] for the reaction. [1]

(ii) This reaction is significantly faster when a particular enzyme is used. On the same axes, as the graph in **b(i)**, show how the rate of reaction would be affected by the presence of a very small amount of the enzyme. Label this line clearly as "in the presence of enzyme". [2]

(iii) Explain the relationship between [H_2O_2] and the rate of the enzyme catalysed reaction. [2]

(c) A sample of iron(III) nitrate solution is added to a solution of hydrogen peroxide. It was found that upon mixing of the chemicals, vigorous effervescence was observed. The yellow iron(III) solution turned brown upon mixing and after a while, the colour of the mixture turned yellow again.

(i) The solution of iron(III) was found to give a dark orange colour with universal indicator. Explain this observation with the use of a relevant equation. [2]

(ii) A possible mechanism for the iron(III) catalysed decomposition of hydrogen peroxide, is provided below. In this mechanism, the HO_2^- ligand on one of the complex ions represents the H–O–O⁻ ion and the O represents an oxygen atom.

Step 1 $[Fe(H_2O)_6]^{3+}(aq) + H_2O_2(aq)$ Ý $[Fe(H_2O)_5(HO_2)]^{2+}(aq) + H_3O^+(aq)$

Step 2 $[Fe(H_2O)_5(HO_2)]^{2+}(aq) \rightarrow OH^-(aq) + [Fe(H_2O)_5O]^{3+}(aq)$

Step 3 $[Fe(H_2O)_5O]^{3+}(aq) + H_2O_2(aq) \rightarrow [Fe(H_2O)_6]^{3+}(aq) + O_2(g)$

Step 4 $H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l)$

Explain fully how you can tell that the $[Fe(H_2O)_6]^{3+}$ ion is acting as a catalyst in this reaction, using evidence from the observations provided in **(c)** and the mechanism. [2]

(iii) The transition metals such as iron tend to have variable oxidation states, whereas s-block elements such as calcium do not. Suggest an explanation for this difference. [2]

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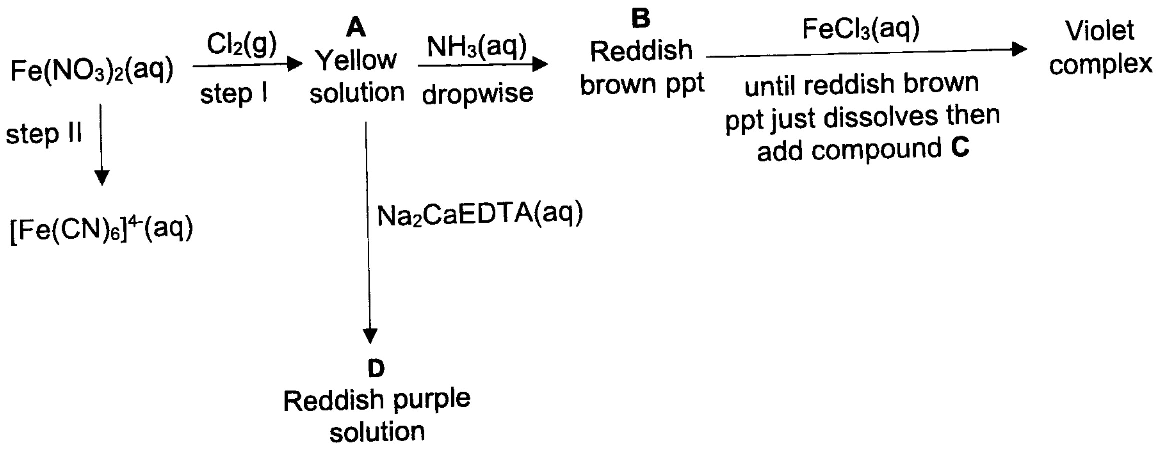
(d) The following scheme shows the reactions of iron and its compounds.



(i) Identify compounds **B** and **C**. [2]

(ii) Explain why **A** and **D** have different colours. [2]

(iii) Write an ionic equation for the formation of **D** from **A**. [1]

(iv) State the types of reactions that occurred in steps I and II. [2]

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[Total: 20]

Section B

Answer **one** question from this section.

4 Glucose comes from the Greek word for "sweet". It is the simplest carbohydrate with molecular formula $C_6H_{12}O_6$ and is the major free sugar circulating in the blood of mammals, serving as the primary source of energy for cell function.

(a) The oxidative breakdown of glucose by our body to produce energy is called respiration. The reaction for the complete combustion of glucose is

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$$

$$\Delta H^{\ominus} = -2816\ \text{kJ mol}^{-1}$$

$$\Delta S^{\ominus} = +181\ \text{J mol}^{-1}\ \text{K}^{-1}$$

(i) Write a half-equation to represent the oxidative breakdown of glucose. [1]

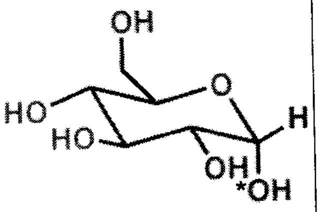
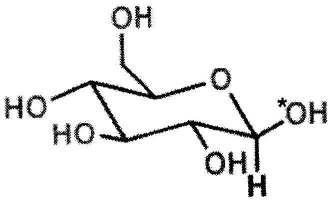
(ii) The energy value of food is measured in Calorie. One Calorie is defined as the amount of heat needed to raise the temperature of 1 kg of water by 1 °C. Use the given information, together with data from the *Data Booklet*, to calculate the number of Calories in 1 g of glucose. [2]

(iii) Comment on the sign of $\Delta S^{\ominus}$ for the combustion of glucose. [1]

(iv) If this combustion reaction could be harnessed as a fuel cell, calculate $\Delta G^{\ominus}$ and hence the theoretical voltage, $E^{\ominus}_{\text{cell}}$, that could be produced under standard conditions. [3]

Glucose exists in two forms, α-glucose and β-glucose, with the *OH group occupying different spatial arrangement in each form. Some information about the two forms is given in Table 4.1.

Table 4.1

	α-glucose	**β-glucose**
		
Melting point / °C	146	150
Angle of rotation of plane-polarised light for a 1 mol dm^{-3} sample / °	+20.2	+3.4

(b) **(i)** Suggest a reason for the difference in melting points between α-glucose and β-glucose. [1]

If a solution of α-glucose is left for some time, it will come into dynamic equilibrium with β-glucose.

$$\alpha\text{-glucose} \rightleftharpoons \beta\text{-glucose}$$

(ii) Explain what is meant by *dynamic equilibrium*. [1]

(iii) 1 dm^3 of a freshly prepared solution of 1.0 mol dm^{-3} solution of α-glucose is left to stand at 298 K. At equilibrium, the solution was found to rotate plane-polarised light by +9.45 °. Given angle of rotation of plane-polarised light is directly proportional to concentration of isomer, use information from Table 4.1 to determine [β-glucose] at equilibrium. [1]

(iv) Hence calculate the value of the equilibrium constant, K_c, for the conversion of α-glucose to β-glucose at 298 K. If you were unable to determine [β-glucose] at equilibrium, assume the value is 0.60. Note 0.60 is **not** the correct answer for **(b)(iii)**. [1]

(v) The conversion of α-glucose into β-glucose is catalysed by acids. What will be the effect on the equilibrium position if the conversion is now carried out in the presence of dilute sulfuric acid? Explain your answer. [1]

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(c) Fig. 4.1 shows the mechanism for the conversion of α-glucose into β-glucose.

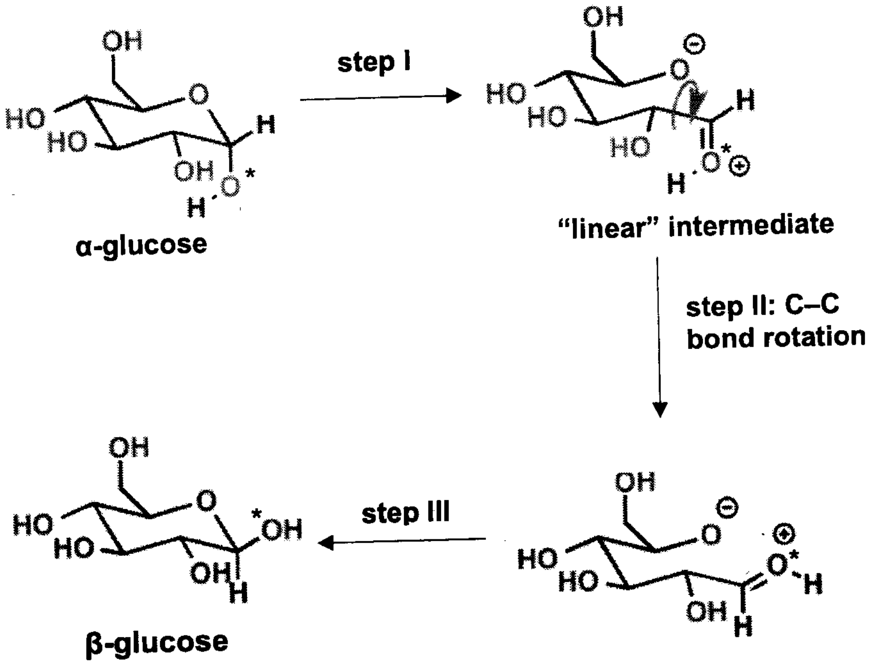

Fig. 4.1

(i) Explain, with reference to the Valence Shell Electron Pair Repulsion theory, why the bond angle around O^* increases in step I of the mechanism. [2]

(ii) Complete Fig. 4.1 to suggest the mechanism for steps I and III. Show all relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]

(iii) Suggest the types of reaction taking place in steps I and III. [2]

(iv) A proton transfer can occur between the charged groups in the "linear" intermediate to form another stable electrically neutral intermediate. Identify the new functional group present in this other intermediate and hence suggest a suitable chemical test to confirm its presence during the conversion of glucose. [2]

[Total: 20]

5(a) Table 5.1 lists the pK_a values for some weak acids.

Table 5.1

Compound	pK_a
H_2S	7.05
H_2O_2	11.7
H_2O	14.0

(i) Using the data provided, and given that NaSH is a weak base, calculate the pH of 0.10 mol dm^{-3} NaSH solution. [2]

(ii) Suggest an explanation for the different pK_a values for H_2S, H_2O_2 and H_2O. [2]

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(b) Hydrogen peroxide acts as an oxidising agent in both acidic and alkaline conditions.

(i) Using suitable data from the *Data Booklet*, calculate the $E^\ominus_{cell}$ for the oxidation of Fe(II) ions by hydrogen peroxide under the two conditions. [2]

(ii) Hence, calculate $\Delta G^\ominus$ for the two reactions, and deduce whether the oxidation of Fe(II) ions by hydrogen peroxide is more feasible under acidic or basic conditions. Explain your answer. [2]

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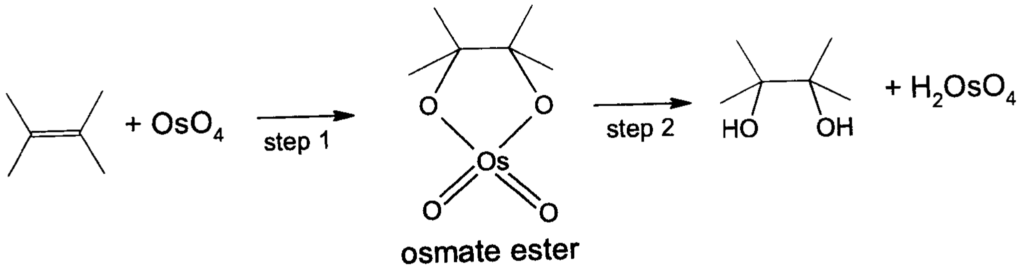
(c) Osmium, Os, is a hard, brittle, bluish-white transition metal that is found as a trace element in alloys. Osmium is among the rarest elements in the Earth's crust, making up only 50 parts per trillion (ppt). Osmium tetroxide, OsO_4, is a mild oxidant and oxidises alkenes to give excellent yields of vicinal diols as shown in Fig. 5.1.

- Osmium tetroxide reacts with alkenes to form an osmate ester,
- which then reacts with water to form the vicinal diols in good yields.
- $NaIO_4$, sodium periodate is added to regenerate osmium tetroxide, thus permitting the use of this expensive and toxic reagent in minimum amounts.



$$H_2OsO_4 + IO_4^- \xrightarrow[\text{step 3}]{} OsO_4 + IO_3^- + H_2O$$

Fig. 5.1

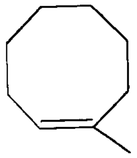
The oxygen atoms add to the same face of the C=C bond. Thus, OsO_4 forms vicinal diols by *syn* addition.

(i) Using VSEPR (valence shell electron pair repulsion) theory, state and explain the bond angles in OsO_4 and IO_3^-. [3]

(ii) Explain why OsO_4 is expected to be very volatile. [1]

(iii) Step 1 in Fig. 5.1 is initiated by an electrophilic attack on OsO_4 by the alkene.

Write out an equation and draw curly arrows to show how the osmate ester intermediate is formed if the alkene is 1-methyl-1-cyclooctene. In your answer, use hash and wedge bonds to show the stereochemistry of the ester intermediate. [3]

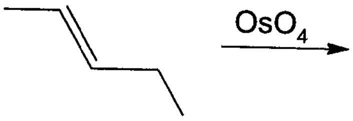


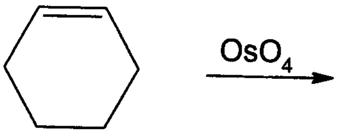
1 –methyl–1–cyclooctene

(iv) By considering the structural formulae and reagents shown above, suggest the type of reaction taking place in step 2 in Fig. 5.1. [1]

When an alkene reacts with osmium tetroxide, stereocenters can form in the diol product. Cis alkenes give meso products and trans alkenes give racemic mixtures. Meso compounds contain 2 or more chiral centres, but they are achiral and have a internal plane of symmetry.

(v) Give the skeletal formulae of the products (including all stereoisomers) of the following reactions. Indicate the presence of any chiral centres in the products with an asterisk *.





[4]

[Total: 20]

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Additional answer space

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

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JC2 PRACTICAL PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME

CLASS	2	1			
CENTRE NUMBER	S				

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CHEMISTRY

Paper 4 Practical

9729/04

18 August 2022

2 hour 30 minutes

Candidates answer on the Question Paper

Additional Materials: As listed in the Confidential Instructions

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Give details of the practical shift and laboratory, where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 19 and 20.

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.

Shift
Laboratory

For Examiner's Use	
1	/ 17
2	/ 16
3	/10
4	/ 12
Total	/55

This document consists of **20** printed pages and **0** blank pages.

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

1 An investigation of the chemistry of some vanadium ions

FA 1 is a solution of a dilute acid.
FA 2 contains vanadate(V) ions, VO_3^-, of concentration 0.50 mol dm^{-3}.

Ammonium vanadate(V), NH_4VO_3, is a crystalline solid that is slightly yellow in colour. It has a relatively low solubility in water at room temperature.

Vanadium, like all transition metals, is able to exhibit variable oxidation states in its compounds.

You are provided with a solution, **FA 2**, which was produced by reacting NH_4VO_3 with aqueous sodium hydroxide. In this reaction, the anion remains unreacted.

(a) Write an equation for the reaction between ammonium vanadate(V) and sodium hydroxide to produce **FA 2**.

Describe how, using a simple chemical test, you can confirm that this reaction occurred during the preparation of **FA 2**.

DO NOT carry out this test.

equation ....

test ....

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....[1]

Relevant standard electrode potential data of some species are given in Table 1.1.

Table 1.1

$V^{3+}(aq) + e^-$ green	$\rightleftharpoons$	$V^{2+}(aq)$ purple	$E^\ominus = -0.26$ V
$VO^{2+}(aq) + 2H^+ + e^-$ blue	$\rightleftharpoons$	$V^{3+}(aq) + H_2O(l)$ green	$E^\ominus = +0.34$ V
$VO_2^+(aq) + 2H^+ + e^-$ yellow	$\rightleftharpoons$	$VO^{2+}(aq) + H_2O(l)$ blue	$E^\ominus = +1.00$ V
$Zn^{2+} + 2e^-$	$\rightleftharpoons$	Zn	$E^\ominus = -0.76$ V
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\rightleftharpoons$	$Mn^{2+}(aq) + 4H_2O(l)$	$E^\ominus = +1.51$ V

(b) (i) When **FA 2** is acidified and reacted with zinc powder, VO_3^- ions are reduced stepwise.

Carry out the following tests. Carefully record your observations in Table 1.2.

Test and identify any gases evolved.

Table 1.2

tests		observations
1	Using a measuring cylinder, transfer 1 cm^3 of **FA 2** into a boiling tube. To this same boiling tube, use a measuring cylinder to add 4 cm^3 of **FA 1** and stir the mixture. This is solution **W**. Retain solution **W** for use in test 2.	
2	To solution **W** in the boiling tube, add a spatula of zinc powder using a metal spatula. Swirl the mixture gently and record your observations. Continue to add more zinc powder one spatula at a time with swirling, until about 4 spatulas of zinc powder is added. Record all colour changes observed throughout the initial **10 minutes**.	
When no further changes are seen, decant the reaction mixture into a test-tube. This is solution **X** which contains one of the reduction product of the vanadium ion originally present in **W**. Retain solution **X** for use in test 3.		
3	Pour 1 cm^3 of **X** into a test-tube. Observe this solution for at least **5 minutes**.	

[6]

(ii) State the ion formed when **FA 1** is added to **FA 2** in test 1. Write an ionic equation for this reaction.

ion formed ....

ionic equation ....[1]

(iii) Suggest which ion is responsible for the final colour observed in test 2. Explain your answer in terms of the $E^\ominus$ values given in Table 1.1.

ion...

explanation..

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....[2]

(iv) Suggest an explanation for your observations in test 3.

explanation..

....[1]

(v) When aqueous sodium hydroxide was added dropwise till excess into a solution containing the complex ion $[V(H_2O)_6]^{3+}$, a brown precipitate is observed.

State the type of reaction and write an equation to explain the observation.

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....[2]

(c) The identity of **FA 1** could be hydrochloric acid, nitric acid or sulfuric acid.

(i) Devise a test that will positively identify hydrochloric acid, nitric acid, and sulfuric acid respectively. For each of the possible acids, you should indicate the expected observations in the table below. Your tests should be based on the Qualitative Analysis Notes on pages 19–20 and should use only the bench reagents provided.

	tests	expected observations
1		
2		
3		

[3]

(ii) Perform your tests on **FA 1** to confirm its identity.

Any test requiring heating MUST be performed in a boiling tube.

FA 1.. [1]

[Total: 17]

2 Investigation on how rate of reaction is affected by the concentration of iodide ions

In acidic solutions iron(III) ions are reduced by iodide ions to form iron(II) ions. The iodide ions are oxidised to iodine.

$$2Fe^{3+}(aq) + 2I^{-}(aq) \downarrow 2Fe^{2+}(aq) + I_2(aq)$$

The rate of this reaction can be investigated by using starch indicator, which turns blue-black in the presence of iodine. Sodium thiosulfate is added to the reaction mixture to react with iodine as it is formed. The blue-black colour is seen when all the thiosulfate has reacted.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \downarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$$

You will investigate how the rate of reaction is affected by changing the concentration of the iodide ions.

FA 3 is 0.0500 mol dm^{-3} potassium iodide, KI.
FA 4 is 0.0500 mol dm^{-3} acidified iron(III) chloride, $FeCl_3$.
FA 5 is 0.00500 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.
FA 6 is starch indicator.

Read through the whole method before starting any practical work.

(a) Method

Prepare a table on page 8 for your results. You will need to include the volume of **FA 3**, volume of water, reaction time and rate of reaction for each of five experiments.

Experiment 1

1. Fill the burette with **FA 3**. Run 20.00 cm^3 of **FA 3** into the 100 cm^3 beaker.
2. Using appropriate measuring cylinders, transfer to the beaker:
    - 20.0 cm^3 of **FA 5**
    - 10.0 cm^3 of **FA 6**.
3. Stir the contents of the beaker using a glass rod.
4. Use the 10 cm^3 measuring cylinder to transfer 10.0 cm^3 of **FA 4** to the beaker. Start the stopwatch during this addition.
5. Mix the contents in the beaker by **thoroughly** stirring.
6. Stop the stopwatch when the solution **first** turns blue-black. Record the time to the nearest second.
7. Carefully wash out the beaker. Stand it upside down on a paper towel to drain.

Experiment 2

8. Fill the second burette with distilled water.

9. Run 10.00 cm^3 of **FA 3** into another 100 cm^3 beaker.

10. Run 10.00 cm^3 of distilled water into the beaker containing **FA 3**.

11. Using appropriate measuring cylinders, transfer to the beaker:
    - 20.0 cm^3 of **FA 5**
    - 10.0 cm^3 of **FA 6**.

12. Stir the contents of the beaker using a glass rod.

13. Use the 10 cm^3 measuring cylinder to transfer 10.0 cm^3 of **FA 4** to the beaker. Start the stopwatch during this addition.

14. Mix the contents in the beaker by **thoroughly** stirring.

15. Stop the stopwatch when the solution **first** turns blue-black. Record the time to the nearest second.

16. Carefully wash out the beaker. Stand it upside down on a paper towel to drain.

Experiments 3 – 5

17. Carry out three further experiments to investigate how the reaction time changes with different volumes of potassium iodide, **FA 3**.

    Remember
    - The combined volume of **FA 3** and distilled water must always be 20.00 cm^3.
    - Do **not** use a volume of **FA 3** that is less than 6.00 cm^3.
    - You should record all your results in a single table.

Results

The rate of reaction can be calculated as shown:

$$\text{rate} = \frac{1000}{\text{reaction time}}$$

Candidate's ratio	

[5]

(b) Use the grid below to plot a graph of rate (y-axis) against volume of **FA 3** (x-axis). Include the origin, (0,0), in your scales. Draw a line of best fit. [3]

I	
II	
III	

(c) **Use your graph** to calculate the time to the nearest second that the reaction would have taken if 12.00 cm^3 of **FA 3** had been used. **Show on the graph** how you obtained your answer.

time = ... s [1]

(d) **(i)** Using data from **Experiments 1** and **2**, show by calculation that the volume of aqueous potassium iodide, **FA 3**, used was directly proportional to the concentration of iodide ions.

[2]

(ii) Explain, by referring to your graph, how the rate of reaction is affected by an increase in the concentration of aqueous potassium iodide, **FA 3**.

....

....

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....

....

....[2]

(e) Thiosulfate ions can reduce iron(III) ions and also react with acid to form sulfur, sulfur dioxide and water.

Write an ionic equation for the reaction between thiosulfate ions and hydrogen ions in aqueous solution. Include state symbols.

....[1]

(f) Another student investigates the effect of iron(III) concentration on the rate of this reaction at a different temperature. The student carries out another experiment, **Experiment 6**, and the rate is compared to that of **Experiment 2**. In **Experiment 2**, the volumes used were:

reagent	volume / cm^3
FA 3	10.00
FA 4	10.0
FA 5	20.0
FA 6	10.0
distilled water	10.00

(i) Suggest the volumes the student could use for **Experiment 6**.

reagent	volume / cm^3
FA 3	
FA 4	
FA 5	
FA 6	
distilled water	

[1]

(ii) This student records a time of 178 s for **Experiment 2**

The rate of reaction is directly proportional to the concentration of iron(III) ions.

Suggest how long it would take the reaction mixture proposed for **Experiment 6** in **(f)(i)** to turn blue-black. Assume that **Experiment 6** is carried out at the same temperature as **Experiment 2**.
Do not carry out Experiment 6.

time = ... s [1]

[Total: 16]

3 Planning

Baker's yeast is a useful enzyme which can be used to catalyse the decomposition of hydrogen peroxide.

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2$$

You are provided with

Apparatus:

- 1 × 100 cm^3 conical flask, fitted with rubber bung and rubber tubing
- 1 × gas syringe (possible capacities of 10, 20, 50 or 100 cm^3)
- stopwatch
- all other common laboratory equipment

Reagents:

- 100 cm^3 of yeast suspension
- 30 cm^3 of 3% (by weight) hydrogen peroxide
- distilled water

When 8.00 cm^3 of the yeast suspension, 4.00 cm^3 of H_2O_2 and 18.0 cm^3 of distilled water are mixed in one of the experimental runs, 10 cm^3 of oxygen gas was produced in 90 seconds.

Use the above information and the reagents provided to design an experiment to prove that the reaction is first order reaction with respect to yeast by a graphical method.

In your experiment, you should perform a total of five experimental runs (including the above run) to measure the volume of oxygen gas produced at regular intervals in each run.

(a) Suggest suitable volumes used for each reagent in the table below.

run	volume of yeast / cm^3	volume of H_2O_2 / cm^3	volume of water / cm^3
1			
2	8.00	4.00	18.0
3			
4			
5			

[2]

(b) In your plan, you should include brief details of:

- the calculations to determine the appropriate capacity of the gas syringe by assuming that the density of H_2O_2 is 1.00 g cm^{-3} and conditions are at r.t.p.,
- the apparatus you would use,
- the measurements you would make to determine the initial rate for each run and the order with respect to yeast.

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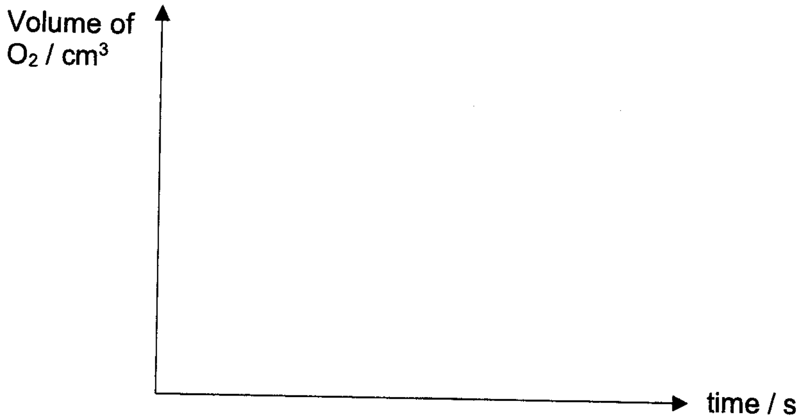
.... [5]

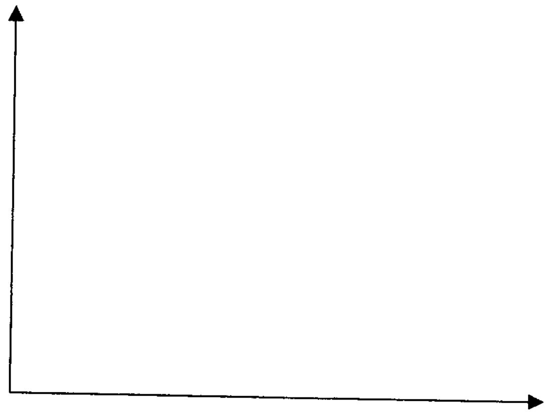
(c) **(i)** Sketch the graph you would expect to obtain in run 2.



[1]

(ii) On the same graph in **(c)(i)**, show how you would obtain the initial rate in run 2. [1]

(d) Hence, sketch a suitable graph to show that the reaction is first order reaction with respect to yeast.



[1]

[Total: 10]

4 **Determination of percentage purity of a sample of contaminated sodium carbonate**

FA 7 is a solution of the contaminated sodium carbonate. You will first dilute **FA 7** and then titrate the diluted solution using hydrochloric acid.

$$2HCl(aq) + Na_2CO_3(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

FA 7 was prepared by dissolving 125 g of contaminated sodium carbonate, Na_2CO_3, in distilled water and making the solution up to 1 dm^3.
FA 8 is 0.100 mol dm^{-3} hydrochloric acid, HCl.
methyl orange indicator

(a) **Method**

Dilution

1. Fill the burette with **FA 7**.
2. Run between 13.00 and 13.50 cm^3 of **FA 7** into the 250 cm^3 volumetric (graduated) flask.
   Record the volume in the space below.

   volume of **FA 7** = ... cm^3

3. Fill the volumetric flask to the line with distilled water. Stopper the flask and shake it to ensure thorough mixing. This flask is **FA 9**.

Titration

4. Fill the burette with **FA 8**.
5. Use the pipette to transfer 25.0 cm^3 of **FA 9** into a conical flask.
6. Add 5 – 10 drops of methyl orange indicator.
7. Titrate the mixture in the conical flask until the end-point is reached.
8. Record your titration results in the space provided on page 17.
9. Repeat steps 5 to 8 until consistent results are obtained.

Titration results

I	
II	
III	
IV	

Teacher's ratio	
Candidate's ratio	
difference	

[6]

(b) From your accurate titration results, obtain a suitable volume of **FA 8** to be used in your calculations.
Show clearly how you obtained this value.

25.0 cm^3 of **FA 9** required .... cm^3 of **FA 8**. [1]

(c) **Calculations**

Show your working and appropriate significant figures in the final answer to **each** step of your calculations. [1]

(i) Calculate the amount of hydrochloric acid present in the volume of **FA 8** calculated in **(b)**. Hence, calculate the amount of sodium carbonate present in 25.0 cm^3 of **FA 9**.

amount of HCl = ... mol

amount of Na_2CO_3 = ... mol

[1]

(ii) Calculate the concentration, in mol dm^{-3}, of sodium carbonate in **FA 9**.

concentration of Na_2CO_3 in **FA 9** = ... mol dm^{-3} [1]

(iii) Calculate the concentration, in mol dm^{-3}, of sodium carbonate in **FA 7**.

concentration of Na_2CO_3 in **FA 7** = ... mol dm^{-3} [1]

(iv) Calculate the percentage purity by mass of sodium carbonate in the contaminated sample used to prepare solution **FA 7**.
(A_r: C, 12.0; O, 16.0; Na, 23.0)

percentage purity by mass = ... % [1]

[Total: 12]

Qualitative Analysis Notes
[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

[Turn over

(b) Reactions of anions

anion	***reaction***
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Tests for gases

gas	***test and test result***
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	***colour of element***	***colour in aqueous solution***	***colour in hexane***
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I	black solid / purple gas	brown	purple