

NANYANG JUNIOR COLLEGE  
JC 2 PRELIMINARY EXAMINATION  
Higher 2

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## CHEMISTRY

9729/01

Paper 1 Multiple Choice

21 September 2021

1 hour

Additional Materials: Multiple Choice Answer Sheet  
Data Booklet

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### READ THESE INSTRUCTIONS FIRST

Write in soft pencil.

Do not use staples, paper clips, 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.

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This document consists of **14** printed pages..

[Turn Over

- 1 The mass percentage of magnesium in a mixture of magnesium chloride and magnesium nitrate was found to be 21.25 %. What mass of magnesium chloride is present in 100 g of the mixture?
- A 47 g                      B 53 g                      C 56 g                      D 61 g
- 2 10.00 cm<sup>3</sup> of 0.500 mol dm<sup>-3</sup> of a metal oxide, M<sub>2</sub>O<sub>n</sub>, reacted exactly with 20.00 cm<sup>3</sup> of 0.300 mol dm<sup>-3</sup> of acidified potassium manganate(VII) solution.
- Given that the oxidation state of M in the product is +6, what is the value of n?
- A 1                              B 2                              C 3                              D 4
- 3 The first six ionisation energies of an element, Q, in kJ mol<sup>-1</sup> are shown.
- 660; 1267; 2218; 3313; 7863; 9500
- What can be inferred from the data provided?
- A Q is a Period 3 element.
- B Q forms an oxide with a giant molecular structure.
- C Q is likely to form a chloride with the formula QC<sub>4</sub> when reacted with chlorine.
- D Q has a lower first ionisation energy than the element preceding it in the Periodic Table.
- 4 Which of the following statements are correct?
- 1 The van der Waals radius of chlorine is larger than the van der Waals radius of argon.
  - 2 The boiling point of N<sub>2</sub>H<sub>4</sub> is higher than CH<sub>3</sub>CH<sub>2</sub>CHO as hydrogen bonds between N<sub>2</sub>H<sub>4</sub> molecules are more extensive than the hydrogen bonds between CH<sub>3</sub>CH<sub>2</sub>CHO molecules.
  - 3 The carbon–carbon bond length is longer in diamond than in graphite.
- A 1, 2 and 3                      B 1 and 2 only                      C 2 and 3 only                      D 3 only

- 5 What is the pressure (in Pa) of a sample of hydrogen gas that has density of  $8 \text{ g m}^{-3}$  at  $300 \text{ }^\circ\text{C}$ ?

A  $\frac{573 \times 4 \times 22.7 \times 10^5}{273}$

B  $\frac{573 \times 8 \times 22.7 \times 100}{273}$

C  $\frac{273 \times 8 \times 22.7 \times 10^5}{573}$

D  $\frac{573 \times 4 \times 22.7 \times 100}{273}$

- 6 Given the following enthalpy changes,

	enthalpy change/ $\text{kJ mol}^{-1}$
$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$	-92
$\text{N}_2(\text{g}) + 4\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{NH}_4\text{Cl}(\text{s})$	-629
$\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$	-176

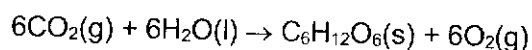
What is the standard enthalpy change of formation of gaseous hydrogen chloride?

- A  $-46.3 \text{ kJ mol}^{-1}$   
 B  $-92.5 \text{ kJ mol}^{-1}$   
 C  $-180 \text{ kJ mol}^{-1}$   
 D  $-361 \text{ kJ mol}^{-1}$

- 7 Some  $\Delta H_f^\ominus$  values are given below.

compound	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
$\text{H}_2\text{O}(\text{l})$	-286
$\text{CO}_2(\text{g})$	-394
$\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$	-1273

The overall reaction in photosynthesis can be represented by the following equation.



Which of the following statements are correct?

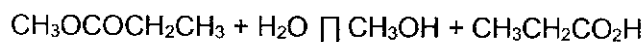
- 1 The enthalpy change of the reaction is  $+2807 \text{ kJ mol}^{-1}$ .
- 2 In the formation of products, the system becomes less disordered.
- 3 The reaction is not spontaneous at all temperatures.

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

- 8 The decomposition of a sample of  $\text{H}_2\text{O}_2$  solution is a first order reaction with a rate constant of  $7.70 \times 10^{-4} \text{ s}^{-1}$ . What is the initial concentration of the  $\text{H}_2\text{O}_2$  solution, in  $\text{mol dm}^{-3}$ , if its concentration has dropped to  $0.0315 \text{ mol dm}^{-3}$  in 80 min?

**A** 0.109      **B** 0.158      **C** 1.01      **D** 1.27

- 9 For the hydrolysis of methyl propanoate,  $\text{CH}_3\text{OCOCH}_2\text{CH}_3$ , in dilute  $\text{HCl}$ , the following rates of reactions were measured at  $25^\circ\text{C}$ .



experiment	[methyl propanoate] / $\text{mol dm}^{-3}$	[HCl] / $\text{mol dm}^{-3}$	initial rate / $\text{mol dm}^{-3} \text{min}^{-1}$
1	0.10	0.20	0.192
2	0.15	0.10	0.144
3	0.10	0.10	0.096
4	0.30	0.15	?

Which statements are **incorrect**?

- The initial rate for experiment 4 is  $0.432 \text{ mol dm}^{-3} \text{ min}^{-1}$ .
- The rate constant is  $9.6 \text{ mol}^{-2} \text{ dm}^6 \text{ min}^{-1}$ .
- If the half-life of methyl propanoate in experiment 1 is 6 minutes, then the half-life of methyl propanoate in experiment 4 is 8 minutes.

- A 1, 2 and 3      B 2 and 3 only      C 3 only      D 2 only
- 10 At a total pressure of 1.0 atm and a temperature of  $60^\circ\text{C}$ , dinitrogen tetraoxide is 50 % dissociated according to the following equation:



What is the value of the equilibrium constant,  $K_p$ , for the dimerisation of  $\text{NO}_2$  at  $60^\circ\text{C}$ ?

- A  $\frac{2}{3}$       B  $\frac{3}{4}$       C  $\frac{4}{3}$       D  $\frac{3}{2}$

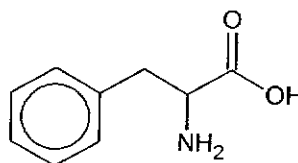
- 11 Nitrogen is discharged from wastewater treatment facilities into rivers and streams, usually as  $\text{NH}_3$  and  $\text{NH}_4^+$ .

The fraction of the total nitrogen present in the water to be discharged as  $\text{NH}_3$  is defined as:

$$\frac{[\text{NH}_3]}{[\text{NH}_3] + [\text{NH}_4^+]}$$

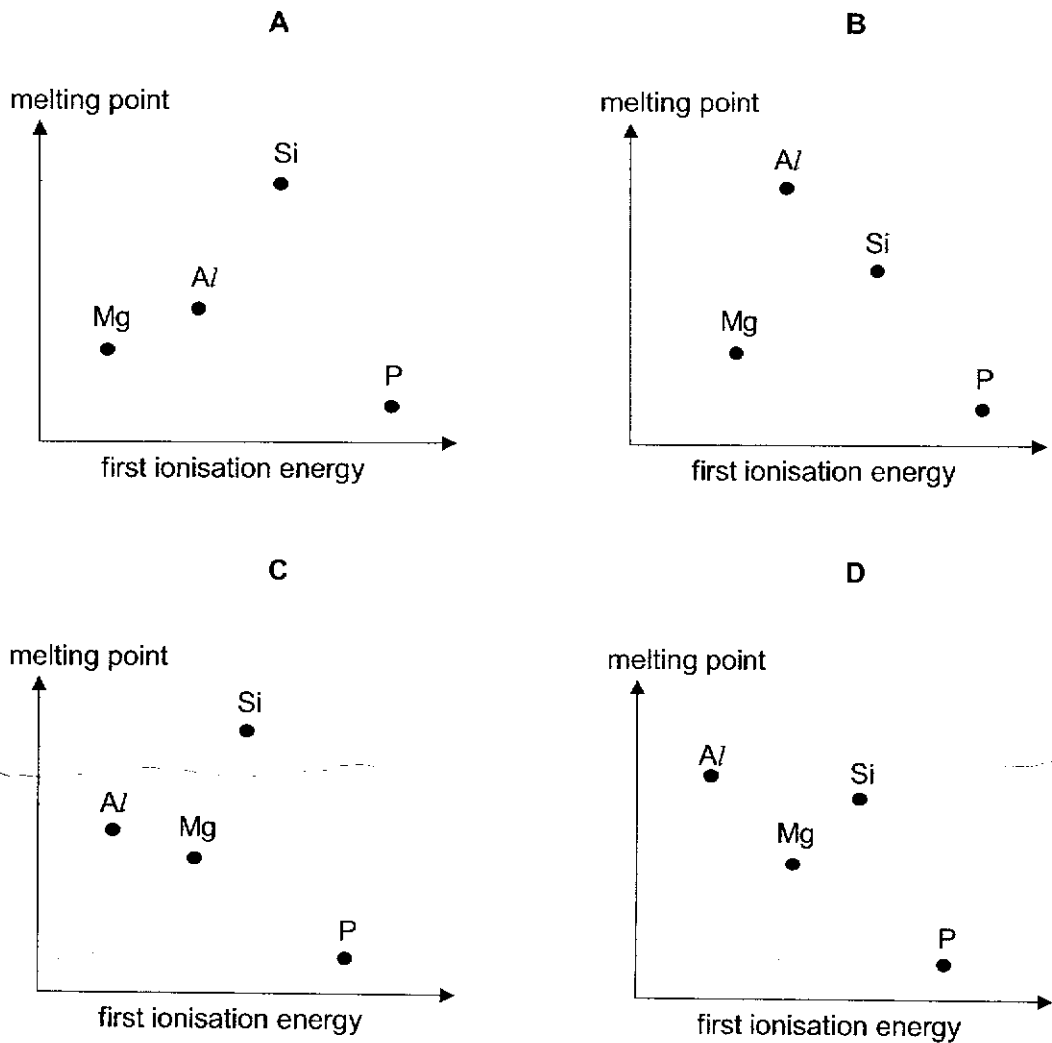
Given that the base dissociation constant,  $K_b$  of  $\text{NH}_3$  is  $1.76 \times 10^{-5} \text{ mol dm}^{-3}$ , what is the fraction of the total nitrogen in the water to be discharged as  $\text{NH}_3$  at pH 7?

- A  $9.94 \times 10^{-1}$   
 B  $5.00 \times 10^{-1}$   
 C  $5.65 \times 10^{-3}$   
 D  $1.76 \times 10^{-3}$
- 12 Which solution's pH will **not** change significantly when a small amount of alkali is added?
- 20  $\text{cm}^3$  of  $0.15 \text{ mol dm}^{-3}$  of ethanoic acid mixed with 10  $\text{cm}^3$  of  $0.20 \text{ mol dm}^{-3}$  of potassium hydroxide
  - 10  $\text{cm}^3$  of  $0.25 \text{ mol dm}^{-3}$  of  $\text{K}_2\text{HPO}_4$  mixed with 5  $\text{cm}^3$  of  $0.15 \text{ mol dm}^{-3}$  of  $\text{KH}_2\text{PO}_4$



- 3 20  $\text{cm}^3$  of  $0.10 \text{ mol dm}^{-3}$  phenylalanine,
- A 1, 2 and 3    B 1 and 2 only    C 1 and 3 only    D 2 only

- 13 Which graph correctly shows the relative melting points of the elements Mg, Al, Si and P plotted against their relative first ionisation energies?



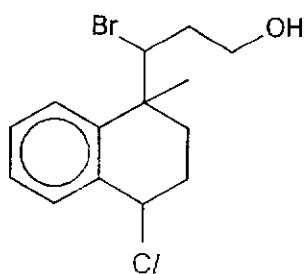
- 14 Which property of Group 2 elements (magnesium to barium) or their compounds increases with increasing proton number?
- A the first ionisation energies of the elements
  - B the acidity of aqueous solutions of the chlorides
  - C the solubility of Group 2 sulfates
  - D the decomposition temperature of the carbonates

15 Which trends concerning halogens from fluorine to iodine and their compounds are **incorrect**?

- 1 The volatility of hydrogen halides decreases down the group.
- 2 The thermal stability of hydrogen halides increases down the group.
- 3 The reducing power of halide ions increases down the group.

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

16 What is the total number of stereoisomers exhibited by the product formed when the following compound reacts with excess ethanolic sodium hydroxide?



**A** 2    **B** 4    **C** 8    **D** 16

17 A non-cyclic organic molecule contains only carbon atoms, hydrogen atoms and one oxygen atom. The molecule is a ketone and contains a chiral carbon atom.

How many carbon atoms can the molecule contain?

- 1 five
- 2 six
- 3 seven

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



- 18 Both maleic acid and fumaric acid are organic compounds with the formula  $\text{HO}_2\text{CCH}=\text{CHCO}_2\text{H}$ .

Data about the acids are given below.

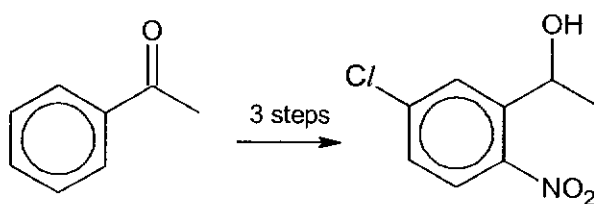
	$\text{p}K_{\text{a}1}$	$\text{p}K_{\text{a}2}$	boiling point / $^{\circ}\text{C}$
maleic acid	1.9	6.2	202
fumaric acid	3.0	4.4	522

Which of the statements are true?

- 1 Maleic acid is the cis-isomer while fumaric acid is the trans-isomer.
- 2 Boiling point of fumaric acid is higher as it has a more elongated shape and a larger surface area of contact, hence more energy is required to overcome the stronger intermolecular forces.
- 3  $\text{CH}(\text{OH})(\text{CO}_2\text{H})\text{CH}(\text{Br})\text{CO}_2\text{H}$  can be prepared using  $\text{HO}_2\text{CCH}=\text{CHCO}_2\text{H}$  as a starting material.
- 4 Four moles of  $\text{CO}_2$  are produced when it is treated with hot alkaline potassium manganate(VII).

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

- 19 The following synthesis takes place in three steps.



Which route forms the highest yield of the product?

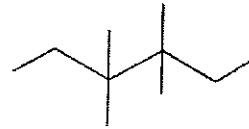
	step 1	step 2	step 3
A	$\text{H}_2$ , Pt	conc $\text{HNO}_3$ , conc $\text{H}_2\text{SO}_4$	$\text{Cl}_2$ , $\text{FeCl}_3$
B	$\text{Cl}_2$ , $\text{FeCl}_3$	$\text{H}_2$ , Pt	conc $\text{HNO}_3$ , conc $\text{H}_2\text{SO}_4$
C	$\text{H}_2$ , Pt	$\text{Cl}_2$ , $\text{FeCl}_3$	conc $\text{HNO}_3$ , conc $\text{H}_2\text{SO}_4$
D	$\text{Cl}_2$ , $\text{FeCl}_3$	conc $\text{HNO}_3$ , conc $\text{H}_2\text{SO}_4$	$\text{H}_2$ , Pt

- 20 In the free radical substitution of 2-methylbutane with bromine, a mixture of mono-brominated compounds was obtained.

Which statements are correct?

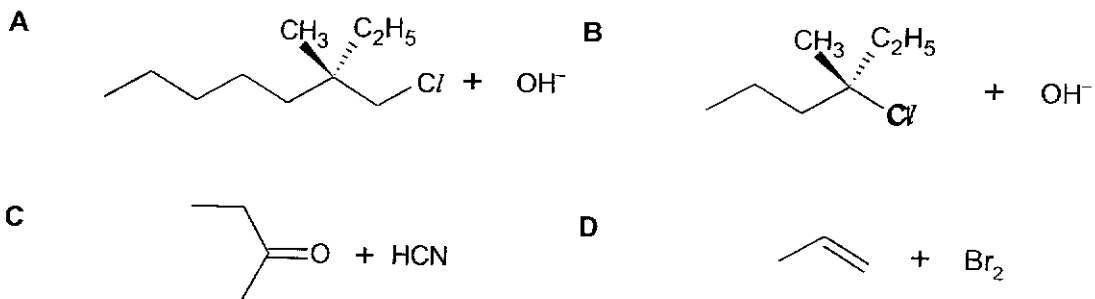
- 1 The statistical ratio of the two compounds with the highest yield is 1 : 2.
- 2 Homolytic fission only occurs in the initiation step.

- 3 One of the products formed in this reaction is



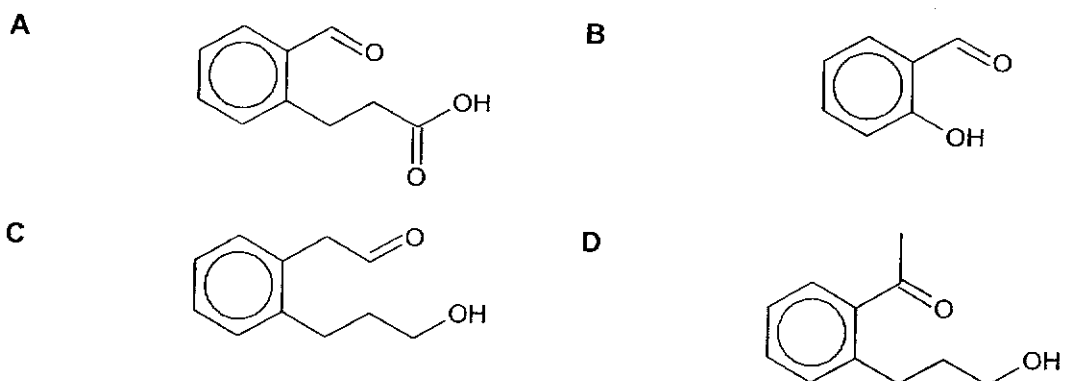
- A 1 and 2 only    B 1 and 3 only    C 2 and 3 only    D 1 only

- 21 Which reaction will **not** produce a mixture of two enantiomers in aqueous solution?

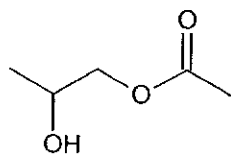


- 22 Compound R gives a positive result when separate samples were treated with  $[\text{Ag}(\text{NH}_3)_2]^+$  and  $\text{PCl}_5$  but a negative result when treated with alkaline  $\text{Cu}(\text{II})$  complex.

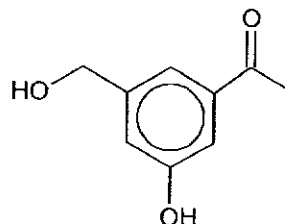
What could R be?



- 23 The following two compounds reacted with alkaline aqueous iodine to form a yellow precipitate. What is the number of moles of sodium hydroxide required to react with one mole of compound S and one mole of compound T respectively?



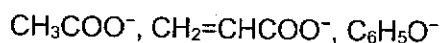
compound S



compound T

	compound S	compound T
<b>A</b>	6	4
<b>B</b>	7	4
<b>C</b>	6	5
<b>D</b>	7	5

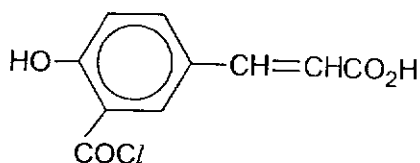
- 24 An equal amount of each of the following species was dissolved separately in  $1 \text{ dm}^3$  of water. The pH of the resultant solutions were measured.



Which row is correct?

	lowest pH	—————→	highest pH
<b>A</b>	$\text{C}_6\text{H}_5\text{O}^-$	$\text{CH}_3\text{COO}^-$	$\text{CH}_2=\text{CHCOO}^-$
<b>B</b>	$\text{CH}_3\text{COO}^-$	$\text{CH}_2=\text{CHCOO}^-$	$\text{C}_6\text{H}_5\text{O}^-$
<b>C</b>	$\text{CH}_2=\text{CHCOO}^-$	$\text{CH}_3\text{COO}^-$	$\text{C}_6\text{H}_5\text{O}^-$
<b>D</b>	$\text{CH}_2=\text{CHCOO}^-$	$\text{C}_6\text{H}_5\text{O}^-$	$\text{CH}_3\text{COO}^-$

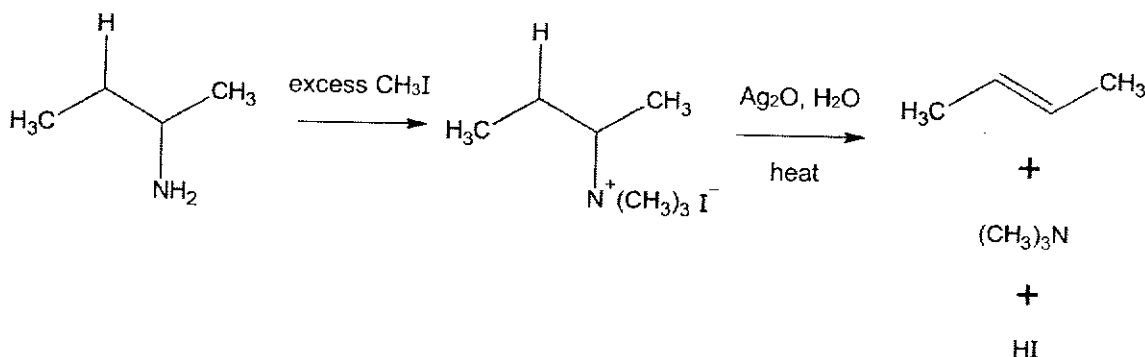
- 25 Compound V is dissolved in heavy water,  $D_2O$ , to form compound W. Compound V contains a number of hydrogen atoms which can easily be replaced by deuterium, D. [D, deuterium =  $^2_1H$ ]



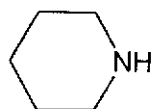
compound V

What is the maximum number of deuterium atoms present in one molecule of compound W?

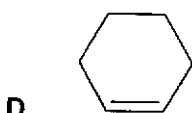
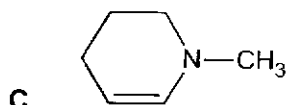
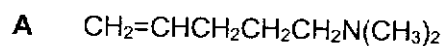
- A 1                      B 2                      C 3                      D 4
- 26 The Hofmann elimination is a process where an amine undergoes treatment with excess methyl iodide to form an intermediate, which is then treated with silver oxide, water and heat to form an alkene.



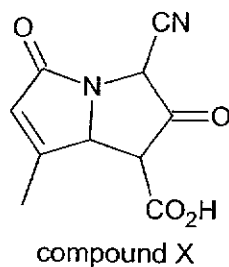
What is the structure of the alkene formed when piperidine, undergoes the Hofmann elimination?



piperidine



- 27 The structure of compound X is shown below.



Compound X reacts with excess  $\text{LiAlH}_4$  in dry ether to yield compound Y.

Which statement about compound Y is correct?

- A One mole of Y reacts with two moles of  $\text{HBr}$ .
- B One mole of Y reacts with two moles of  $\text{SOCl}_2$ .
- C One mole of Y reacts with four moles of  $\text{CH}_3\text{COCl}$ .
- D One mole of Y reacts with sodium metal to produce three moles of  $\text{H}_2$  gas.
- 28 Upon complete hydrolysis, a tetrapeptide Z gives the following amino acids.

amino acid	Structure	$M_r$	mass of amino acid obtained from hydrolysis / g
aspartic acid	$\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{N}-\text{C}-\text{COOH} \\   \\ \text{CH}_2\text{COOH} \end{array}$	133	53.2
glutamine	$\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{N}-\text{C}-\text{COOH} \\   \\ \text{CH}_2\text{CH}_2\text{CONH}_2 \end{array}$	146	29.2
proline		115	23.0

What is the  $M_r$  of tetrapeptide Z?

- A 340                      B 394                      C 473                      D 527

- 29 Use of the Data Booklet is relevant to this question.

A student connects a  $\text{Zn}^{2+}/\text{Zn}$  half-cell to a  $\text{Fe}^{3+}/\text{Fe}^{2+}$  half-cell. The voltage measured across the electrodes is found to be +1.50 V.

Which of the following could be a reason for the discrepancy between the measured value above and the  $E^{\ominus}_{\text{cell}}$  expected?

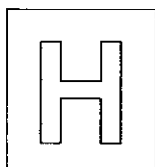
- A Water is added to the  $\text{Zn}^{2+}/\text{Zn}$  half-cell.
  - B Water is added to the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  half-cell.
  - C The piece of zinc in the  $\text{Zn}^{2+}/\text{Zn}$  half-cell used is too small.
  - D A small amount of  $\text{NaOH}(\text{aq})$  is added to the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  half-cell.
- 30 Two separate electrolyses were performed as follows, under the same conditions of temperature and pressure.

experiment 1: When molten magnesium chloride was electrolysed for five minutes,  $60 \text{ cm}^3$  of chlorine was collected from the anode.

experiment 2: When aqueous sulfuric acid was electrolysed for five minutes,  $90 \text{ cm}^3$  of oxygen was collected from the anode.

If the current used in experiment 1 was  $I$ , what was the current used in experiment 2?

- A  $0.7I$                       B  $I$                       C  $3I$                       D  $4I$



NANYANG JUNIOR COLLEGE  
JC 2 PRELIMINARY EXAMINATION  
Higher 2

CANDIDATE  
NAME

CLASS

TUTOR'S  
NAME

**CHEMISTRY**

Paper 2 Structured Questions

9729/02

01 September 2021

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.

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	/14
2	/16
3	/20
4	/25
<b>Total</b>	<b>/75</b>

This document consists of 20 printed pages..

[Turn Over

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

- 1 This is a question on the salts of magnesium.
- (a) Struvite,  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , is a fertiliser mineral that can be obtained from wastewaters. It is a salt that contains two cations and one anion.
- (i) Draw a dot-and-cross diagram of  $\text{MgNH}_4\text{PO}_4$ .

[2]

- (ii) Explain why  $\text{MgNH}_4\text{PO}_4$  is only slightly soluble in water.

.....

.....

.....

..... [1]

- (iii) Thermal decomposition of  $\text{MgNH}_4\text{PO}_4$  produces an alkaline gas, water and a white powder of magnesium pyrophosphate,  $\text{Mg}_2\text{P}_2\text{O}_7$ . Write an equation with state symbols for this reaction.

..... [1]

- (b) The value of the solubility products and melting points of some magnesium salts at 298 K are shown in Table 1.1.

**Table 1.1**

salt	value of solubility product	melting point / °C
magnesium chloride, $\text{MgCl}_2$		714
magnesium hydroxide, $\text{Mg}(\text{OH})_2$	$1.8 \times 10^{-11}$	350
magnesium phosphate, $\text{Mg}_3(\text{PO}_4)_2$	$4.0 \times 10^{-25}$	1184

In this question, give each of your numerical answers to two significant figures.

Magnesium phosphate is widely used in medication to support the relaxation of muscles. This compound is used to prevent the cramping of muscles and vitamin E deficiency.

- (i) With an appropriate equation, define the *lattice energy of magnesium phosphate*.

.....

.....

..... [2]



- (ii) Suggest an explanation, in terms of structure and bonding, for the difference in melting points between magnesium chloride and magnesium phosphate.

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

- (iii) Write an expression for the solubility product of magnesium phosphate, stating its units.

..... [1]

- (iv) Determine the  $[Mg^{2+}(aq)]$  of a saturated solution of magnesium phosphate.

[2]

- (v) Solid magnesium chloride was slowly added to a solution containing  $0.15 \text{ mol dm}^{-3}$  of sodium hydroxide and  $0.32 \text{ mol dm}^{-3}$  of sodium phosphate at 298 K.

Calculate the concentration of hydroxide ions in the solution when the first trace of magnesium phosphate appears.

[3]

[Total: 14]

- 2 Nitrogen dioxide,  $\text{NO}_2$ , is a significant air pollutant. It is a precursor for a number of harmful secondary air pollutants such as ozone and particulate matter, and plays a role in the oxidation of atmospheric sulfur dioxide.

PM refers to particulate matter in the atmosphere that are so small they can only be detected using an electron microscope. Most of these particles form in the atmosphere as a result of pollution emitted from power plants, industries and automobiles.  $\text{PM}_{10}$  is particulate matter  $10\ \mu\text{m}$  or less in diameter,  $\text{PM}_{2.5}$  is particulate matter  $2.5\ \mu\text{m}$  or less in diameter. Due to their small size, they can penetrate the deepest parts of the lungs as well as access the gas exchange regions of the lung via diffusion.

To safeguard public health, concentration of  $\text{NO}_2$ ,  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  around Singapore are closely monitored.

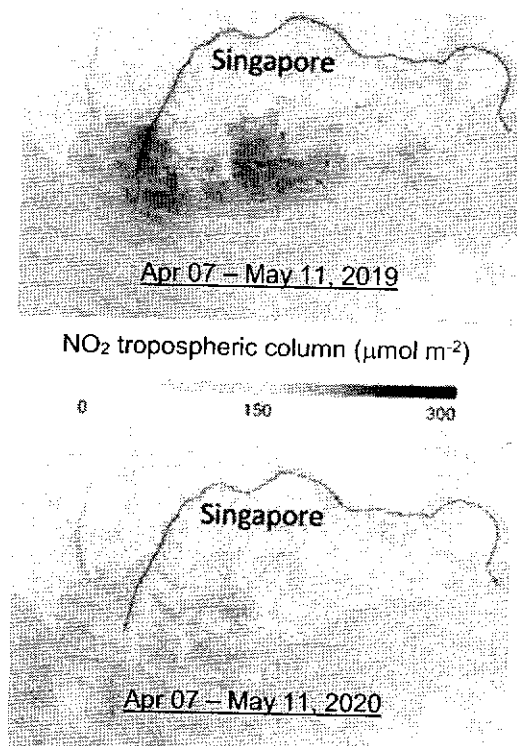


Fig. 2.1

Fig. 2.1 shows mean atmospheric concentrations of  $\text{NO}_2$  from 7 April to 11 May 2019 (top) and 2020 (bottom) imaged using data obtained from the ESA Copernicus Sentinel 5P satellite.

Table 2.1 shows change of air quality parameters in Singapore during the Circuit Breaker period of 2020, a stay-at-home order and cordon sanitaire implemented by the Government of Singapore in response to the COVID-19 pandemic in the country on 7 April 2020. During this period, all non-essential workplaces were closed and all schools transitioned to home-based learning.

Table 2.1

	average reading over last 4 years	reading during Circuit Breaker
$\text{NO}_2$ ( $\mu\text{g m}^{-3}$ )	33.1	15.1
$\text{PM}_{10}$ ( $\mu\text{g m}^{-3}$ )	29.8	23
$\text{PM}_{2.5}$ ( $\mu\text{g m}^{-3}$ )	14.4	10.1

- (a) (i) Describe and explain, with the aid of suitable equations, the role of  $\text{NO}_2$  in the oxidation of atmospheric sulfur dioxide.

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

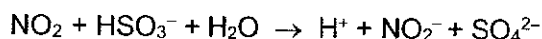
- (ii) Using your understanding of the source of  $\text{NO}_2$ , suggest a reason for the trend shown in Table 2.1.

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

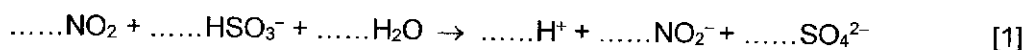
- (iii) Suggest why the measured  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  did not change as significantly as  $\text{NO}_2$ .

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

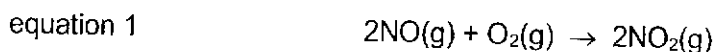
- (b) Haze events have been occurring in China megacities in recent years. These hazes mainly consist of aqueous sulfates,  $\text{SO}_4^{2-}$ , produced as a result of  $\text{SO}_2$  and  $\text{NO}_2$  reacting under particularly adverse meteorological conditions. One possible reaction is shown by the following unbalanced equation, where  $\text{NO}_2$  undergoes reduction to form  $\text{NO}_2^-$ .



Complete the chemical equation for the reaction.



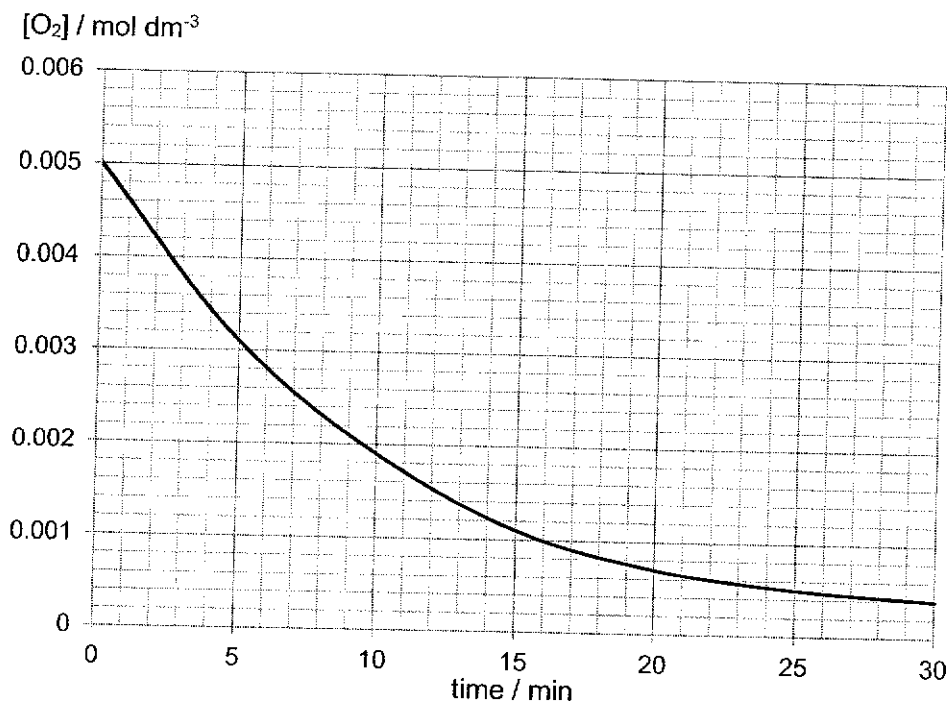
- (c)  $\text{NO}_2$  can be formed from  $\text{NO}$ , as shown in equation 1.



Three experiments were carried out to determine order of reaction with respect to  $\text{NO}$  and  $\text{O}_2$ , and hence the rate constant for this reaction.

Experiment 1 was carried out with initial concentrations of  $\text{NO}$  and  $\text{O}_2$  at  $0.10 \text{ mol dm}^{-3}$  and  $0.0050 \text{ mol dm}^{-3}$  respectively.

Fig. 2.2 shows the concentration of  $\text{O}_2$  recorded against time for this experiment.



**Fig. 2.2**

The experiment was repeated to find the initial rate of reaction at different initial concentrations of  $\text{NO}$  and  $\text{O}_2$ . The results of these experiments are shown in Table 2.2.

**Table 2.2**

Experiment	Initial $[\text{NO}] / \text{mol dm}^{-3}$	Initial $[\text{O}_2] / \text{mol dm}^{-3}$	Initial rate of formation of $\text{NO}_2 / \text{mol dm}^{-3} \text{ s}^{-1}$
2	0.001	0.002	$5.55 \times 10^{-10}$
3	0.002	0.003	$3.33 \times 10^{-9}$

- (i) Define the terms *order of reaction* and *rate constant*.

.....

.....

.....

.....

[2]

- (ii) Explain why NO is used in large excess in experiment 1.

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

- (iii) Using the data given, determine the order of reaction with respect to each of the reactants and hence, calculate the rate constant, stating its units.

[3]

- (iv) Determine the initial rate of depletion of O<sub>2</sub> when [NO] = 0.002 mol dm<sup>-3</sup> and [O<sub>2</sub>] = 0.002 mol dm<sup>-3</sup>.

[2]

- (d) The removal of  $\text{NO}_2$  is important because of its significant environmental impact. The solution to this problem is to enforce the installation of catalytic converter onto the exhaust pipes of vehicles. With the aid of a Maxwell Boltzmann distribution curve, explain how catalytic converters help to reduce the release of  $\text{NO}_2$  into the environment.

.....

.....

.....

.....

..... [3]

[Total: 16]

- 3 (a) State and explain the relative Brønsted-Lowry acidity of phenol, nitrophenol and ethanoic acid.

.....

.....

.....

.....

.....

.....

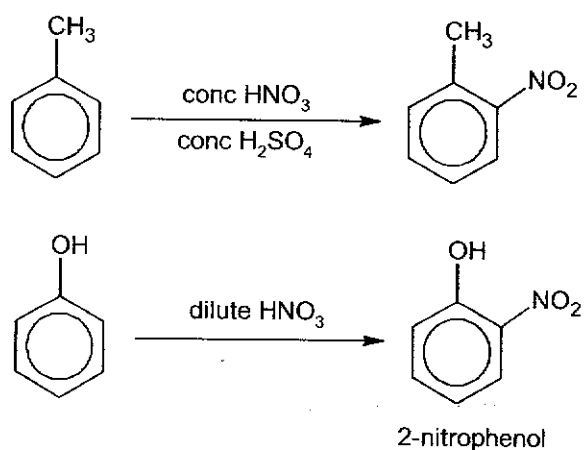
.....

.....

.....

..... [3]

- (b) Both methylbenzene and phenol react with nitric acid, but under different conditions.



- (i) Describe the mechanism of the reaction between methylbenzene and concentrated nitric acid, showing curly arrows, charges and any relevant lone pairs.

[3]

- (ii) Explain why different conditions are needed for these two reactions.

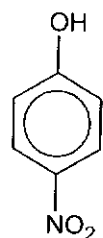
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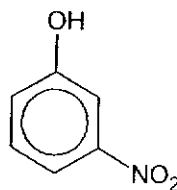
.....

..... [2]

When phenol reacts with dilute nitric acid, two other isomers, 4-nitrophenol and 3-nitrophenol are formed in the reaction mixture.



4-nitrophenol



3-nitrophenol

- (iii) Explain why 3-nitrophenol is the isomer least likely to form in this reaction.

.....

.....

..... [1]

- (iv) The boiling points of two isomers are shown in Table 3.1.

Table 3.1

compound	boiling point / °C
2-nitrophenol	216
4-nitrophenol	279

Suggest a reason for the difference in boiling points between 2-nitrophenol and 4-nitrophenol. Include a diagram to illustrate your answer.

.....

.....

.....

..... [2]



Phenol can be synthesised from nitrobenzene through the following reaction scheme.

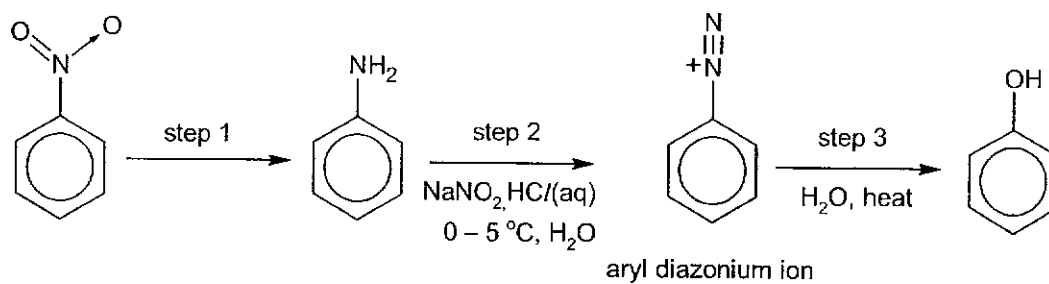


Fig. 3.1

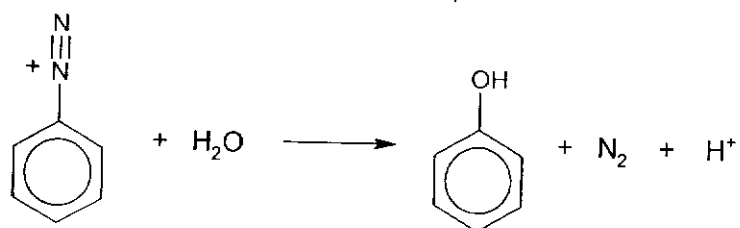
- (c) (i) Explain, in terms of change in oxidation number of N atom, why step 1 is a reduction reaction.

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

- (ii) Write a balanced equation for the reduction of nitrobenzene to phenylamine. Use [H] to represent the reducing agent.

..... [1]

(iii) Aryl diazonium ion reacts with water to form phenol.



aryl diazonium ion

The reaction proceeds via nucleophilic substitution ( $S_N1$ ) mechanism.

- The first step is the rate determining step. Nitrogen gas is produced.
- This is followed by the water molecule acting as a nucleophile to attack the carbocation formed.
- The third step involves deprotonation to form phenol.

Suggest the mechanism for this reaction, showing curly arrows, charges and any relevant lone pairs.

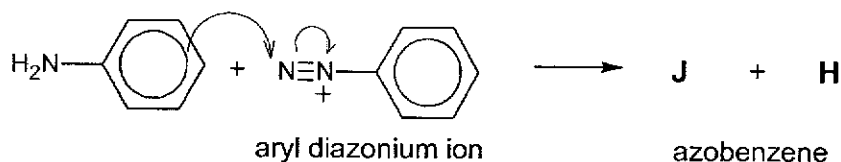
[2]

- (iv) The aryl diazonium ion reacts similarly with ethanol.

Draw the structure of the organic compound. Suggest how the overall rate of reaction will be affected when ethanol is used in the reaction.

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

- (d) (i) In step 3 of Fig. 3.1, a side reaction can occur. The electron deficient aryl diazonium ion can undergo electrophilic substitution with phenylamine to form an azobenzene which contains the diazenyl functional group,  $-N=N-$ . Two cis-trans isomeric azobenzene **J** and **H** are formed.



Draw the structures of **J** and **H**.

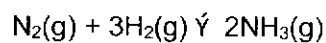
[2]

- (ii) Suggest why cis-azobenzene is less stable than trans-azobenzene.

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

[Total: 20]

- 4  $\text{NH}_3$  is produced from  $\text{N}_2$  and  $\text{H}_2$  in the presence of a catalyst. When  $\text{NH}_3$  is heated in a sealed reactor, the following equilibrium is established.



- (a) (i) Write an expression for  $K_p$  for this equilibrium, stating the units.

[1]

- (ii) In an experiment,  $\text{N}_2$  and  $\text{H}_2$  are placed in a sealed reactor in the molar ratio 1:3. Fig. 4.1 shows the variation in the amounts of  $\text{N}_2$  and  $\text{NH}_3$  in the system with time. The reactor is maintained at a temperature of 750 K and the total pressure is 197 atm.

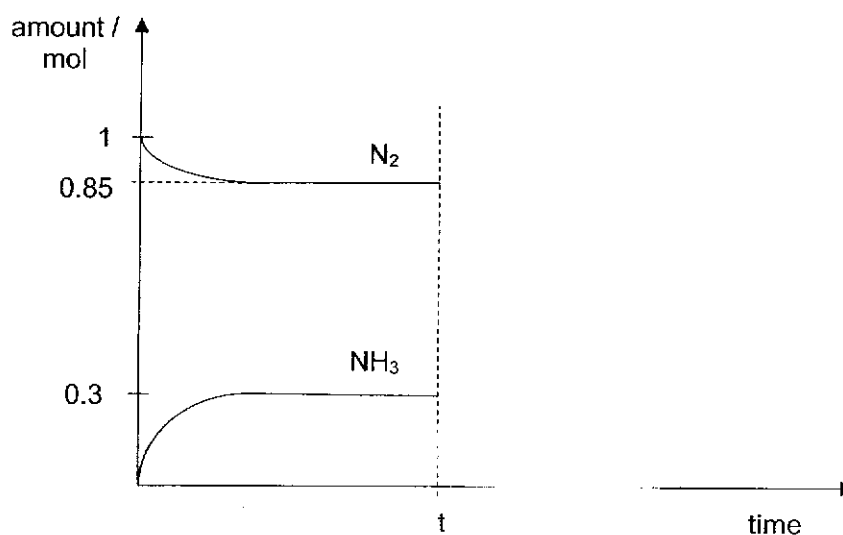


Fig. 4.1

Use the information provided above and data from Fig. 4.1 to calculate the value of  $K_p$  for the equilibrium at 750 K.

[2]

- (iii) Of the three gases at 750 K, the behaviour of  $\text{NH}_3$  deviates the most from ideal gas behaviour and  $\text{N}_2$  behaves less ideally than  $\text{H}_2$ .

Explain the relative deviations from ideal gas behaviour of these gases.

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

- (iv) At time  $t$ , gases in the sealed reactor were passed into a condenser.  $\text{NH}_3$  gas is cooled and removed from the system. The remaining gases were then recycled and passed back into the reactor.

Assuming that the pressure and temperature in the sealed reactor remains unchanged, sketch the changes in amount of  $\text{N}_2$  and  $\text{NH}_3$  that would be observed from  $t$  min in Fig. 4.1. [1]

- (v) The reaction to produce  $\text{NH}_3$  is repeated with the same amounts of  $\text{N}_2$  and  $\text{H}_2$  at 750 K in a smaller reactor. State the effects, if any, of this change on the yield of ammonia and on the value of  $K_p$ . Explain your answer.

- effect on yield of ammonia

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

- effect on the value of  $K_p$

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

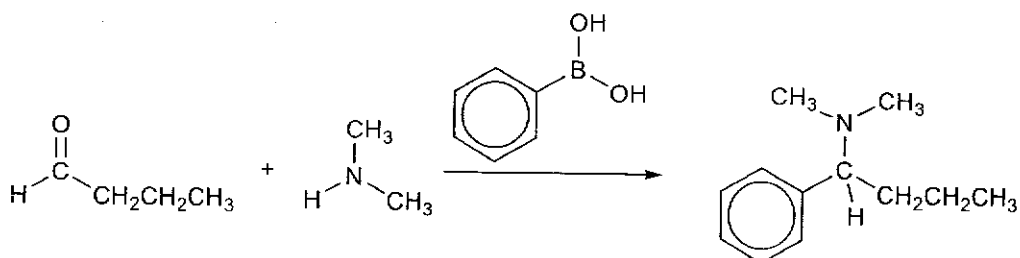
Direct treatment of ammonia and amine with an alkylating agent like alkyl halides, will result in the formation of by-products. With the help of carbonyl compounds, one substituted amine compound rather than a mixture can be obtained. Parts (b) and (c) introduce two such methods.

**(b) Method 1: Petasis reaction**

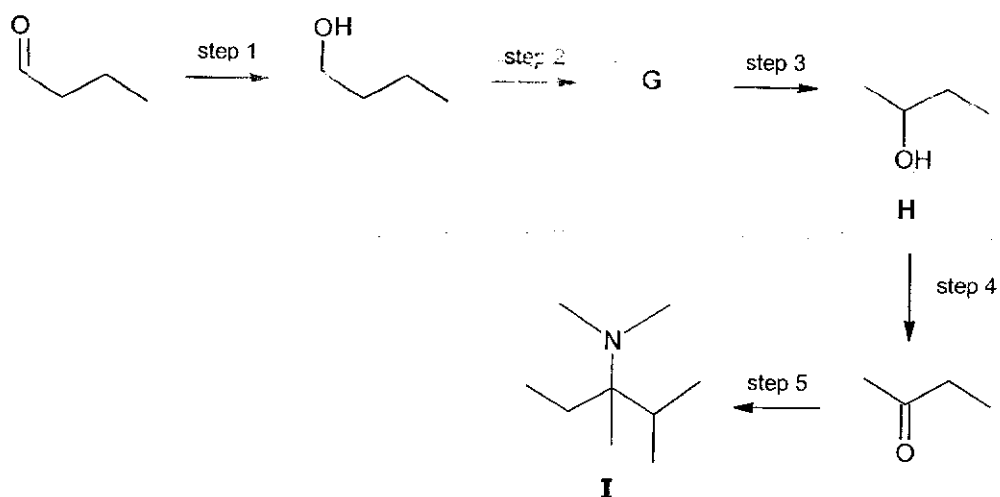
In the Petasis reaction, carbonyl compounds react with amines in the presence of suitable boronic acids to form substituted amines.

The general structure of a boronic acid is  $B(OH)_2R$  where R is an alkyl or aryl group.

An example of the Petasis reaction is given below.



The Petasis reaction can be used in step 5 of the following synthesis of compound **I** from butanal.



(i) Suggest the structure of compound **G**.

[1]

- (ii) Suggest reagents and conditions for steps 1, 2, 3 and 5.

step 1 .....

step 2 .....

step 3 .....

step 5 .....

[4]

- (iii) State the type of stereoisomerism shown by compound **H** and hence draw the structures of the isomers.

type of stereoisomerism .....

[2]

## (c) Method 2: Reductive amination

In the reductive amination of carbonyl compounds, ketones and aldehydes react with primary amine in the presence of an acid catalyst via an iminium ion intermediate. The iminium ion formed is then reduced by  $\text{NaBH}_3\text{CN}$  to form the desired substituted amine.

An example of the reductive amination reaction is given below.



The mechanism for the above reaction involved a series of five steps as shown in Fig. 4.2.

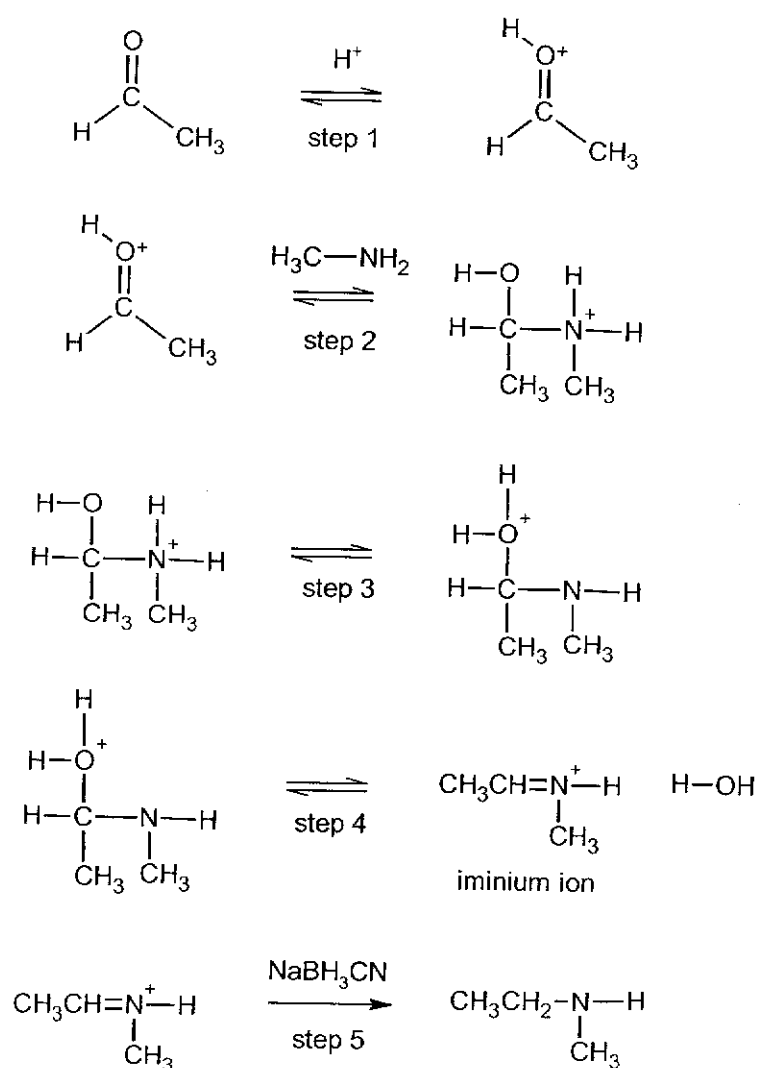


Fig. 4.2



- (i) Complete Fig. 4.2 to suggest a mechanism for steps 1 to 4 of the formation of N-ethylmethanamine. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]
- (ii) The iminium ion intermediate formed in step 4 of the reductive amination reaction displays stereoisomerism.

State the type of stereoisomerism. With the aid of a labelled diagram, showing how the orbitals overlap, explain how this stereoisomerism arise.

type of stereoisomerism .....

.....  
 .....  
 .....  
 ..... [3]

- (iii) Benzaldehyde can also be used in the reductive amination reaction. Other than the use of alkaline aqueous  $I_2$ , outline a simple chemical test that you could carry out to distinguish benzaldehyde from ethanal. Hence, write a balanced equation for the reaction that occur.

test .....

observations .....

.....  
 .....

balanced equation

[2]

- (d) Both N-ethylmethylamine and N-methylethanamine are examples of nitrogen compounds.

Table 4.1

Lewis base	type of hybridisation of N atom
$\text{CH}_3\text{CH}_2\text{NHCH}_3$ N-ethylmethylamine	
$\text{CH}_3\text{CH}=\text{NCH}_3$ N-methylethanamine	

- (i) Explain how the two nitrogen compounds act as Lewis bases. Illustrate your answer with an equation using one of the Lewis bases stated in Table 4.1.

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

- (ii) Complete Table 4.1 and hence explain why N-ethylmethylamine is more basic than N-methylethanamine.

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

[Total: 25]