

**NATIONAL JUNIOR COLLEGE**  
**SH2 PRELIMINARY EXAMINATION**  
 Higher 2

CANDIDATE  
NAME

SUBJECT  
CLASS

REGISTRATION  
NUMBER

**CHEMISTRY**

Paper 3 Free Response

**9729/03**  
**27 August 2021**  
**2 hours**

Candidates answer on Question Paper.  
 Additional Materials: Data Booklet

**READ THE INSTRUCTIONS FIRST**

Write your subject class, registration number and name on all the work you hand in.

Write in dark blue or black pen.

You may use a soft pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

**Section A**

Answer **all** questions.

**Section B**

Answer **one** question.

A Data Booklet is provided.

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

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

For Examiner's Use	
<b>Section A</b>	
1	/20
2	/16
3	/24
<b>Section B</b>	
4	/20
5	/20
<b>Paper 3 Total</b>	<b>/80</b>

This document consists of **24** printed pages.

## Section A

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

- 1 (a) Nicotine ( $C_{10}H_{14}N_2$ ) is a drug present in tobacco. In aqueous solution, nicotine ionises as shown.



- (i) Calculate the pH of a  $0.100 \text{ mol dm}^{-3}$   $C_{10}H_{14}N_2$  solution. [2]

$C_{10}H_{14}N_2$  is a weak base,

$$[OH^-] = \sqrt{10^{-6} \times 0.100} = 3.162 \times 10^{-4} \text{ mol dm}^{-3}$$

$$pOH = -\lg[OH^-] = 3.50$$

$$pH = 14 - pOH = 10.5$$

- (ii) Suggest a suitable indicator for the titration of aqueous nicotine with  $HNO_3(aq)$ . Explain your answer. [2]  
Methyl orange [1]. The equivalence point pH would be less than 7 [1/2], the working range of methyl orange (pH 3-5) would overlap with the region of rapid pH change at equivalence point. [1/2]

Note: The salt,  $C_{10}H_{15}N_2^+$ , (with  $K_a$  value) is the conjugate acid of weak base  $C_{10}H_{14}N_2$  ( $K_b$ ). Hence the salt is acidic and has a pH of  $< 7$  at equivalence point.

- (iii) Calculate the pH of a  $5.00 \text{ dm}^3$  solution consisting of  $0.100 \text{ mol dm}^{-3}$   $C_{10}H_{14}N_2$  and  $0.200 \text{ mol dm}^{-3}$   $C_{10}H_{15}N_2^+$ . [1]  
The mixture contains a weak base and its conjugate acid, it is a buffer solution.

$$\begin{aligned} pOH &= pK_b + \lg \frac{[\text{conjugate acid}]}{[\text{weak base}]} \\ &= 6.0 + \lg \frac{0.2}{0.1} \\ &= 6.30 \text{ [1/2]} \end{aligned}$$

$$pH = 14 - 6.30 = 7.70 \text{ [1/2]}$$

- (iv) Calculate the number of moles of  $\text{HNO}_3$  that needs to be added to the solution in (a)(iii) to obtain a buffer solution of pH 7.40. [2]  
 Weak base  $\text{C}_{10}\text{H}_{14}\text{N}_2$  of the buffer will react with the  $\text{HNO}_3$  added, use ICF table (in mol) to determine limiting reagent.

Initial amount of  $\text{C}_{10}\text{H}_{14}\text{N}_2 = 5 \times 0.100 = 0.5 \text{ mol}$

Initial amount of  $\text{C}_{10}\text{H}_{15}\text{N}_2^+ = 5 \times 0.200 = 1.0 \text{ mol}$

Let amount of  $\text{HNO}_3$  added =  $x \text{ mol}$

	$\text{C}_{10}\text{H}_{14}\text{N}_2$	+ $\text{H}^+$	$\rightarrow$	$\text{C}_{10}\text{H}_{15}\text{N}_2^+$
I / mol	0.5	x		1.0
C / mol	-x	-x		+x
F / mol	$0.5 - x$	0		$1 + x$

$$\text{pH} = 7.40, \text{pOH} = 6.60$$

$$\text{pOH} = \text{p}K_b + \lg \frac{[\text{conjugate acid}]}{[\text{weak base}]}$$

$$6.60 = 6.0 + \lg \left( \frac{1+x}{0.5-x} \right)$$

$$\lg \left( \frac{1+x}{0.5-x} \right) = 0.60$$

$$\left( \frac{1+x}{0.5-x} \right) = 10^{0.60} \text{ [1] or similar idea}$$

$$\frac{1+x}{0.5-x} = 3.981$$

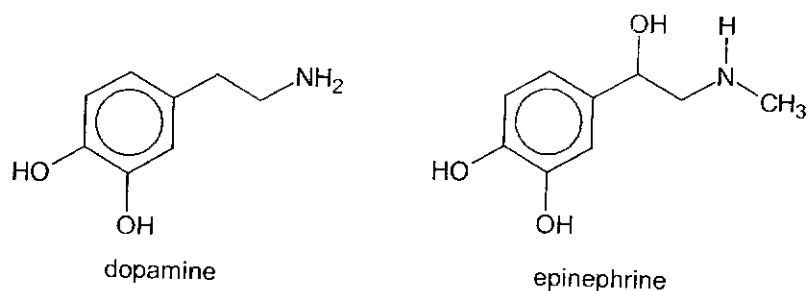
$$1+x = 1.991 - 3.981x$$

$$4.981x = 0.991$$

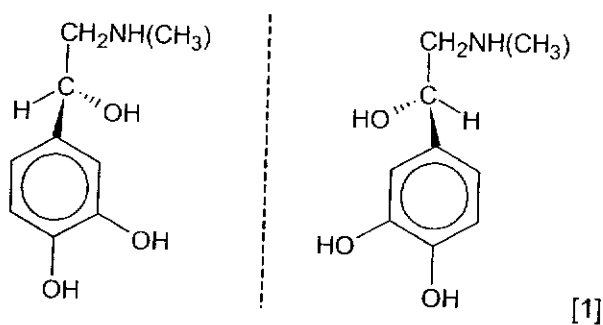
$$x = 0.199$$

Amount of  $\text{HNO}_3$  needed = 0.199 mol

When a cigarette is smoked, nicotine-rich blood stimulates the release of many chemical messengers including dopamine and epinephrine.

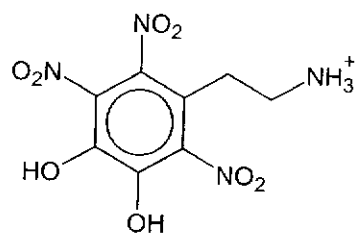


- (b) (i) Name the type of isomerism exhibited by epinephrine and draw the isomers. [2]  
Optical isomerism / enantiomerism [1]



Note : must show 3D tetrahedral drawing around the chiral carbon.

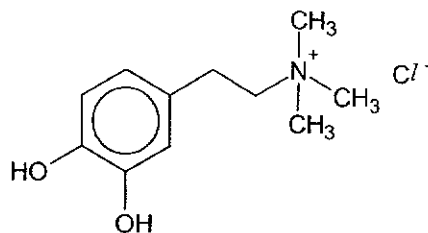
- (ii) Give the structure of the product when dopamine is reacted with excess concentrated  $\text{HNO}_3$ . [2]



1m for 3 × E.sub of  $-\text{NO}_2$  on phenol (0m if monosub of  $-\text{NO}_2$ )  
1m for acid base reaction with  $-\text{NH}_2$  to give  $-\text{NH}_3^+$

Note: conc  $\text{HNO}_3$  lead to tri sub of  $-\text{NO}_2$  at 2,4,6 position of EACH phenol.

- (iii) A reaction between dopamine and chloromethane,  $\text{CH}_3\text{Cl}$ , forms a compound with formula  $\text{C}_{11}\text{H}_{18}\text{NO}_2\text{Cl}$ . Suggest a structure for this compound and how the yield of this compound can be maximised. [2]



React Dopamine with **excess  $\text{CH}_3\text{Cl}$** . [1m]

Note: dopamine,  $\text{C}_8\text{H}_{11}\text{NO}_2$  reacts with 3 mol of  $\text{CH}_3\text{Cl}$  to obtain 11 C.  
Amine group function as the nucleophile to react with C-Cl.

- (iv) Suggest a chemical test to distinguish the two chemical messengers, dopamine and epinephrine. [2]

1m chemical test for 2° alcohol in epinephrine.

1m observations

Anhydrous  $\text{PCl}_5$  or  $\text{SOCl}_2$

White fumes of  $\text{HCl}$  observed for epinephrine but no white fumes for dopamine.

$\text{K}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4(\text{aq}), \text{heat}$

Orange  $\text{K}_2\text{Cr}_2\text{O}_7$  turns green for epinephrine but  $\text{K}_2\text{Cr}_2\text{O}_7$  remains orange for dopamine.

Do not accept hot  $\text{KMnO}_4$  as both compounds would undergo benzene side chain oxidation.

Cigarette smoke contains many harmful chemicals such as Period 4 elements, chromium, nickel and arsenic.

- (c) Give the full electronic configuration of chromium and arsenic. [2]

Cr :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$

As :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$  (Group 15 configuration)

- (d) Chromium and nickel are transition elements.

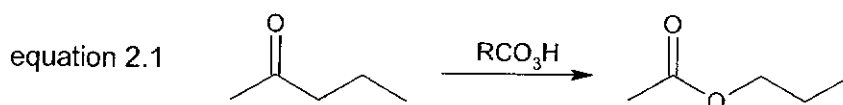
- (i) State what is meant by the term *transition elements*. [1]  
Transition elements concept

- (ii) Suggest why the first ionisation energies of chromium and nickel are similar. [2]  
Transition elements concept

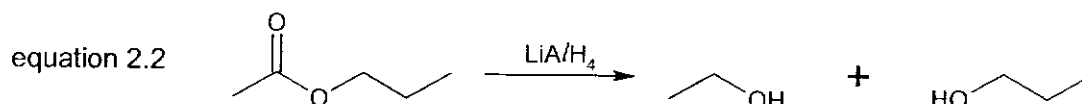
[Total : 20]

2 Baeyer-Villiger reaction is an organic reaction that forms an ester from a ketone.

Pentan-2-one can be converted into propyl ethanoate using a peroxyacid,  $\text{RCO}_3\text{H}$ .

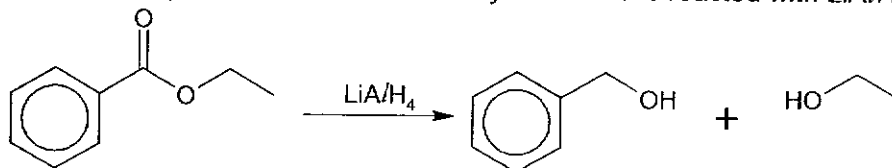


Ester can be reduced by  $\text{LiAlH}_4$  to give alcohols. An example of the reduction of propyl ethanoate is shown below.



(a) (i) Suggest the type of reaction shown in equation 2.1. [1]  
Oxidation [gain O atom]

(ii) Suggest the products formed when ethyl benzoate is reacted with  $\text{LiAlH}_4$ . [2]



(b) Fig 2.1 shows a reaction scheme involving a cyclic ester, compound C.

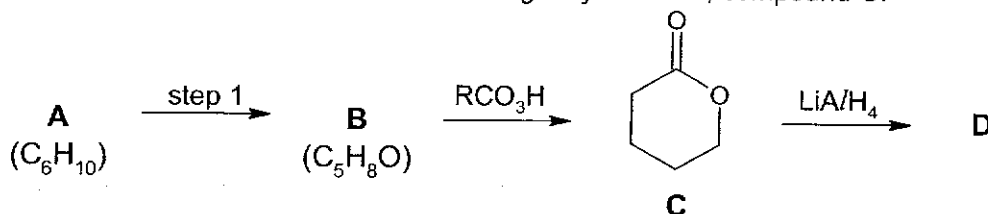
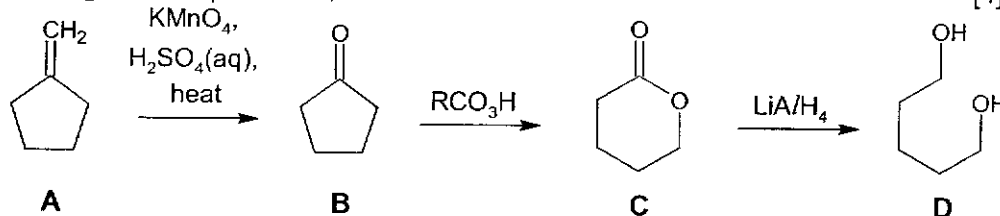


Fig 2.1

(i) State the reagents and conditions required for step 1 and suggest structures for the organic compounds A, B and D. [4]



1m for step 1

B to C follows the reaction stated in equation 2.1. B must be a carbonyl compound.

C to D follows the reaction stated in equation 2.2. D contains 2 -OH groups after the ester reacts with  $\text{LiAlH}_4$ .

A must be an alkene with  $=\text{CH}_2$  such that it loses one C atom as  $\text{CO}_2$  after vigorous oxidation with hot acidified  $\text{KMnO}_4$

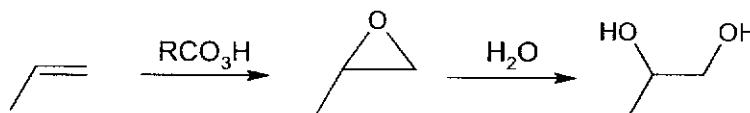
(ii) Compound **C** can also be synthesised from  $\text{HOOC}(\text{CH}_2)_3\text{CH}_2\text{OH}$ .

Suggest the reagents and conditions required for this synthesis. [1]  
Concentrated  $\text{H}_2\text{SO}_4$ , heat

Note: The  $-\text{COOH}$  and  $-\text{OH}$  group undergoes intramolecular condensation to form cyclic ester.

(c) Peroxyacid,  $\text{RCO}_3\text{H}$ , also converts alkene into epoxide, a cyclic ether with three-atom ring that approximates an equilateral triangle.

Epoxide reacts with water readily to give a diol.

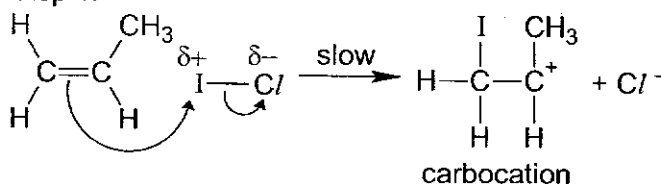


Use your knowledge of VSEPR theory to explain the high reactivity of epoxide. [2]  
Based on VSEPR theory, the C (or O atoms) in epoxide should have a **bond angle of  $109.5^\circ$  ( $105^\circ$  for O)** respectively to minimise electron pair repulsion [1/2]

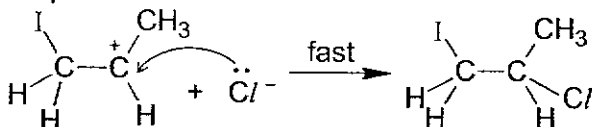
However, in the three-atom ring of epoxide, the bond angle of  **$60^\circ$  is smaller than predicted by VSEPR** [1/2], which causes **significant bond pair-bond pair repulsion (or ring strain)** [1/2], the C-O **bonds are easier to break / unstable**. [1/2]

(d) Describe the mechanism for the reaction of propene with  $\text{Cl}-\text{I}$ .  
In your answer, show any relevant charges, dipoles or lone pairs of electrons you consider important in this mechanism. [3]  
Electrophilic addition [1m]

Step 1:



Step 2:

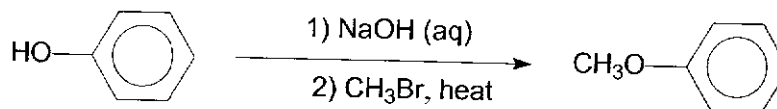


-1/2m for each mistake

Note: must show the more stable carbocation (formed in higher proportion) that lead to the formation of major product.

- (e) Organic halogen compounds are widely used in synthetic reactions.

Bromoalkanes are often used in the synthesis of ethers from phenols in the Williamson ether synthesis, an example of which is shown below.



- (i) Suggest why aqueous NaOH is required in this reaction. [1]  
 NaOH remove  $\text{H}^+$  from phenol to generate **phenoxide**, with higher electron density on O. It is **a stronger nucleophile** than phenol. [1]
- (ii) The rate of the synthesis decreases when  $\text{CH}_3\text{Cl}$  is used in place of  $\text{CH}_3\text{Br}$ .

With the use of the *Data Booklet*, suggest an explanation for this difference in the rate of reaction. [2]

$\text{BE}(\text{C}-\text{Cl}) = 340 \text{ kJ mol}^{-1}$  and  $\text{BE}(\text{C}-\text{Br}) = 280 \text{ kJ mol}^{-1}$ . [1m]

More energy is required to overcome the stronger  $\text{C}-\text{Cl}$  bond in  $\text{CH}_3\text{Cl}$ , leading to a slower rate of reaction. [1m]

[Total : 16]



- 3 (a) Some data on three nitrogen-containing compounds are given in the table below:

compound	boiling point/ °C
NO <sub>2</sub>	21
N <sub>2</sub> O <sub>4</sub>	21
N <sub>2</sub> O <sub>5</sub>	47

- (i) With reference to the structure and bonding, explain why the boiling points of NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> are the same. [3]

Both compounds have **simple molecular / covalent structure**. [1/2]

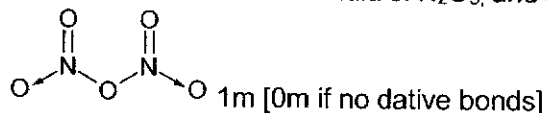
NO<sub>2</sub> is polar with **permanent dipole-permanent dipole (pd-pd) interaction** [1/2] while N<sub>2</sub>O<sub>4</sub> is non polar with **instantaneous dipole-induced dipole (id-id) interaction**. [1/2]

As size of **electron cloud of N<sub>2</sub>O<sub>4</sub> is large** [1/2], its electron cloud is more easily polarised, **increasing the strength of id-id forces**. [1/2]

The strength of **intermolecular forces for NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> are comparable** [1/2] and hence their boiling points are the same.

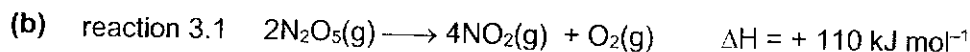
- (ii) N<sub>2</sub>O<sub>5</sub> is a symmetrical molecule O<sub>2</sub>N-O-NO<sub>2</sub>.

Draw the full structural formula of N<sub>2</sub>O<sub>5</sub>, and suggest the N-O-N bond angle. [2]



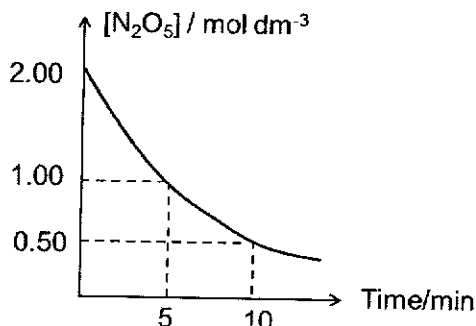
Note: N is not able to form 2 × N=O and 1 × N-O, hence a dative bond is necessary.

There are 2 bond pair regions and 2 lone pair regions around O of N-O-N  
Bond angle is 104.5° or 105° (bent)



The overall order of reaction for reaction 3.1 is one and the reaction proceeds via a two-step mechanism.

- (i) Sketch a graph of concentration of  $\text{N}_2\text{O}_5$  against time for reaction 3.1. The reaction has a half-life of 5 minutes and  $\text{N}_2\text{O}_5$  at an initial concentration of  $2.00 \text{ mol dm}^{-3}$ . [1]



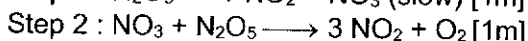
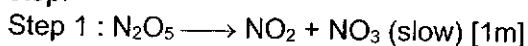
- (ii) Determine the value of the rate constant,  $k$ , for reaction 3.1, stating its units. [1]

For first order reaction,  $t_{1/2} = \frac{\ln 2}{k}$

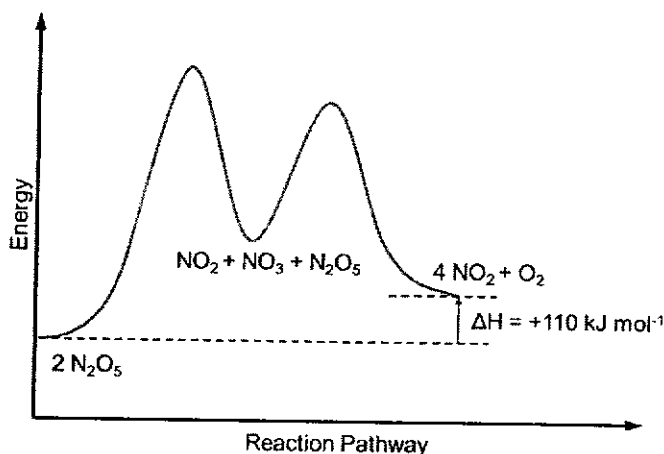
$$k = \frac{\ln 2}{5} = 0.139 \text{ min}^{-1}$$

- (iii) The slow step of the two-step reaction mechanism produces a  $\text{NO}_3$  intermediate.

Write equations to show a possible reaction mechanism for reaction 3.1. [2]  
Since it is first order w.r.t  $\text{N}_2\text{O}_5$ , only 1 molecule of  $\text{N}_2\text{O}_5$  is involved in the slow step.



- (iv) Sketch an energy profile diagram for the proposed mechanism for reaction 3.1. Label your diagram clearly, including the reactants and the products formed. [2]

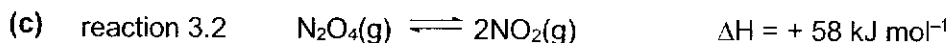


Show 2-step reaction with higher  $E_a$  for first step [1/2]

Show and label positive  $\Delta H$  (product is higher energy level than reactant) [1/2]

Label the reactants and products clearly [1/2]

Label the intermediate as the sum of product of step 1 + 2<sup>nd</sup>  $\text{N}_2\text{O}_5$  [1/2]



Some amount of dinitrogen tetroxide,  $\text{N}_2\text{O}_4$ , is placed in a gas syringe and allowed to achieve the equilibrium. At room temperature and pressure, 0.100 g of an equilibrium mixture of reaction 3.2 takes up a volume of 31.7  $\text{cm}^3$ .

- (i) Write the  $K_p$  expression for reaction 3.2. [1]

$$K_p = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}}$$

- (ii) Calculate the average relative molecular mass of the mixture. [1]

$$\text{Amount of gas} = \frac{31.7}{24000} = 0.001321 \text{ mol [1/2]}$$

$$\text{Average } M_r = \frac{0.100}{0.00132} = 75.7 \text{ [1/2]}$$

- (iii) Use your answers to (c)(ii) to calculate the percentage of  $\text{N}_2\text{O}_4$  in the equilibrium mixture and hence the value of  $K_p$  (in atm) for reaction 3.2 at r.t.p. [3]

Let % of  $\text{N}_2\text{O}_4$  be  $x$  and % of  $\text{NO}_2$  be  $(100-x)$

$$\frac{x}{100} \times (14.0 \times 2 + 16.0 \times 4) + \frac{100-x}{100} \times (14.0 + 16.0 \times 2) = 75.70$$

$$92x + 4600 - 46x = 7570$$

$$46x = 2970$$

$$x = 64.57$$

$$\% \text{ N}_2\text{O}_4 = 64.6\% \text{ [1]}$$

$$P_{\text{N}_2\text{O}_4} = \frac{64.57}{100} \times 1 = 0.6457 \text{ atm [1/2]}$$

$$P_{\text{NO}_2} = \frac{35.43}{100} \times 1 = 0.3543 \text{ atm [1/2]}$$

$$K_p = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} = \frac{(0.3543)^2}{0.6457} = 0.1944 \approx 0.194 \text{ atm [method 1m]}$$

- (iv) The gas mixture is compressed to a volume of 20  $\text{cm}^3$ . Explain how would the percentage of  $\text{N}_2\text{O}_4$  be affected as compared to your answer in (c)(iii). [2]  
When the gas mixture is compressed, total **gas pressure increases**. [1/2] By Le Chatelier's Principle, the equilibrium would try to partially offset the increase in pressure by **reducing the number of gas particles**. [1/2] **Position of equilibrium would shift to the left, and percentage of  $\text{N}_2\text{O}_4$  increases**. [1]

(d)  $\text{NO}_2$ , an air pollutant, is sometime found in car exhaust emissions.

- (i) Give one environmental impact of  $\text{NO}_2$ . [1]
- formation of smog through reaction with other air pollutants. Smog is harmful to plants and humans.
  - formation of ozone at lower atmosphere. High concentration of ozone at lower atmosphere causes respiratory problems.
  - $\text{NO}_2$  acts as a catalyst for the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$ ,  $\text{SO}_3$  dissolves in rainwater to cause acid rain ( $\text{H}_2\text{SO}_4$ ).
- Any of the above.
- (ii) Explain how  $\text{NO}_2$  is produced in car engine. [1]  
During combustion of petrol,  **$\text{N}_2$  reacts with  $\text{O}_2$  under high temperature.**
- (iii) To reduce pollution from motor vehicles, catalytic converters containing rhodium and platinum are fixed onto the exhaust pipes. These catalysts convert the pollutants to less harmful compounds.

Write an equation to show how catalytic converter removes CO and  $\text{NO}_2$ . [1]  
 $4\text{CO} + 2\text{NO}_2 \longrightarrow 4\text{CO}_2 + \text{N}_2$

(e)  $\text{NH}_3$ ,  $\text{CH}_3\text{CONH}_2$  and  $\text{C}_6\text{H}_5\text{NH}_2$  are nitrogen containing compounds.

Arrange these compounds in order of increasing basicity. Explain your answer. [3]  
 $\text{CH}_3\text{CONH}_2 < \text{C}_6\text{H}_5\text{NH}_2 < \text{NH}_3$  [1]

The lone pair electrons on nitrogen atom of  $\text{CH}_3\text{CONH}_2$  is delocalised significantly to adjacent C=O with highly electronegative O atom, hence, it is **not available** to accept  $\text{H}^+$ . [1] Thus, amide is neutral/not basic.

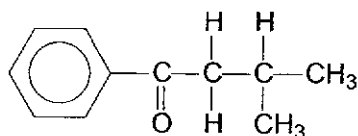
For  $\text{C}_6\text{H}_5\text{NH}_2$ , due to slight delocalization of lone pair electrons on N into the benzene ring, this decreases the electron density on N atom and it is less available to accept  $\text{H}^+$  as compared to  $\text{NH}_3$ . [1] Hence  $\text{C}_6\text{H}_5\text{NH}_2$  is a weaker base than  $\text{NH}_3$ .

[Total: 24]

## Section B

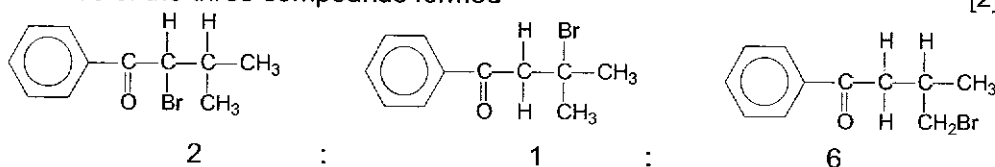
Answer **one** question from this section.

- 4 (a) When phenyl-3-methylbutanone reacts with bromine in the presence of UV light, three mono-brominated compounds are formed.



phenyl-3-methylbutanone

- (i) Draw the structures of the three mono-brominated compounds and hence predict the ratio of the three compounds formed [2]



1m for each correct structure

1m for correct ratio

- (ii) After bromination is carried out, the products are analysed. It is found that the three mono-brominated compounds are formed in approximately equal amount.

Suggest an explanation for the difference between this ratio and the one you gave in (a)(i) [2]

The relative stability of the carbon radical intermediate is  $3^\circ$  radical  $>$   $2^\circ$  radical  $>$   $1^\circ$  radical. Greater number of electron donating alkyl group stabilises the carbon radical to a larger extent. [1]

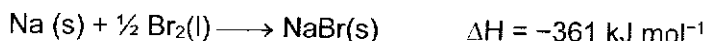
The more stable radical is formed at a greater rate OR larger % than expected. [1]

- (b) With reference to the data given below and any relevant data from the *Data Booklet*, answer the following questions concerning the chemistry of sodium bromide.

Standard enthalpy change of formation of solid sodium bromide	- 361 kJ mol <sup>-1</sup>
First electron affinity of bromine	- 325 kJ mol <sup>-1</sup>
Standard enthalpy change of atomisation of sodium	+ 107 kJ mol <sup>-1</sup>
Lattice energy of sodium bromide	- 753 kJ mol <sup>-1</sup>

- (i) Define standard enthalpy change of formation of solid sodium bromide. [1]  
The **heat evolved** when **1 mol of NaBr(s) is formed from** its constituent element in their standard state **Na(s) and Br<sub>2</sub>(l)** under **standard conditions of 298 K and 1 bar**.

OR

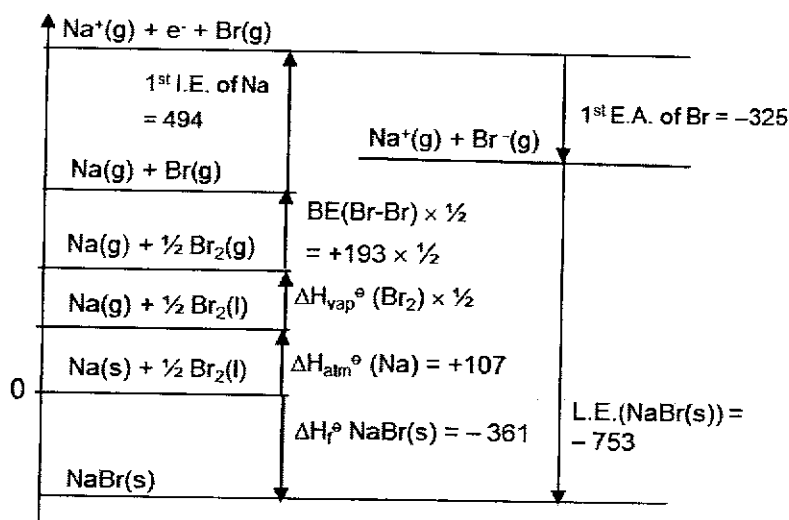


(must include sign of  $\Delta H$  if define using equation)

Note: standard state of Br<sub>2</sub> is liquid, refer to QA table in Data Booklet.

- (ii) Construct an energy level diagram and use it to calculate the standard enthalpy change of vapourisation of bromine. [5]

Enthalpy/ kJ mol<sup>-1</sup>



4m for energy level diagram  
-1/2 for each mistake

By Hess' Law

$$-361 = 107 + \frac{1}{2} \times \Delta H_{\text{vap}} \text{ Br}_2 + 193 \times \frac{1}{2} + 494 - 325 - 753$$

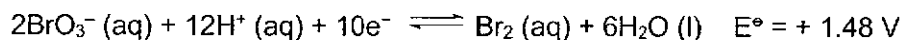
$$\frac{1}{2} \times \Delta H_{\text{vap}} \text{ Br}_2 = 19.5$$

$$\Delta H_{\text{vap}} \text{ Br}_2 = +39.0 \text{ kJ mol}^{-1} \quad [1]$$

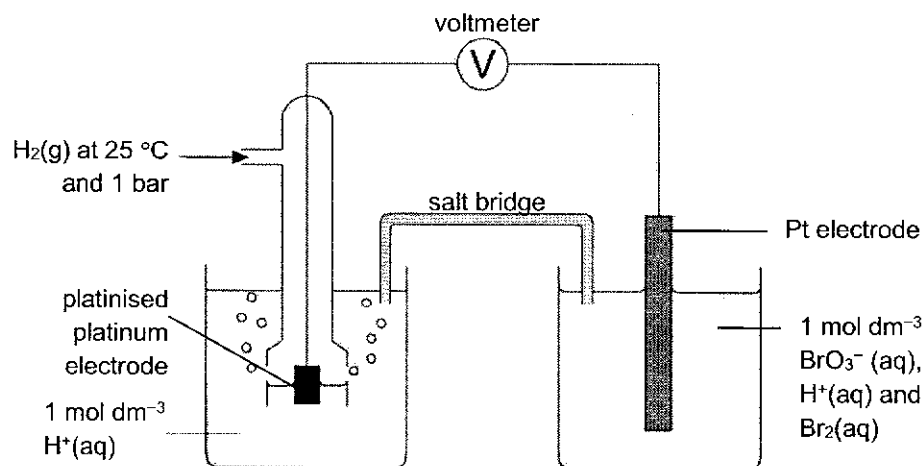
Note: vaporisation is conversion of **1 mol of Br<sub>2</sub>(l)** to Br<sub>2</sub>(g)

- (c) Long-term exposure to bromate(V) ions may increase consumers' risk of cancer, according to the US government's Environmental Protection Agency.

Aqueous bromate(V) ions acts as a strong oxidising agent in acidic solution as shown in the equation below:



- (i) Draw a labelled diagram to show how the standard electrode potential of the  $\text{BrO}_3^- (\text{aq})/\text{Br}_2 (\text{aq})$  electrode can be measured. [3]



1m for each half-cell (-1/2 for each mistake),

Note:  $\text{H}^+$  is required for the  $\text{BrO}_3^-$  and  $\text{Br}^-$  half cell, as shown in the half equation.

½m for 298K, 1bar and 1 mol dm<sup>-3</sup> for all ions

½m for voltmeter and salt bridge

- (ii) When  $\text{AgNO}_3 (\text{aq})$  is added to the  $\text{BrO}_3^- (\text{aq})/\text{Br}_2 (\text{aq})$  half-cell in the (c)(i) set-up, white precipitate is formed.

Explain the effect on the electrode potential of the half-cell. [2]

$\text{Ag}^+$  reacts with  $\text{BrO}_3^-$  to form the white precipitate,  $[\text{BrO}_3^-]$  decreases. [1/2]

By Le Chatelier's Principle, the position of the equilibrium shifts to the left [1/2]

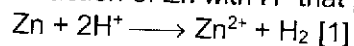
Electrode potential of the half-cell decreases (less positive) [1]

Note: There are no  $\text{Br}^-$  in the  $\text{BrO}_3^-/\text{Br}_2$  half cell. Hence it is wrong to identify the ppt as  $\text{AgBr}$ .

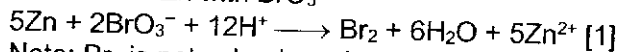
- (iii) Effervescence is observed when excess zinc is added to acidified bromate(V) ions. The final solution is colourless.

Write balanced equations for the reactions.

Reaction of Zn with  $H^+$  that produces  $H_2(g)$  (Effervescence) [3]

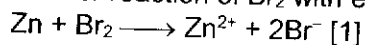


Reaction of Zn with  $BrO_3^-$



Note:  $Br_2$  is not colourless, hence there must be a further reaction of  $Br_2$ .

Further reaction of  $Br_2$  with excess Zn



- (d) Describe and explain how the volatilities of the halogens vary from chlorine to iodine. [2]  
Volatilities of non-polar halogen **decrease** from  $Cl_2$  to  $I_2$  [1/2] due to their **increasing electron cloud size** [1/2]; **strength of the intermolecular instantaneous dipole-induced dipole interactions increases**, [1/2] more energy is required to vapourise the halogens from  $Cl_2$  to  $I_2$ . [1/2]

Note: Volatility is the measure of how ready a substance vapourise. It involves the breaking of intermolecular forces, NOT covalent bond.

[Total : 20]





- (b) Ethanedioic acid,  $\text{H}_2\text{C}_2\text{O}_4$ , is a toxic substance found in rhubarb leaves.

20.0 g of rhubarb leaves was crushed, and the ethanedioic acid present was extracted using water. The volume of the extracted sample was made up to  $50.0 \text{ cm}^3$  using water.

$10.0 \text{ cm}^3$  of the solution containing ethanedioic acid was pipetted into a conical flask and titrated with  $0.020 \text{ mol dm}^{-3}$  acidified potassium manganate(VII),  $\text{KMnO}_4$ . The following reaction occurs.



The average titre was  $9.25 \text{ cm}^3$ .

- (i) State the endpoint colour change of this titration. [1]  
When the solution in conical flask turns from colourless into first permanent pink. (Due to one excess drop of purple  $\text{KMnO}_4$  from burette)
- (ii) Calculate the percentage mass of ethanedioic acid,  $\text{H}_2\text{C}_2\text{O}_4$ , present in the rhubarb leaves sample. [3]

$$\text{Amount of } \text{MnO}_4^- \text{ used} = \frac{9.25}{1000} \times 0.020 = 0.000185 \text{ mol [1/2]}$$

$$\text{Amount of } \text{C}_2\text{O}_4^{2-} \text{ in } 10.0 \text{ cm}^3 = \frac{5}{2} \times 0.000185 = 0.0004625 \text{ mol [1/2]}$$

$$\text{Amount of } \text{C}_2\text{O}_4^{2-} \text{ in } 50.0 \text{ cm}^3 = 5 \times 0.0004625 = 0.002313 \text{ mol [1/2]}$$

$$\text{Mass of } \text{H}_2\text{C}_2\text{O}_4 = 0.002313 \times (1.0 \times 2 + 12.0 \times 2 + 16.0 \times 4) = 0.2082 \text{ g [1/2]}$$

$$\% \text{ mass of } \text{H}_2\text{C}_2\text{O}_4 \text{ in } 20.0 \text{ g sample} = \frac{0.2082}{20.0} \times 100\% = 1.04\% [1]$$

Note: we **cannot** use the mol ratio of  $\text{MnO}_4^-$  to  $\text{H}^+$  to determine amount of  $\text{H}_2\text{C}_2\text{O}_4$  as  $\text{H}^+$  is contributed by  $\text{H}_2\text{C}_2\text{O}_4$  and acidified medium of  $\text{KMnO}_4$ .

- (c) One of the uses of carbon dioxide is in the manufacture of carbonated drinks.

Cylinders of pressurised carbon dioxide are used to produce cola, a carbonated drink. A commercial cola drink was manufactured using such cylinders, each with internal volume of  $5 \text{ dm}^3$  and contains 2.58 kg of carbon dioxide.

- (i) Calculate the pressure the carbon dioxide would exert inside the cylinder at  $25^\circ\text{C}$ . [1]

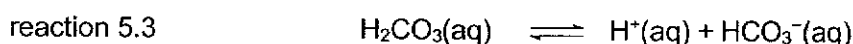
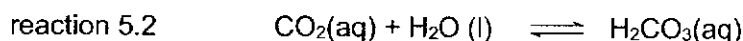
$$pV = nRT \quad (P \text{ in Pa, } V \text{ in m}^3, T \text{ in K})$$

$$p \times 5 \times 10^{-3} = \frac{2.58 \times 1000}{44.0} \times 8.31 \times 298$$

$$p = 2.90 \times 10^7 \text{ Pa}$$

- (ii) The actual pressure inside each of the cylinder was found to smaller than the pressure you calculated in (c)(i). Explain this observation. [1]  
 $\text{CO}_2$  has **significant intermolecular forces of attraction** [1/2] (instantaneous dipole-induced dipole). This gas molecules are **attracted closer together** and **reduces the force of collision of gas molecules (pressure exerted)** against the wall of containers. [1/2]

The amount of carbon dioxide dissolved in a carbonated drink is affected by three reversible reactions.



- (iii) Henry's law state that the amount of dissolved gas in a liquid is proportional to its partial pressure above the liquid.

$$K_H = \frac{[\text{CO}_2(\text{aq})]}{P_{\text{CO}_2}}$$

The Henry's law constant,  $K_H$ , for  $\text{CO}_2$  is  $3.4 \times 10^{-2} \text{ mol dm}^{-3} \text{ atm}^{-1}$  at  $25^\circ\text{C}$ .

The pressure of  $\text{CO}_2(\text{g})$  in an unopened sealed bottle is 250 kPa at  $25^\circ\text{C}$ .

Calculate the concentration of dissolved  $\text{CO}_2$  in the unopened bottle at  $25^\circ\text{C}$ . [1]

$$[\text{CO}_2(\text{aq})] = 3.4 \times 10^{-2} \text{ mol dm}^{-3} \text{ atm}^{-1} \times \left( \frac{250000}{101325} \text{ atm} \right)$$

$$= 0.08388 \approx 0.0839 \text{ mol dm}^{-3}$$

Note: Take note of units for  $K_H$ , hence pressure need to be in atm.

- (iv) Deduce the effect on the pH of the drink when the bottle is opened. Explain your reasonings in terms of the effect on the equilibrium reactions above. No calculation is required for this question. [3]  
 When the bottle is opened, some  $\text{CO}_2$  escapes (or  $P_{\text{total}}$  decreases),  $[\text{CO}_2(\text{g})]$  decreases. The equilibrium of reaction 5.1 shifts left and  $[\text{CO}_2(\text{aq})]$  decreases. [1]  
 Decrease in  $[\text{CO}_2(\text{aq})]$  further causes equilibrium of reaction 5.2 to shifts left and  $[\text{H}_2\text{CO}_3(\text{aq})]$  decreases. [1]  
 Decrease in  $[\text{H}_2\text{CO}_3(\text{aq})]$  then causes equilibrium of reaction 5.3 to shift left too.  
 Overall,  $[\text{H}^+]$  decreases and hence the pH of the drink increases. [1]



## (b) Reactions of anions

<i>anion</i>	<i>Reaction</i>
carbonate, $\text{CO}_3^{2-}$	$\text{CO}_2$ liberated by dilute acids
chloride, $\text{Cl}^-(\text{aq})$	gives white ppt. with $\text{Ag}^+(\text{aq})$ (soluble in $\text{NH}_3(\text{aq})$ )
bromide, $\text{Br}^-(\text{aq})$	gives pale cream ppt. with $\text{Ag}^+(\text{aq})$ (partially soluble in $\text{NH}_3(\text{aq})$ )
iodide, $\text{I}^-(\text{aq})$	gives yellow ppt. with $\text{Ag}^+(\text{aq})$ (insoluble in $\text{NH}_3(\text{aq})$ )
nitrate, $\text{NO}_3^-(\text{aq})$	$\text{NH}_3$ liberated on heating with $\text{OH}^-(\text{aq})$ and Al foil
nitrite, $\text{NO}_2^-(\text{aq})$	$\text{NH}_3$ liberated on heating with $\text{OH}^-(\text{aq})$ and Al foil; $\text{NO}$ liberated by dilute acids (colourless $\text{NO} \rightarrow$ (pale) brown $\text{NO}_2$ in air)
sulfate, $\text{SO}_4^{2-}(\text{aq})$	gives white ppt. with $\text{Ba}^{2+}(\text{aq})$ (insoluble in excess dilute strong acids)
sulfite, $\text{SO}_3^{2-}(\text{aq})$	$\text{SO}_2$ liberated with dilute acids; gives white ppt. with $\text{Ba}^{2+}(\text{aq})$ (soluble in dilute strong acids)

## (c) Tests for gases

<i>Gas</i>	<i>test and test result</i>
ammonia, $\text{NH}_3$	turns damp red litmus paper blue
carbon dioxide, $\text{CO}_2$	gives a white ppt. with limewater (ppt. dissolves with excess $\text{CO}_2$ )
chlorine, $\text{Cl}_2$	bleaches damp litmus paper
hydrogen, $\text{H}_2$	"pops" with a lighted splint
oxygen, $\text{O}_2$	relights a glowing splint
sulfur dioxide, $\text{SO}_2$	turns aqueous acidified potassium manganate(VII) from purple to colourless

## (d) Colour of halogens

<i>halogen</i>	<i>colour of element</i>	<i>colour in aq. solution</i>	<i>colour in hexane</i>
chlorine, $\text{Cl}_2$	greenish yellow gas	pale yellow	pale yellow
bromine, $\text{Br}_2$	reddish brown gas / liquid	orange	orange-red
iodine, $\text{I}_2$	black solid / purple gas	brown	Purple

### Qualitative Analysis Notes

[ppt. = precipitate]

#### (a) Reactions of aqueous cations

cation	reaction with	
	NaOH(aq)	NH <sub>3</sub> (aq)
aluminium, Al <sup>3+</sup> (aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH <sub>4</sub> <sup>+</sup> (aq)	ammonia produced on heating	–
barium, Ba <sup>2+</sup> (aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca <sup>2+</sup> (aq)	white ppt. with high [Ca <sup>2+</sup> (aq)]	no ppt.
chromium(III), Cr <sup>3+</sup> (aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu <sup>2+</sup> (aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe <sup>2+</sup> (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 <sup>3+</sup> (aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg <sup>2+</sup> (aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn <sup>2+</sup> (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 <sup>2+</sup> (aq)	white ppt. soluble in excess	white ppt. soluble in excess