

NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
 Higher 2

CANDIDATE
NAME

SUBJECT
CLASS

REGISTRATION
NUMBER

CHEMISTRY

Paper 2 Structured Questions

9729/02

24 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 on both sides of the paper.
 You may use a soft pencil for any diagrams, graphs or rough working.

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

Answers **all** questions.

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

For Examiner's Use	
1	/8
2	/12
3	/8
4	/11
5	/17
6	/19
Paper 2 Total	/75

	Marks	Weightings
Paper 1	/30	15%
Paper 2	/75	30%
Paper 3	/80	35%
Paper 4	/55	20%

Overall Percentage	
Grade	

This document consists of **23** printed pages and **1** blank page.

Answer all the questions in the spaces provided.

- 1 (a) Iodine can undergo a reaction with aqueous potassium hydroxide to form iodate and iodide ions as shown in the following equation.



This reaction has a potential application in times of nuclear catastrophe when radioactive and volatile iodine-131 is produced. Spraying alkalis into the nuclear reactors can convert the volatile iodine into non-volatile iodate and iodide ions, thus minimizing the damaging radioactive effects.

- (i) Name the type of reaction for the above equation.
Disproportionation

Note : I is simultaneously oxidized from O.S. = 0 in I_2 to O.S. = +5 in IO_3^- and reduced from O.S. = 0 in I_2 to O.S. = -1 in I^-

[1]

- (ii) Write the two balanced half-equations for the above reaction.
[O] $\text{I}_2 + 12\text{OH}^- \longrightarrow 2\text{IO}_3^- + 6\text{H}_2\text{O} + 10\text{e}^-$
(construct by following the steps in balancing half equation)

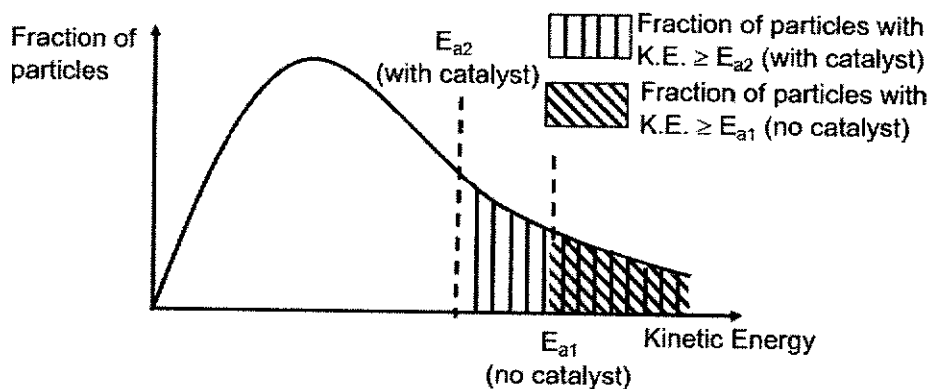
[R] $\text{I}_2 + 2\text{e}^- \longrightarrow 2\text{I}^-$ (obtained from Data Booklet)
State symbols not required

[2]

- (b) The reaction of iodide and peroxydisulfate ions is very slow and can be catalysed by using a homogeneous catalyst.



- (i) Explain why the rate of the above reaction is slow.
The rate of the reaction is very slow because the activation energy is very high due to the collision of two ions of the same charges. [1]
- (ii) With the aid of the Boltzmann distribution, explain how addition of a homogeneous catalyst helps to increase the rate of a reaction.



A catalyst provides an alternative reaction pathway with lower activation energy (E_{a2}).

The fraction of particles with $\text{K.E.} \geq E_a$ increases as shown in the Boltzmann distribution.

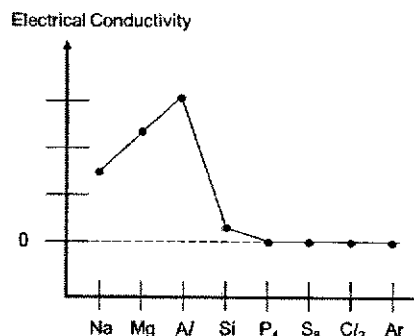
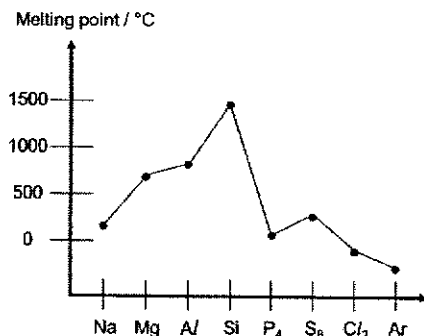
The frequency of effective collisions increases hence rate of reaction increases.

1m diagram
1m explanation

[2]

2 (a) The Period 3 elements vary in their physical properties.

(i) On the axes below, sketch the melting point and electrical conductivity trends for the **stated elements**.



Note:

Melting point trend

For metals, Na to Al, mp increases because of **stronger metallic bond strength** between cations and sea of delocalized electrons as the charge of cations increases and number of delocalised electrons increases.

Si has giant covalent lattice structure. **Much energy** is required to break the strong covalent bonds between Si atoms.

P₄, S₈, Cl₂ and Ar have simple molecular structure. **Little energy** is required to overcome the weaker id-id between molecules.

As strength of id-id \propto no. of electrons in a molecule/atom,
mp decrease in order: **S₈ > P₄ > Cl₂ > Ar**

Electrical conductivity trend

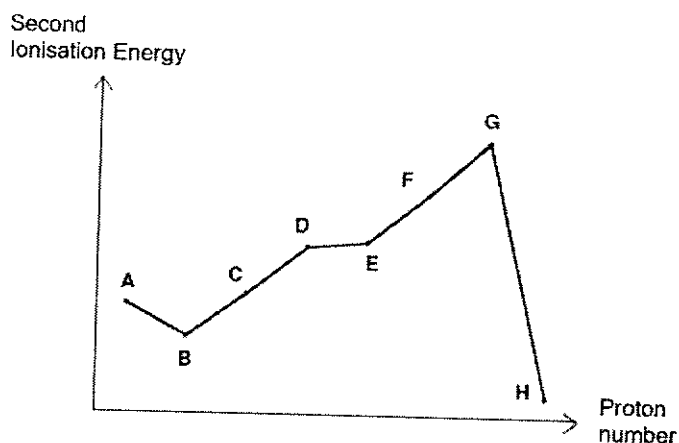
For metals, electrical conductivity **increases** as no. of delocalized electrons (mobile charge carriers) increases from Na to Al.

Si is a **metalloid** which behaves as a semi-conductor and have some electrical conductivity.

P₄, S₈, Cl₂ and Ar are **non-conductor** of electricity as they do not have mobile charge carriers.

[2]

- (ii) Sulfur is an element in Period 3 of the Periodic Table. The graph below shows the second ionisation energies of eight elements with consecutive proton number.



Which of the elements **A** to **H** represents sulfur? Explain your answer.

The sharp drop in 2nd I.E. from **G** to **H** indicates that **H** is in Group 2 where its 2nd I.E. involves the removal of the most loosely held electron from an outer principal quantum shell as compared to that of **G**.

OR

The sharp drop of 2nd I.E. from **G** to **H** indicates that **G** is in Group 1 where its 2nd I.E. involves the removal of an electron from the inner quantum shell, which is much closer to the nucleus as compared to that of **H**.

1m explanation

Hence **D** is a Group 16 element and it is sulfur. [1]

[2]

- (b) A 0.400 g solid sample of a mineral, $XY(\text{CO}_3)_2$ (where X and Y are Group 2 elements) was heated strongly to give a mixture of oxides of X and Y and carbon dioxide. The solid mixture has a total mass of 0.275 g.

The solid mixture was added to excess water and stirred. The suspension was filtered, and the oxide of X was obtained as a residue. The dried residue weighed 0.057 g.

- (i) Write a balanced equation for the decomposition of $XY(\text{CO}_3)_2$
- $$XY(\text{CO}_3)_2 \longrightarrow XO + YO + 2\text{CO}_2$$

[1]

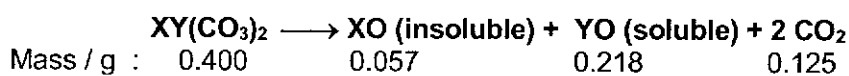
- (ii) Calculate the mass of carbon dioxide produced.

$$\text{Mass of CO}_2 = 0.400 - 0.275 = 0.125 \text{ g}$$

[1]

- (iii) Hence, or otherwise, identify the metals, X and Y , showing your working clearly.

$$\text{Mass of YO} = 0.275 - 0.057 = 0.218 \text{ g}$$



Let A_r of X be a and A_r of Y be b

$$\text{Amt of CO}_2 = \frac{0.125}{44.0} = 0.00284 \text{ mol [1/2]}$$

$$\text{Amt of XO} = \text{Amt of YO} = \frac{0.284}{2} = 0.00142 \text{ mol [1/2]}$$

$$\text{For XO,} \\ \frac{0.057}{a + 16.0} = 0.00142$$

$$a = 24.1, X \text{ is Mg [1]}$$

$$\text{For YO,} \\ \frac{0.218}{b + 16.0} = 0.00142$$

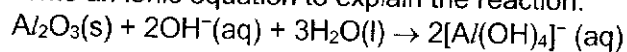
$$b = 137.5, Y \text{ is Ba [1]}$$

[3]

(c) Aluminium is commonly extracted from its oxide, Al_2O_3 .

(i) Al_2O_3 dissolves in hot aqueous solution of sodium hydroxide.

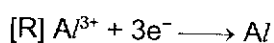
Write an ionic equation to explain the reaction.



Must include state symbol for ionic equation and exclude $Na^+(aq)$ spectator ion [1]

(ii) Al_2O_3 is dissolved in molten cryolite. The mixture is electrolysed using graphite electrodes. The cell operates at a very high current of 50 000 A.

Calculate the time needed to obtain 1 kg of pure aluminium.



$$\text{Amount of Al to be produced} = \frac{1000}{27.0} = 37.04 \text{ mol [1/2]}$$

$$\text{Amount of electrons required} = 3 \times 37.04 = 111.1 \text{ mol [1/2]}$$

$$Q = I \times t = n_e \times F$$

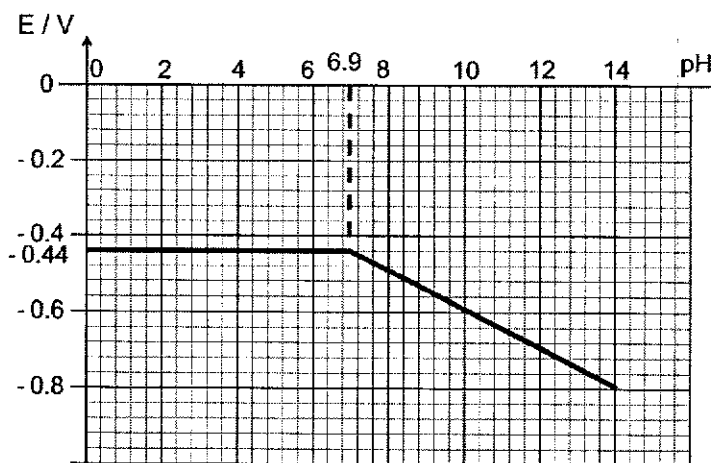
$$t = \frac{111.1 \times 96500}{50000} = 214 \text{ s [1]}$$

[2]

[Total : 12]

- 3 A student wanted to investigate the effect of pH on the electrode potential, E , of an iron(II)/ iron half-cell.

She started the experiment with $1 \text{ mol dm}^{-3} \text{ Fe}^{2+}$ with Fe electrode at pH 0. NaOH(aq) was added dropwise to the solution and the following data was collected.



- (i) Using the information provided, show that the green $\text{Fe}(\text{OH})_2$ precipitate is produced at approximately pH 6.9.

(Solubility product, K_{sp} , of $\text{Fe}(\text{OH})_2 = 6.0 \times 10^{-15} \text{ mol}^3 \text{ dm}^{-9}$ at 25°C)

For ppt to occur, Ionic Product $\geq K_{\text{sp}}$

$$[\text{Fe}^{2+}] \times [\text{OH}^-]^2 = 6.0 \times 10^{-15}$$

$$(1.0) \times [\text{OH}^-]^2 = 6.0 \times 10^{-15}$$

$$[\text{OH}^-]^2 = 6.0 \times 10^{-15}$$

$$[\text{OH}^-] = 7.746 \times 10^{-8} \text{ [1m]}$$

$$\text{pOH} = -\lg [\text{OH}^-] = (7.746 \times 10^{-8}) = 7.1$$

$$\text{pH} = 14 - 7.1 = 6.9 \text{ [1m]}$$

OR

At pH = 6.9, pOH = 7.1

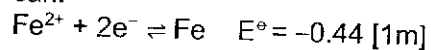
$$[\text{OH}^-] = 10^{-7.1} = 7.943 \times 10^{-8} \text{ mol dm}^{-3}$$

$$\begin{aligned} \text{Ionic Product of } \text{Fe}(\text{OH})_2 &= [\text{Fe}^{2+}] \times [\text{OH}^-]^2 \\ &= (1.0) \times (7.943 \times 10^{-8})^2 \\ &= 6.29 \times 10^{-15} > K_{\text{sp}} \end{aligned}$$

Since ionic product $> K_{\text{sp}}$, ppt will be formed.

[2]

- (ii) With the use of the *Data Booklet*, explain the shape of the graph as fully as you can.



From pH 0 to 6.9,
the Fe^{2+}/Fe half-cell contains $1.0 \text{ mol dm}^{-3} \text{ Fe}^{2+}$, hence E° is -0.44V . [1m]

After pH 6.9, $\text{Fe}(\text{OH})_2$ precipitate starts to form. $[\text{Fe}^{2+}(\text{aq})]$ decreases as pH continues to increase. The position of equilibrium shifts to the left and E becomes more negative. [1m]

[3]

- (iii) Explain why $\text{Fe}(\text{OH})_2$ is green.
Transition Element concepts

[3]

[Total : 8]

- 4 (a) Nitroglycerin, $C_3H_5(NO_3)_3$, is a flammable oil commonly used to manufacture dynamite. The atomisation of nitroglycerin is represented by the equation:

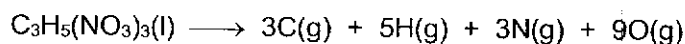
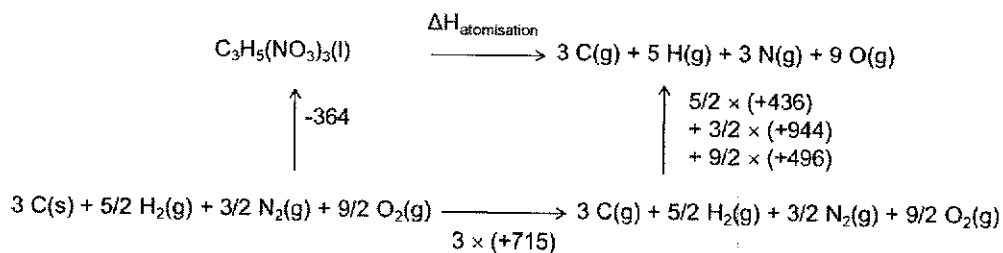


Table 4.1

Standard enthalpy change of formation of nitroglycerin(l) / kJ mol^{-1}	-364
Standard enthalpy change of atomisation of carbon (graphite) / kJ mol^{-1}	+715
Standard enthalpy change of formation of $H_2O(g)$ / kJ mol^{-1}	-242
Standard enthalpy change of formation of $CO_2(g)$ / kJ mol^{-1}	-394

- (i) Using data from Table 4.1 and relevant values from the *Data Booklet*, draw an energy cycle and use it to calculate the standard enthalpy change of atomisation of nitroglycerin.

**By Hess' law**

$$\Delta H_{\text{atm}}^{\circ} = +364 + 3 \times (+715) + 5/2 \times (+436) + 3/2 \times (+944) + 9/2 \times (+496)$$

$$\Delta H_{\text{atm}}^{\circ} = +7247 \approx +7250 \text{ kJ mol}^{-1}$$

Cycle 2m

-1m for missing state symbol/label of enthalpy

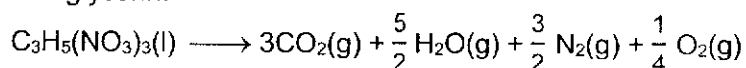
-1m for not balanced equation

Final answer 1m

[3]

- (ii) At high temperature, nitroglycerin decomposes to produce nitrogen, oxygen, carbon dioxide and steam.

Write a balanced equation, with state symbols, for the decomposition of nitroglycerin.



[1]

- (iii) Using data from Table 4.1, calculate the standard enthalpy change of decomposition of nitroglycerin.

$$\begin{aligned} \Delta H^\circ_{\text{decomposition}} &= \Sigma \Delta H^\circ_{\text{formation}} (\text{Products}) - \Sigma \Delta H^\circ_{\text{formation}} (\text{Reactants}) \\ &= [3(-394) + 5/2(-242)] - (-364) \\ &= -1423 \\ &\approx -1420 \text{ kJ mol}^{-1} \end{aligned}$$

Note: $\Delta H^\circ_{\text{decomposition}}$ should be based on per mol of nitroglycerin used.

[1]

- (iv) Given that $\Delta S^\circ = +208 \text{ J K}^{-1}\text{mol}^{-1}$, calculate ΔG° for this decomposition and hence predict the spontaneity of the reaction.

$$\begin{aligned} \Delta G^\circ_{\text{decomposition}} &= \Delta H^\circ_{\text{decomposition}} - T\Delta S^\circ \\ &= -1423 - [298 \times (+208/1000)] \\ &= -1485 \approx -1490 \text{ kJ mol}^{-1} \quad [1\text{m}] \end{aligned}$$

Since ΔG° is negative, the reaction is spontaneous at 25 °C. [1m]

Note: temperature of standard condition is 298 K.

[2]

- (v) Is the reaction spontaneous at all temperatures? Explain.

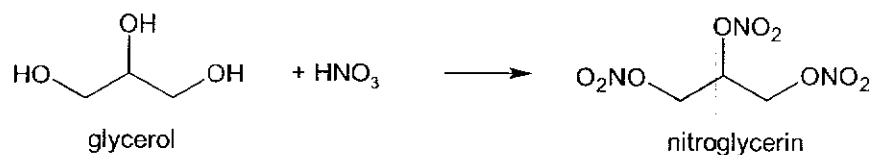
$\Delta H^\circ_{\text{decomposition}}$ is negative. T is always positive and ΔS° is positive, hence ΔG is always < 0 . [1m]

i.e. $\Delta G = \Delta H - T\Delta S = \text{negative} - [(\text{positive}) \times (\text{positive})] = \text{negative}$

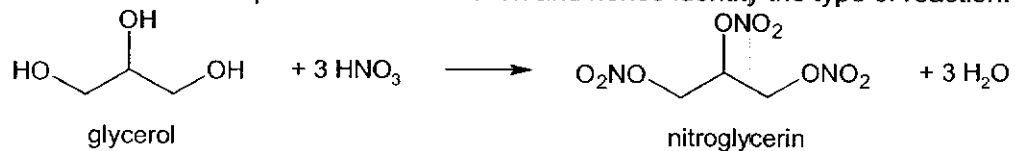
Thus, the decomposition reaction of nitroglycerin is spontaneous at all

[1]

- (b) Nitroglycerin can be produced by reaction of glycerol with nitric acid.



- (i) Write a balanced equation for the reaction and hence identify the type of reaction.



Type of reaction : Condensation

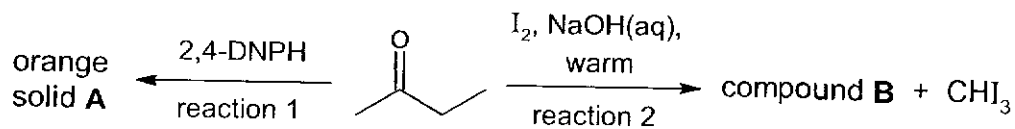
[2]

- (ii) Give the IUPAC name for glycerol.
Propane-1,2,3-triol

[1]

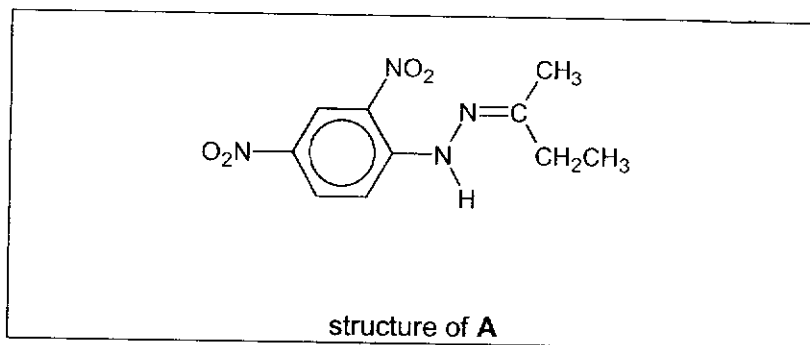
[Total : 11]

- 5 (a) Butanone, $\text{CH}_3\text{COCH}_2\text{CH}_3$, is a commonly used organic solvent.



- (i) Butanone reacts with 2,4-dinitrophenylhydrazine to give an orange solid **A**. Suggest the type of reaction and draw the structure of **A**.

Type of reaction : Condensation



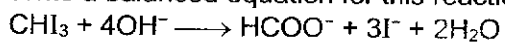
[2]

- (ii) Suggest the identity of compound **B**.
 $\text{CH}_3\text{CH}_2\text{COO}^-\text{Na}^+$ or $\text{CH}_3\text{CH}_2\text{COONa}$ (No net charge for compound)

[1]

- (iii) When CHI_3 is heated strongly with $\text{OH}^-(\text{aq})$, a mixture containing HCOO^- and I^- is obtained.

Write a balanced equation for this reaction.



[1]

- (iv) The use of the table of characteristic infra-red absorption frequencies for some selected bonds in the *Data Booklet* is relevant to this question.

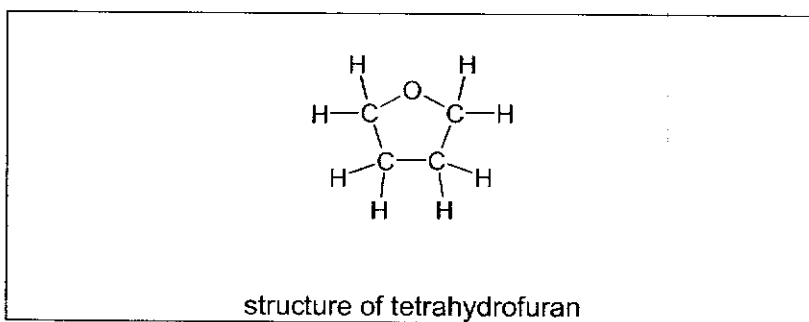
Tetrahydrofuran is a functional group isomer of butanone and has no reaction with anhydrous SOCl_2 nor $\text{Br}_2(\text{aq})$.

Infra-red absorptions can be used to identify functional groups in organic compounds. For example, butanone shows absorption at 1680 cm^{-1} due to the $\text{C}=\text{O}$ bond.

The analysis of tetrahydrofuran shows infra-red absorption at 1000 cm^{-1} .

Identify the bond present in tetrahydrofuran and suggest its structure.

Bond present : C-O



Note: no $-\text{OH}$ and no $\text{C}=\text{C}$ functional group.
Also accept any other cyclic ether.

[2]

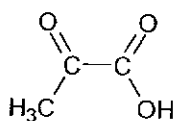
- (b) Compound **C** has the molecular formula $C_7H_{14}O$. It contains two functional groups.

Data about the reactions of **C** are given in Table 5.1.

Table 5.1

reaction	reagent	Result
b1	Na(s)	colourless gas evolved.
b2	I_2 in CCl_4	one organic product formed with $M_r = 367.8$
b3	$KMnO_4$, $H_2SO_4(aq)$, heat	butanone and compound D , $C_3H_4O_3$, formed.

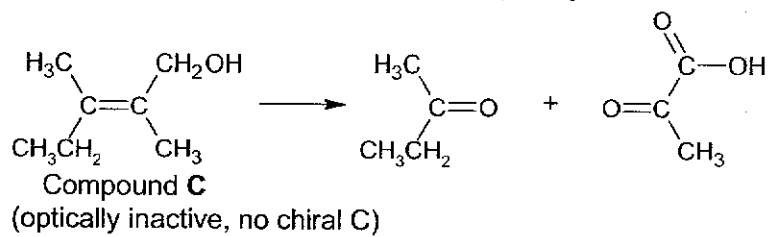
- (i) Name the functional group that reaction **b1** shows to be present in **C**.
Alcohol or hydroxy [1]
- (ii) Write the balanced equation for reaction **b1**.
 $C_7H_{14}O + Na \longrightarrow C_7H_{13}ONa + \frac{1}{2} H_2$ [1]
- (iii) Deduce the molecular formula of the organic product formed in reaction **b2**.
 $C_7H_{14}OI_2$ ($M_r = 367.8$)
Note: Electrophilic Addition of I_2 to $C=C$ [1]
- (iv) Draw the structure of compound **D** produced from reaction **b3**.



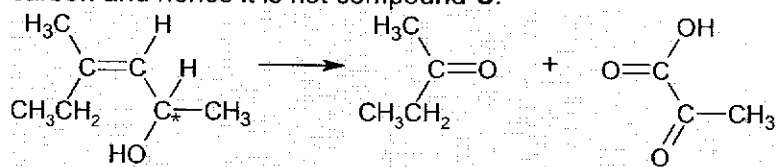
Note: Vigorous oxidation of $C=C$ and alcohol group. Molecular formula of **D** suggests presence of both the ketone and carboxylic acid group.

[1]

- (v) Draw the structure of **C** given that it is optically inactive.

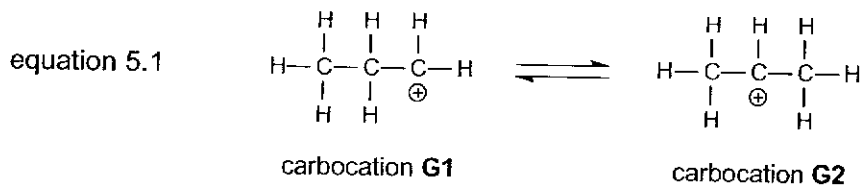


Note: The following compound will give the same products, however it has a chiral carbon and hence it is not compound **C**.

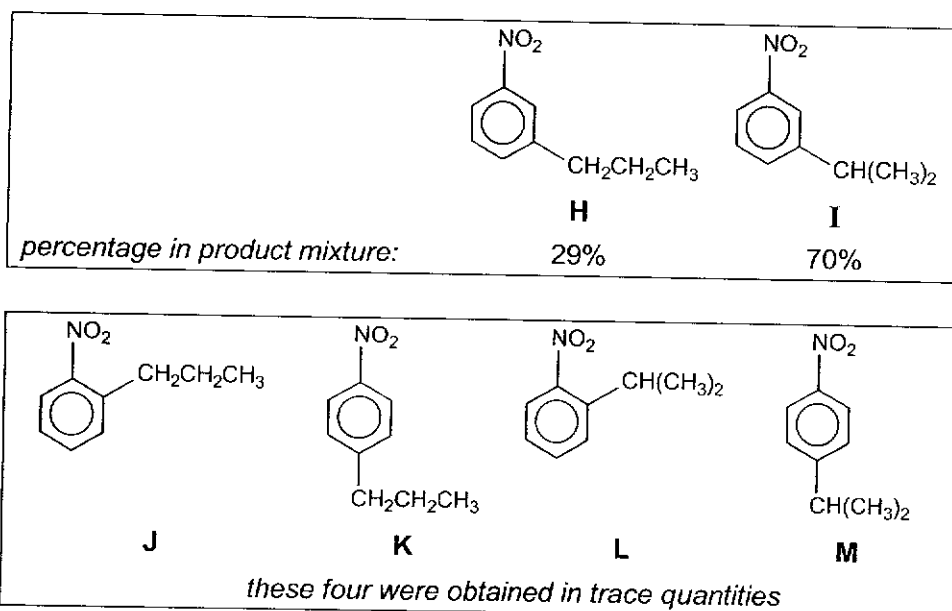


[1]

- (c) Propene can undergo protonation by an acid to give a mixture of two carbocations that co-exist in equilibrium:



When the equilibrium mixture of the two carbocations was added to nitrobenzene, the following products were obtained.



- (i) Suggest a reason why **J**, **K**, **L** and **M** were obtained in trace quantities only.
 -NO₂ group in nitrobenzene is 3-directing.

[1]

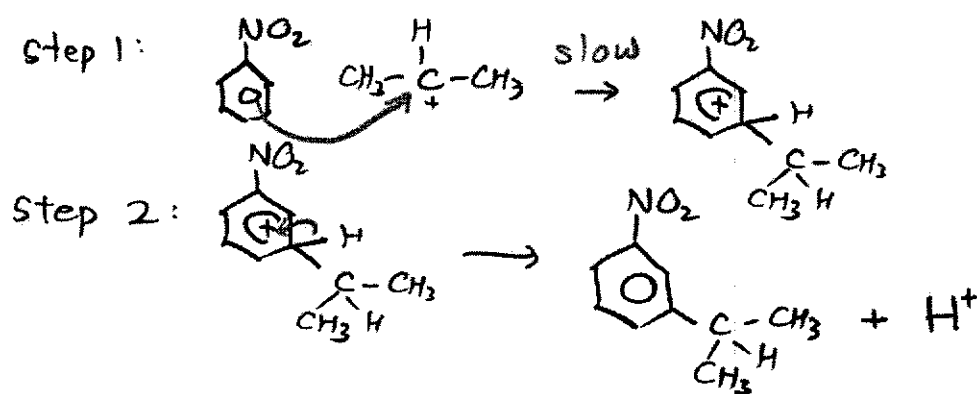
- (ii) By considering the position of equilibrium for equation 4.1, suggest why **I** was obtained in larger quantity than **H**.
Carbocation **G2** is more stable due to the greater number of electron donating alkyl group that stabilizes the positive charge of the carbocation. [1/2]

Carbocation **G2** exist in a greater proportion than carbocation **G1**. [1/2] Hence during the reaction with nitrobenzene, a larger quantity of **I** is obtained.

Note: Discuss the stability of the carbocation intermediate, NOT stability of compound **H** and **I**.

[1]

- (iii) Describe the mechanism for the formation of **I** from nitrobenzene.
In your answer, show any relevant charges, dipoles or lone pairs of electrons you consider important in this mechanism.
Electrophilic substitution [1m]



2m mechanism
-½ for each mistake

[3]

- (iv) **H** can be reduced to 3-propylphenylamine.

Suggest a suitable reagents and conditions for this reaction.

- 1) Sn, conc HCl, heat
- 2) followed by excess NaOH(aq)

Note: NaOH (aq) is required in step 2 to remove the excess HCl in order to generate basic phenylamine.

[1]

[Total : 17]

- 6 Bubble tea is a popular beverage in Singapore. NJC Chemistry department has conducted extensive studies on the effect of bubble tea on health.

- (a) Bubble tea drinks are acidic in nature due to the presence of acids such as malic acid. Malic acid can undergo an elimination reaction to produce but-2-enedioic acid.

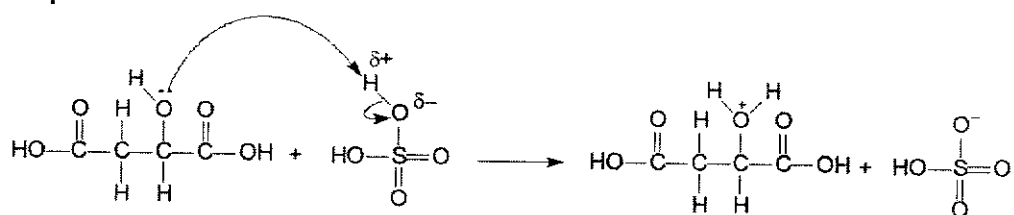


The mechanism of the elimination reaction occurs in three steps.

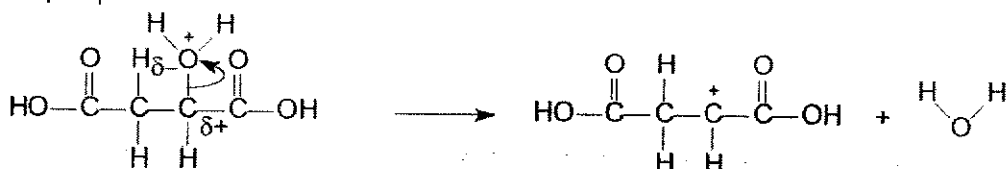
Complete the mechanism in Fig. 6.1 by showing clearly lone pair electrons and movement of electrons by curly arrows.

Fig. 6.1

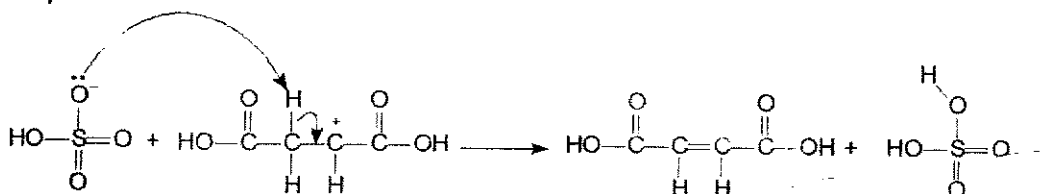
Step 1:



Step 2:



Step 3:



Note: Identify the bond broken/formed for each step.

For breaking of polar bond, identify the $\delta+$ and $\delta-$ of the atoms involved in the bond, electron pair from the bond will move to the more electronegative element involved in the bond.

For bond formation, electron pair move from electron rich region (lone pair electrons or existing bond) to target atom.

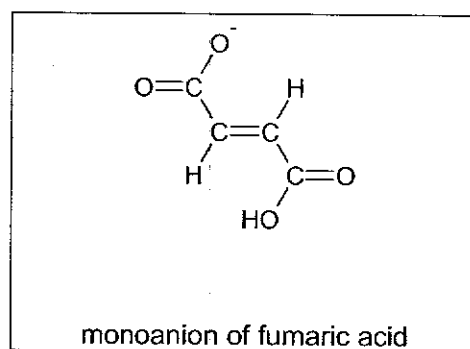
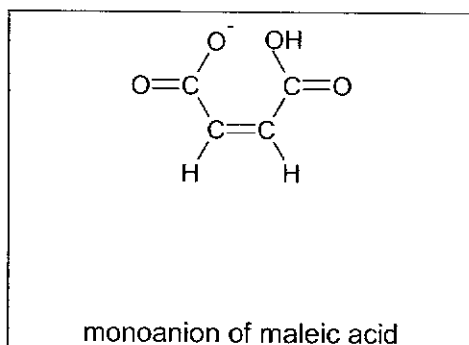
For step 3, formation of pi bond involves the movement of electron pair to existing sigma bond.

[3]

(b) But-2-enedioic acid exhibits cis-trans isomerism.

	pK_{a1}	pK_{a2}
maleic acid (cis-isomer)	1.9	6.0
fumaric acid (trans-isomer)	3.0	4.4

(i) Draw the monoanion of the two isomers.



[1]

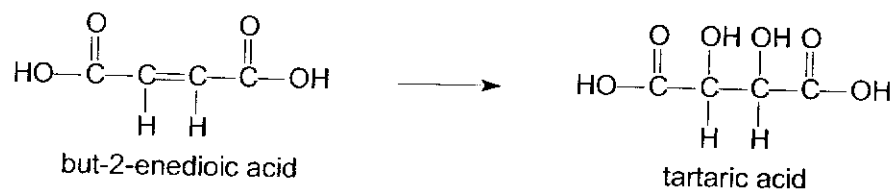
(ii) Hence or otherwise, explain why pK_{a1} of maleic acid is smaller than that of fumaric acid.

The monoanion of maleic acid (cis-isomer) is stabilized by intramolecular H-bonding, and it is more stable than the monoanion of fumaric acid. [1]

Dissociation of maleic acid into its monoanion and H^+ is more favourable than fumaric acid. Hence maleic acid is more acidic and has a smaller pK_{a1} . [1]

[2]

- (c) But-2-enedioic acid can be converted to tartaric acid.



- (i) State the reagents and conditions to convert but-2-enedioic acid to tartaric acid.
 KMnO_4 , $\text{NaOH}(\text{aq})$, cold, followed by $\text{H}_2\text{SO}_4(\text{aq})$
 Also accept KMnO_4 , $\text{H}_2\text{SO}_4(\text{aq})$, cold

Note: The $-\text{COOH}$ group will be neutralized by $\text{NaOH}(\text{aq})$, hence we will need to acidify the reaction mixture to convert back to $-\text{COOH}$.

[1]

- (ii) But-2-enedioic acid can also undergo an enzyme catalysed reaction to produce tartaric acid.

A reactant in an enzymatic reaction is known as a substrate. The effect of substrate concentration on the rate of reaction is shown in Fig. 6.2.

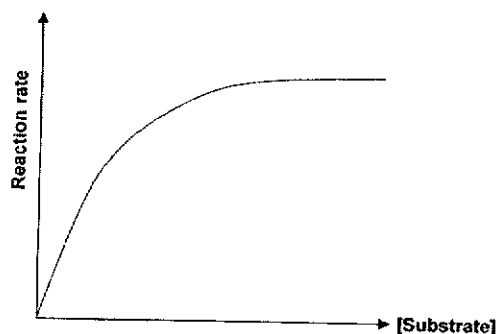


Fig. 6.2

Explain the shape of the graph at low [substrate] and high [substrate].
 At low [substrate], not all of the active sites are occupied. The rate of reaction increases proportionally with substrate concentration. [1m]

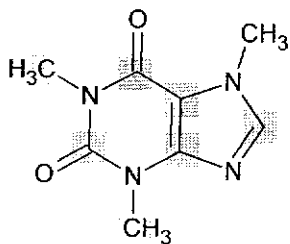
At high substrate concentration, the **active sites of the enzymes are saturated.**
Increase in the concentration of substrate cannot increase the rate of reaction any further. [1m]

[2]

- (d) Bubble tea contains a high amount of caffeine.

Caffeine, a stimulant found in coffee and tea, was discovered by a German chemist, Friedrich Ferdinand Runge, in 1819.

The structure of caffeine is given below.

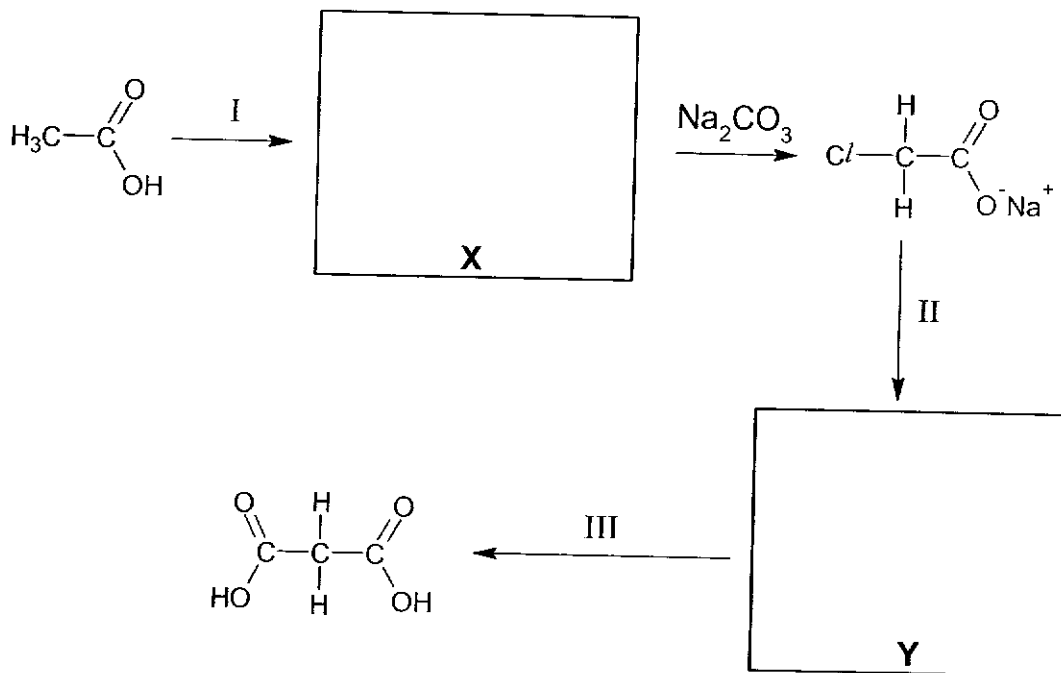


- (i) State the number of sp^2 and sp^3 hybridised carbon atoms in caffeine.
- number of sp^2 hybridised carbon atoms : 5 (highlighted in light blue) [1/2m]
- number of sp^3 hybridised carbon atoms : 3 (highlighted in yellow) [1/2m]

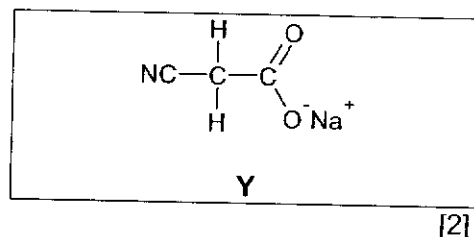
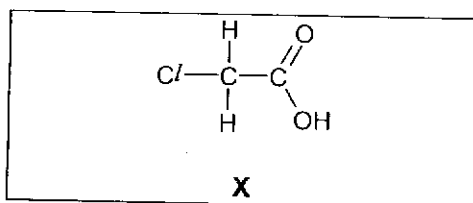
[1]

Caffeine can be synthesised in the laboratory using dimethyl urea, $(\text{CH}_3)_2\text{NHCONH}(\text{CH}_3)$ and malonic acid, $\text{HOOC}(\text{CH}_2)\text{COOH}$.

Malonic acid is usually prepared from ethanoic acid as follows:



(ii) Draw the structures of the intermediates X and Y.



[2]

(iii) Suggest reagents and conditions for step I and II and identify the type of reaction for step III in the reaction sequence

Step I : **limited Cl_2 (g), UV** (Note: limited Cl_2 would favour mono-substitution)

Step II : **KCN in ethanol, heat**

Type of reaction for step III : **Acid hydrolysis**

[3]

- (e) The caffeine content of some beverages is given in Table 6.1.

Table 6.1

	Red Bull (250 ml)	Coca-Cola (250 ml)	Espresso (60 ml)	Bubble tea (400 ml)
Caffeine content/ mg	80	25	100	160

The beverage consumption pattern of an 18-year-old student was monitored across a 12-hours period. The student followed the instructions and did not consume any caffeine containing products two days prior to the research study.

Time	Drinks consumed
0600	Espresso (60 ml)
1000	Coca-Cola (250 ml)
1400	Bubble tea (400 ml)
1800	-

- (i) The Singapore Health Promotion Board recommends teenagers' (13-18 years old) total daily caffeine consumption to not exceed 3mg caffeine per kg of body weight.

Given that the student's weight is 54kg, deduce whether the student has exceeded the recommended daily caffeine intake.

Total daily caffeine intake of the student = $100 + 25 + 160 = 285\text{mg}$ [1]

Recommended daily caffeine intake = $54 \times 3 = 162\text{mg}$ [1/2]

The student has exceeded the recommended daily caffeine intake. [1/2]

[2]

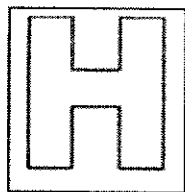
- (ii) Caffeine's biological half-life is approximately 4 hours.

Determine the estimated amount of caffeine (in mg) remaining in the student at time 1800. Show your workings clearly.

Time	Drinks consumed	Caffeine at 1800
0600	Espresso (60 ml)	$100 \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = 12.5\text{mg}$
1000	Coca-Cola (250 ml)	$25 \times \frac{1}{2} \times \frac{1}{2} = 6.25\text{mg}$
1400	Bubble tea (400 ml)	$160 \times \frac{1}{2} = 80\text{mg}$
1800	-	Total caffeine = 98.75mg

[2]

[Total: 19]



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.

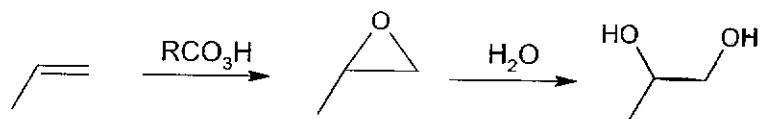
The number of marks is given in brackets [] at the end of each question or part question.

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

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

- (c) Peroxyacid, RCO_3H , 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]

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

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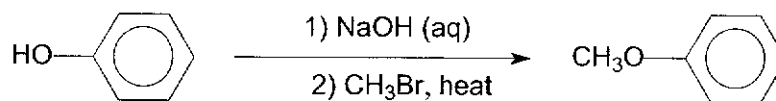
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- (e) Organic halogen compounds are widely used in synthetic reactions.

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]
- (ii) The rate of the synthesis decreases when CH₃Cl is used in place of CH₃Br.

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

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[Total : 16]

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

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

- (i) With reference to the structure and bonding, explain why the boiling points of NO₂ and N₂O₄ are the same. [3]

- (ii) N₂O₅ is a symmetrical molecule O₂N–O–NO₂.

Draw the full structural formula of N₂O₅ and suggest the N–O–N bond angle. [2]

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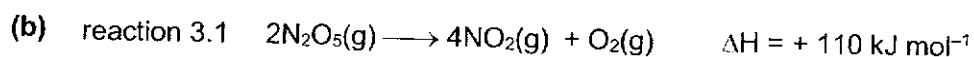
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The overall order of reaction for reaction 3.1 is one and the reaction proceeds via a two-step mechanism.

- (i) Sketch a graph of concentration of N₂O₅ against time for reaction 3.1. The reaction has a half-life of 5 minutes and N₂O₅ at an initial concentration of 2.00 mol dm⁻³. [1]
- (ii) Determine the value of the rate constant, k, for reaction 3.1, stating its units. [1]

(iii) The slow step of the two-step reaction mechanism produces a NO_3 intermediate.

Write equations to show a possible reaction mechanism for reaction 3.1. [2]

(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]

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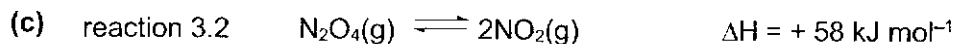
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Some amount of dinitrogen tetroxide, N_2O_4 , is placed in a gas syringe and allowed to achieve the equilibrium. At room temperature and pressure, 0.100 g of an equilibrium mixture of reaction 3.2 takes up a volume of 31.7 cm^3 .

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

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

(iii) Use your answers to (c)(ii) to calculate the percentage of N_2O_4 in the equilibrium mixture and hence the value of K_p (in atm) for reaction 3.2 at r.t.p. [3]

(iv) The gas mixture is compressed to a volume of 20 cm^3 . Explain how would the percentage of N_2O_4 be affected as compared to your answer in (c)(iii). [2]

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(d) NO_2 , an air pollutant, is sometime found in car exhaust emissions.

- (i) Give one environmental impact of NO_2 . [1]
- (ii) Explain how NO_2 is produced in car engine. [1]
- (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 NO_2 . [1]

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(e) NH_3 , CH_3CONH_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]

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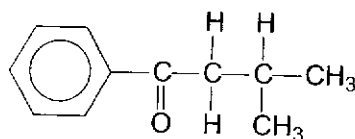
[Total: 24]

PLEASE TURN OVER

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]
- (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]

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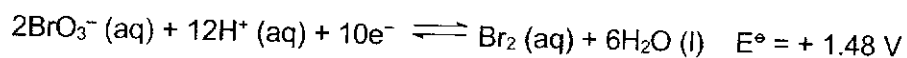
- (b) With reference to the data given below and any relevant data from the *Data Booklet*, answer the following questions concerning the chemistry of sodium bromide.

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

- (i) Define standard enthalpy change of formation of solid sodium bromide. [1]
- (ii) Construct an energy level diagram and use it to calculate the standard enthalpy change of vapourisation of bromine. [5]

- (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]
- (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]

- (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. [3]

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(d) Describe and explain how the volatilities of the halogens vary from chlorine to iodine. [2]

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[Total : 20]

- 5 (a) Ethanedioate ion, $C_2O_4^{2-}$, is found in some food such as spinach and beets.
- (i) Draw the dot-and-cross diagram for $C_2O_4^{2-}$, which contains a C-C bond. [1]
 - (ii) All the carbon-oxygen bond lengths in ethanedioate ion, $C_2O_4^{2-}$ are determined to be a value between the C-O and C=O bond lengths. Account for this observation. [2]
 - (iii) When heated to high temperature, MgC_2O_4 undergoes thermal decomposition to give magnesium oxide, carbon monoxide and carbon dioxide. It is observed that thermal stability of Group 2 ethanedioate increases down the group.

Explain the thermal stability trend of Group 2 ethanedioate. [2]

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- (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 cm^3 using water.

10.0 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), KMnO_4 . The following reaction occurs.



The average titre was 9.25 cm^3 .

- (i) State the endpoint colour change of this titration. [1]
- (ii) Calculate the percentage mass of ethanedioic acid, $\text{H}_2\text{C}_2\text{O}_4$, present in the rhubarb leaves sample. [3]

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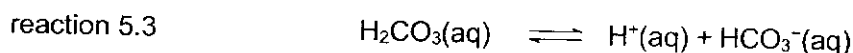
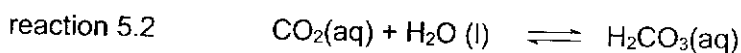
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- (c) One of the uses of carbon dioxide is in the manufacture of carbonated drinks.

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 dm^3 and contains 2.58 kg of carbon dioxide.

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

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 CO_2 is $3.4 \times 10^{-2} \text{ mol dm}^{-3} \text{ atm}^{-1}$ at $25 \text{ }^\circ\text{C}$.

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

Calculate the concentration of dissolved CO_2 in the unopened bottle at $25 \text{ }^\circ\text{C}$. [1]

- (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]

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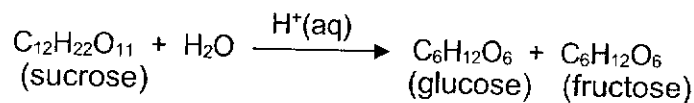
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- (d) Sucrose is the most common natural food sweetener, often known as table sugar. In acidic solution, sucrose is readily hydrolysed to a 1:1 mixture of glucose and fructose. The reaction is catalysed by aqueous H^+ ions.



A series of experiments were carried out at 25 °C to investigate the kinetics of this reaction, using 0.79 mol dm⁻³ sucrose solution and 1.25 mol dm⁻³ hydrochloric acid. The data obtained was presented in Table 5.1.

Table 5.1

Expt	Volume of sucrose /cm ³	Volume of HCl /cm ³	Volume of water /cm ³	Initial rate of reaction /mol dm ⁻³ min ⁻¹
1	20	20	10	0.00125
2	20	30	0	0.00188
3	10	30	10	0.000938

- (i) Explain why varying volume of water was used in the 3 experiments. [1]
- (ii) Using the data in Table 5.1, deduce the rate equation and hence, calculate the rate constant for the reaction, stating its units. [4]

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Additional answer space

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