

NATIONAL JUNIOR COLLEGE SH2 PRELIMINARY EXAMINATION Higher 2

CANDIDATE

SUBJECT CLASS REGISTRATION NUMBER

CHEMISTRY

Paper 3 Free Response

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 24 printed pages.

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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.

$$C_{10}H_{14}N_2 + H_2O \longrightarrow C_{10}H_{15}N_2^+ + OH^- pK_b (C_{10}H_{14}N_2) = 6.0$$

- (i) Calculate the pH of a 0.100 mol dm⁻³ C₁₀H₁₄N₂ 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 HNO₃(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 dm³ solution consisting of 0.100 mol dm⁻³ $C_{10}H_{14}N_2$ and 0.200 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.

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

pH = 14-6.30 = 7.70 [1/2]

(iv) Calculate the number of moles of HNO₃ that needs to be added to the solution in (a)(iii) to obtain a buffer solution of pH 7.40. [2] Weak base C₁₀H₁₄N₂ of the buffer will react with the HNO₃ added, use ICF table (in mol) to determine limiting reagent.

Initial amount of $C_{10}H_{14}N_2 = 5 \times 0.100 = 0.5$ mol Initial amount of $C_{10}H_{15}N_2^+ = 5 \times 0.200 = 1.0$ mol Let amount of HNO₃ added = x mol

	$C_{10}H_{14}N_2$	+ H*	\rightarrow	$C_{10}H_{15}N_{2}^{+}$
I / mol	0.5	X		1.0
C / mol	- x	- x		+χ
F / mol	0.5 – x	0		1 + x

pH = 7.40, pOH = 6.60
pOH = pK_b + lg
$$\frac{[conjugateacid]}{[weakbase]}$$

6.60 = 6.0 + lg $(\frac{1+x}{0.5-x})$
lg $(\frac{1+x}{0.5-x})$ = 0.60
 $(\frac{1+x}{0.5-x})$ = 10^{0.60} [1] or similar idea
 $\frac{1+x}{0.5-x}$ = 3.981
1 + x = 1.991 - 3.981x

Amount of HNO₃ needed = 0.199 mol

4.981 x = 0.991 x = 0.199 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 HNO₃. [2]



1m for $3 \times E$.sub of $-NO_2$ on phenol (0m if monosub of $-NO_2$) 1m for acid base reaction with $-NH_2$ to give $-NH_3^+$

Note: conc HNO₃ lead to tri sub of -NO₂ at 2,4,6 position of EACH phenol.

(iii) A reaction between dopamine and chloromethane, CH₃C*l*, forms a compound with formula C₁₁H₁₈NO₂C*l*. Suggest a structure for this compound and how the yield of this compound can be maximised.



React Dopamine with excess CH₃Cl. [1m]

Note: dopamine, $C_8H_{11}NO_2$ reacts with 3 mol of CH_3Cl 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 PCl_5 or $SOCl_2$ White fumes of HCl observed for epinephrine but no white fumes for dopamine.

 $K_2Cr_2O_7, H_2SO_4(aq)$, heat Orange $K_2Cr_2O_7$ turns green for epinephrine but $K_2Cr_2O_7$ remains orange for dopamine.

Do not accept hot $KMnO_4$ 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] $Cr : 1s^22s^22p^63s^23p^63d^54s^1$ As : $1s^22s^22p^63s^23p^63d^{10}4s^24p^3$ (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, RCO₃H.



Ester can be reduced by LiA/H_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. Oxidation [gain O atom]
 - (ii) Suggest the products formed when ethyl benzoate is reacted with LiA/H₄. [2]

[1]



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



Fig 2.1

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



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 LiA/H₄.

A must be an alkene with = CH_2 such that it loses one C atom as CO_2 after vigorous oxidation with hot acidified KmnO₄

(ii) Compound **C** can also be synthesised from $HOOC(CH_2)_3CH_2OH$.

Suggest the reagents and conditions required for this synthesis. [1] Concentrated H_2SO_4 , heat

Note: The -COOH and -OH group undergoes intramolecular condensation to form cyclic ester.

(c) Peroxyacid, RCO₃H, 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°(105° for O)** respectively to minimise electron pair repulsion [1/2]

However, in the three-atom ring of epoxide, the bond angle of <u>60° is smaller than</u> 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 C*l*-I.
 In your answer, show any relevant charges, dipoles or lone pairs of electrons you consider important in this mechanism.
 [3] Electrophilic addition [1m]





-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 H⁺ from phenol to generate <u>phenoxide</u>, with higher electron density on O. It is <u>a stronger nucleophile</u> than phenol. [1]
- (ii) The rate of the synthesis decreases when CH_3Cl is used in place of CH_3Br .

With the use of the *Data Booklet*, suggest an explanation for this difference in the rate of reaction. [2] $BE(C-Cl) = 340 \text{ kJ mol}^{-1}$ and $BE(C-Br) = 280 \text{ kJ mol}^{-1}$. [1m]

More energy is required to overcome the stronger C-Cl bond in CH_3Cl , 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 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 NO_2 and N_2O_4 are the same. [3] Both compounds have simple molecular / covalent structure. [1/2] NO₂ is polar with permanent dipole-permanent dipole (pd-pd) interaction [1/2] while N₂O₄ is non polar with instantaneous dipole-induced dipole (id-id) interaction. [1/2]

As size of electron cloud of N₂O₄ 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_2 and N_2O_4 are comparable [1/2] and hence their boiling points are the same.

(ii) N_2O_5 is a symmetrical molecule $O_2N-O-NO_2$.

> Draw the full structural formula of N_2O_5 , and suggest the N–O–N bond angle. [2] 0 Ĩ ^{•O} 1m [0m if no dative bonds]

Note: N is not able to form 2 \times N=O and 1 \times 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)

(b) reaction 3.1 $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$ $\Delta H = + 110 \text{ kJ mol}^{-1}$

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

(i) Sketch a graph of concentration of N_2O_5 against time for reaction 3.1. The reaction has a half-life of 5 minutes and N_2O_5 at an initial concentration of 2.00 mol dm⁻³.

[1]

2.00 1.00 0.50 5 10 Time/min

- (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 NO₃ intermediate.

Write equations to show a possible reaction mechanism for reaction 3.1. [2] Since it is first order w.r.t N_2O_5 , only 1 molecule of N_2O_5 is involved in the slow step.

Step 1 : $N_2O_5 \longrightarrow NO_2 + NO_3$ (slow) [1m] Step 2 : $NO_3 + N_2O_5 \longrightarrow 3 NO_2 + O_2$ [1m]

(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]



Reaction Pathway

Show 2-step reaction with higher E_a for first step [1/2] Show and label positive ΔH (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 + 2nd N₂O₅ [1/2] (c) reaction 3.2 $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H = + 58 \text{ kJ mol}^{-1}$

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 cm³.

- (i) Write the $K_{\rm p}$ expression for reaction 3.2. [1] $K_{\rm p} = \frac{(P_{NO2})^2}{P_{N2O4}}$
- (ii) Calculate the average relative molecular mass of the mixture. [1] Amount of gas = $\frac{31.7}{24000}$ = 0.001321 mol [1/2]

Average
$$M_{\rm r} = \frac{0.100}{0.00132} = 75.7$$
 [1/2]

(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.

Let % of N₂O₄ be x and % of NO₂ 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
% N₂O₄ = 64.6% [1]
P_{N2O4} = $\frac{64.57}{100} \times 1 = 0.6457$ atm [1/2]
P_{NO2} = $\frac{35.43}{100} \times 1 = 0.3543$ atm [1/2]
 $\mathcal{K}_{p} = \frac{(P_{NO2})^{2}}{P_{N2O4}} = \frac{(0.3543)^{2}}{0.6457} = 0.1944 \approx 0.194$ atm [method 1m]

(iv) The gas mixture is compressed to a volume of 20 cm³. Explain how would the percentage of N₂O₄ be affected as compared to your answer in (c)(iii). [2] When the gas mixture is compressed, total <u>gas pressure increases</u>. [1/2] By Le Chatelier's Principle, the equilibrium would try to partially offset the increase in pressure by <u>reducing the number of gas particles</u>. [1/2] <u>Position of equilibrium would shift to the left, and percentage of N₂O₄ increases. [1]
</u>

[3]

- (d) NO₂, an air pollutant, is sometime found in car exhaust emissions.
 - (i) Give one environmental impact of NO₂.
 - 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.
 - NO₂ acts as a catalyst for the oxidation of SO₂ to SO₃, SO₃ dissolves in rainwater to cause acid rain (H₂SO₄).
 Any of the above.
 - (ii) Explain how NO₂ is produced in car engine. [1] During combustion of petrol, N_2 reacts with O₂ 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 NO₂. [1] $4CO + 2NO_2 \longrightarrow 4CO_2 + N_2$

(e) NH_3 , CH_3CONH_2 and $C_6H_5NH_2$ are nitrogen containing compounds.

Arrange these compounds in order of increasing basicity. Explain your answer. [3] $CH_3CONH_2 < C_6H_5NH_2 < NH_3$ [1]

The <u>lone pair electrons</u> on nitrogen atom of CH_3CONH_2 is <u>delocalised</u> **significantly** to <u>adjacent C=O</u> with highly electronegative O atom, hence, it is <u>not available to accept</u> <u>H⁺</u>. [1] Thus, amide is neutral/not basic.

For $C_6H_5NH_2$, 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 H⁺ as compared to NH_3 . [1] Hence $C_6H_5NH_2$ is a weaker base than NH_3 .

[Total: 24]

[1]

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° radical > 2° radical > 1° 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 ^{– 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] The <u>heat evolved</u> when <u>1 mol of NaBr(s) is formed from</u> its constituent element in their standard state <u>Na(s) and Br₂(l)</u> under <u>standard conditions of 298 K and</u> <u>1 bar</u>. OR Na (s) + $\frac{1}{2}$ Br₂(l) \longrightarrow NaBr(s) $\Delta H = -361$ kJ mol⁻¹ (must include sign of ΔH if define using equation) Note: standard state of Br₂ 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⁻¹

	$\operatorname{Na}(g) + e + \operatorname{DI}(g)$		
	1 st I.E. of Na = 494	Na⁺(g) + Br ⁻(g)	1 st E.A. of Br = –325
	Na(g) + Br(g)		
		BE(Br-Br) × ½	
	Na(g) + ½ Br ₂ (g)	= +193 × ½	
	Na(g) + ½ Br ₂ (l)	$\Delta H_{vap}^{e} (Br_2) \times \frac{1}{2}$	
0	Na(s) + ½ Br ₂ (l)	ΔH_{atm}^{e} (Na) = +107	
0 -		∆H _f ^e NaBr(s) = – 361	L.E.(NaBr(s)) = – 753
	NaBr(s)		

A Na⁺(g) + e⁻ + Br(g)

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

By Hess' Law

 $\begin{array}{l} -361 = 107 + \frac{1}{2} \times \Delta H_{vap} \; Br_2 + 193 \times \frac{1}{2} + 494 - 325 - 753 \\ \frac{1}{2} \times \Delta H_{vap} \; Br_2 = 19.5 \\ \Delta H_{vap} \; Br_2 = +39.0 \; kJ \; mol^{-1} \; [1] \end{array}$

Note: vaporisation is conversion of **<u>1</u> mol of Br₂(I)** to Br₂(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:

$$2BrO_{3}^{-}(aq) + 12H^{+}(aq) + 10e^{-} = Br_{2}(aq) + 6H_{2}O(I)$$
 E^e = + 1.48 V

(i) Draw a labelled diagram to show how the standard electrode potential of the $BrO_3^{-}(aq)/Br_2(aq)$ electrode can be measured. [3]



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

Note: H⁺ is required for the BrO₃⁻ and Br⁻ half cell, as shown in the half equation.

 $\frac{1}{2}$ m for 298K, 1bar and 1 mol dm⁻³ for all ions $\frac{1}{2}$ m for voltmeter and salt bridge

(ii) When AgNO₃(aq) is added to the BrO₃⁻(aq)/Br₂(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] Ag^+ reacts with BrO_3^- to form the white precipitate, $[BrO_3^-]$ 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 Br^{-} in the BrO_3^{-}/Br_2 half cell. Hence it is wrong to identify the ppt as 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 H₂(g) (Effervescence) Zn + 2H⁺ \longrightarrow Zn²⁺ + H₂ [1] [3]

Reaction of Zn with $BrO_3^ 5Zn + 2BrO_3^- + 12H^+ \longrightarrow Br_2 + 6H_2O + 5Zn^{2+}$ [1] Note: Br_2 is not colourless, hence there must be a further reaction of Br_2 .

Further reaction of Br_2 with excess Zn Zn + $Br_2 \longrightarrow Zn^{2+} + 2Br^{-}$ [1]

(d) Describe and explain how the volatilities of the halogens vary from chlorine to iodine. [2] Volatilities of non-polar halogen decrease from Cl₂ to I₂ [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 Cl₂ to I₂.[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]

- **5** (a) Ethanedioate ion, $C_2O_4^{2-}$, is a 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, C₂O₄²⁻ are determined to be a value between the C-O and C=O bond lengths. Account for this observation.
 [2]

Due to the continuous <u>sideway overlap of</u> the unhybridised <u>**p** orbitals</u> [1/2] of C and O atoms, the <u> π electrons are delocalised</u> [1/2] across the connected C and O atoms.

This leads to a resonance hybrid structure that <u>has partial double bond</u> <u>character/bond order of 1.5</u> [1] in all the carbon-oxygen bonds.

(iii) When heated to high temperature, MgC₂O₄ 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] Down the group, <u>cations</u> of Group 2 metals have the same charge but their size increases. The $\frac{charge}{size}$ ratio of the <u>cation</u> decreases. This leads to a <u>decrease in</u> <u>polarising power</u>. [1/2]

The <u>electron clouds in the $C_2O_4^{2-}$ anion is being distorted to a smaller extent</u> [1/2] down the group and the <u>extent of weakening of C–O bond decreases</u> down the group. [1/2]

More energy is required to break the C–O bonds in the $C_2O_4^{2-}$ anion. [1/2]

Therefore, thermal stability of the Group 2 ethanedioate increases down the group.

Note: It is wrong to say the C-O covalent gets stronger down the group. It is weakened to a smaller extent.

(b) Ethanedioic acid, $H_2C_2O_4$, 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 cm³ using water.

10.0 cm³ of the solution containing ethanedioic acid was pipetted into a conical flask and titrated with 0.020 mol dm⁻³ acidified potassium manganate(VII), KMnO₄. The following reaction occurs.

 $2MnO_4^{-}(aq) + 16H^{+}(aq) + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$

The average titre was 9.25 cm³.

- (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 KMnO₄ from burette)
- (ii) Calculate the percentage mass of ethanedioic acid, H₂C₂O₄, present in the rhubarb leaves sample. [3]

Amount of MnO₄⁻ used = $\frac{9.25}{1000} \times 0.020 = 0.000185$ mol [1/2] Amount of C₂O₄²⁻ in 10.0 cm³ = $\frac{5}{2} \times 0.000185 = 0.0004625$ mol [1/2]

Amount of $C_2O_4^{2-}$ in 50.0 cm³ = 5 × 0.0004625 = 0.002313 mol [1/2]

Mass of $H_2C_2O_4 = 0.002313 \times (1.0 \times 2 + 12.0 \times 2 + 16.0 \times 4) = 0.2082$ g [1/2]

% mass of H₂C₂O₄ in 20.0 g sample = $\frac{0.2082}{20.0} \times 100\% = 1.04\%$ [1]

Note: we **<u>cannot</u>** use the mol ratio of MnO_4^- to H^+ to determine amount of $H_2C_2O_4$ as H^+ is contributed by $H_2C_2O_4$ and acidified medium of KmnO₄.

(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 dm³ and contains 2.58 kg of carbon dioxide.

(i) Calculate the pressure the carbon dioxide would exert inside the cylinder at 25 °C.

pV = nRT (P in Pa, V in m³, T in K) $p \times 5 \times 10^{-3} = \frac{2.58 \times 1000}{44.0} \times 8.31 \times 298$ $p = 2.90 \times 10^7$ 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] CO₂ has <u>significant intermolecular forces of attraction</u> [1/2] (instantaneous dipole-induced dipole). This gas molecules are <u>attracted closer together</u> and <u>reduces the force of collision of gas molecules (pressure exerted)</u> against the wall of containers. [1/2]

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

reaction 5.1	CO ₂ (g)	CO ₂ (aq)
reaction 5.2	CO ₂ (aq) + H ₂ O (I)	➡ H ₂ CO ₃ (aq)
reaction 5.3	H ₂ CO ₃ (aq)	→ H ⁺ (aq) + HCO ₃ ⁻ (aq)

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

$$K_{\rm H} = \frac{[\rm CO_2(aq)]}{P_{\rm CO2}}$$

The Henry's law constant, $K_{\rm H}$, for CO₂ is 3.4×10^{-2} mol dm⁻³ atm⁻¹ at 25 °C.

The pressure of CO₂(g) in an unopened sealed bottle is 250 kPa at 25 °C.

Calculate the concentration of dissolved CO₂ in the unopened bottle at 25 $^\circ$ C.[1]

 $[CO_2(aq)] = 3.4 \times 10^{-2} \text{ mol } dm^{-3} \text{ atm}^{-1} \times (\frac{250000}{101325} \text{ atm})$ $= 0.08388 \approx 0.0839 \text{ mol } dm^{-3}$

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 CO₂ escapes (or P_{total} decreases), [CO₂(g)] decreases. The equilibrium of reaction 5.1 shifts left and [CO₂(aq)] decreases. [1] Decrease in [CO₂(aq)] further causes equilibrium of reaction 5.2 to shifts left and [H₂CO₃(aq)] decreases. [1] Decrease in [H₂CO₃(aq)] then causes equilibrium of reaction 5.3 to shift left too. Overall, [H⁺] decreases and hence the pH of the drink increases. [1]

[1]

(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.

$$\begin{array}{cccc} C_{12}H_{22}O_{11} + H_2O & \xrightarrow{H^+(aq)} & C_6H_{12}O_6 + C_6H_{12}O_6 \\ (sucrose) & (glucose) & (fructose) \end{array}$$

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.

Expt	Volume of sucrose /cm ³	Volume of HC <i>l</i> /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

Table 5.1

- (i) Explain why varying volume of water was used in the 3 experiments. [1] Water is added to maintain a constant total volume of solution for each experiment. This is such that the volume of reagents used would be directly proportional to its concentration in the final reaction mixture.
- (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] Comparing expt 1 and 2, when $[HCl] \times 1.5$ while [sucrose] is kept constant, rate of reaction also $\times 1.5$. It is 1st order w.r.t. HCl. [1]

Comparing expt 2 and 3, when [sucrose] \times 2 while [HC/] is kept constant, rate of reaction also \times 2. It is 1st order w.r.t. sucrose. [1]

Rate = k[sucrose] [HC/] [1]

Using data from any expt to calculate conc of reagents **<u>after mixing</u>** to find k. E.g. from expt 1

[sucrose] = $0.79 \times \frac{20}{50} = 0.316 \text{ mol dm}^{-3}$ [HC/] = $1.25 \times \frac{20}{50} = 0.500 \text{ mol dm}^{-3}$

$$k = \frac{0.00125}{0.316 \times 0.500} = 7.91 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$$

[Total : 20]