



CANDIDATE NAME

SUBJECT CLASS REGISTRATION NUMBER

CHEMISTRY

Paper 3 Free Response

9729/03 14 September 2023 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				
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2	/16			
3	/24			
Section B				
4	/20			
5	/20			
Paper 3 Total	/80			

This document consists of 28 printed pages.

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Section A Answer all the questions in this section.

1 (a) Table 1.1 list physical properties of some Period 4 elements.

property	К	Ca	Fe	As	Se
relative atomic mass	39.1	40.1	55.8	74.9	79.0
atomic radius (metallic) / nm		0.197	0.126		
melting point / K		1112	1808		
density / g cm ⁻³		1.54	7.86		
1 st I.E. / kJ mol⁻¹				944	941
2 nd I.E. / kJ mol ⁻¹	3070	1150			

Table 1.1

(i) Explain why the atomic radius of Fe is less than that of Ca.

[2]

- (ii) Use relevant data from the table to explain why the density of Fe is significantly greater than that of Ca. (no calculations are required) [2]
- (iii) Suggest why the melting point of Fe is significantly higher than the melting point of Ca. [2]
- (iv) With reference to the electronic configuration of K and Ca, explain why the 2nd I.E. of Ca is lower than that of K.
 [2]
- (v) With reference to the electronic configurations of As and Se, explain why the 1st I.E. of Se is lower than that of As.
 [2]
- (i) Fe has higher nuclear charge than Ca as it has more protons. Although Fe has more inner-shell electrons than Ca, the additional 3d electrons are poor shielding electrons. Thus, the increase in nuclear charge outweighs the increase in shielding effect. Overall, the valence electrons in Fe experience a stronger nuclear attraction, resulting in smaller atomic radius than Ca.

(ii) Density = mass/volume

Fe has a smaller atomic radius than Ca and thus more atoms per unit volume. Furthermore, Fe has a larger relative atomic mass than Ca. Hence, Fe has greater mass per unit volume than Ca.

(iii) The small energy difference between 3d and 4s subshells allow Fe to contribute both the 3d and 4s electrons to the sea of delocalised electrons for metallic bonding, whereas Ca contributes only 2 valence electrons (from 4s subshell) to the sea of delocalized electrons. More energy is required to overcome the stronger metallic bonds in Fe and hence the melting point of Fe is significantly higher than that of Ca. (iv) K: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ Ca: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

The second most loosely held electron to be removed from K is from the 3p subshell whereas the second most loosely held electron to be removed from Ca is from the 4s subshell, which experiences greater shielding effect since it has one more filled principal quantum shell and is further away from the nucleus. These factors outweigh the higher nuclear change in Ca. Thus, the nuclear attraction for the second most loosely held electron in Ca is weaker and less energy is required to remove it, resulting in lower 2nd I.E for Ca as compared to K.

(v) As: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$ Se: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$

The most loosely held electron to be removed from Se is a paired 4p electron whereas the most loosely held electron to be removed from As is an unpaired 4p electron. Less energy is required to remove the paired electron since it experiences inter-electronic repulsion, hence, Se has a lower 1st I.E than As.

(b) The Fischer-Tropsch process involves converting a mixture of carbon monoxide and hydrogen, known as syngas, into hydrocarbons, in the presence of catalysts.

One such reaction is shown below:

$$CO(g) + 3H_2(g) \leftarrow CH_4(g) + H_2O(g)$$
 $\Delta H < 0$

- (i) Write an expression for the equilibrium constant, K_p , for this reaction, and state its units. [2]
- (ii) A mixture of CO and H₂ was introduced into a sealed vessel and heated to 1200 K. At equilibrium, it was found that the total pressure was 32 atm, and the mole fractions of CO and CH₄ were 0.5 and 0.12 respectively.

Calculate the equilibrium partial pressures of all gases, and hence calculate the value of K_{p} . [3]

(iii) Higher temperatures and higher pressures can lead to faster reactions. However, in commercial facilities that use the Fischer-Tropsch process, this was avoided. Explain why.

Transition metals such as iron or cobalt, are commonly used as catalysts in the Fischer-Tropsch process.

- (iv) State the type of catalysis in the Fischer-Tropsch process. [1]
- (v) Outline the mode of action of the catalyst in the Fischer-Tropsch process. [2]
- (i) $K_{p} = \frac{P_{CH4} \times P_{H2O}}{P_{CO} \times (P_{H2})^{3}}$ Units = atm⁻²

(ii) When position of equilibrium shifts to the right, equal amount of CH₄ and H₂O are formed

Mole fraction of $CH_4 = H_2O = 0.12$ $P_{CH4} = P_{H2O} = 0.12 \times 32 = 3.84$ atm

Mole fraction of CO = 0.5P_{CO} = $0.5 \times 32 = 16$ atm

Mole fraction of $H_2 = 1 - 0.5 - 0.12 - 0.12 = 0.26$ $P_{H2} = 0.26 \times 32 = 8.32$ atm

$$K_{\rm p} = \frac{3.84 \times 3.84}{16 \times (8.32)^3} = 1.60 \times 10^{-3} \, \text{atm}^{-2}$$

(iii) The forward reaction is exothermic, using a high temperature would favour the backward endothermic reaction instead, resulting in lower yield, hence avoided.

Using a higher pressure will incur higher costs of maintaining the equipment, hence avoided.

- (iv) Heterogeneous catalysis
- (v) Step 1: Adsorption of reactant particles CO(g) and H₂(g) onto the active sites of Fe(s) catalyst surface through weak interactions.
 - Step 2: **Reaction** at the surface occurs at a faster rate as reactant molecules are brought closer together in the correct orientation for reaction and existing bonds within the reactant molecules are weakened, thereby reducing E_a.
 - Step 3: **Desorption** of products CH₄(g) from the Fe(s) catalyst surface. Catalyst is regenerated and there are vacant active sites available for adsorbing other reactant molecules.

[Total: 20]

- 2 Iodine is found naturally in compounds in many different oxidation states.
 - (a) lodide ions, I^- , react with acidified $H_2O_2(aq)$ to form iodine, I_2 , and water. The resultant mixture is then shaken with cyclohexane, C_6H_{12} , to extract the I_2 .

Cyclohexane is immiscible with water.

(i) Identify the role of $H_2O_2(aq)$ in its reaction with I⁻ ions in acidic conditions.

Write an ionic equation for the reaction.

(ii) The partition coefficient (K_{pc}) is the ratio of the concentrations of a solute in two different immiscible solvents in contact with each other when equilibrium has been established at a particular temperature.

The partition coefficient can be expressed as the following equation:

$$K_{\text{pc}} = \frac{[\text{Solute}]_{\text{Organic solvent}}}{[\text{Solute}]_{\text{Water}}}$$

15.0 cm³ of C_6H_{12} is shaken with 20.0 cm³ of an aqueous solution containing I_2 until no further change is seen.

It is found that 0.390 g of I_2 is extracted into C_6H_{12} .

The partition coefficient of I_2 between C_6H_{12} and water, K_{pc} , is 93.8.

Calculate the mass of I_2 that remains in the aqueous layer. [2]

- (iii) Suggest how the value of K_{pc} of I₂ between hexan-2-one and water compares to the value given in (a)(ii).
 Explain your answer. [2]
- (i) Role: oxidising agent lonic equation: $H_2O_2 + 2H^+ + 2I^- \rightarrow 2H_2O + I_2$
- (ii) Amt of I₂ extracted into C₆H₁₂ = $\frac{0.390}{2(126.9)}$ = 0.001537 mol [I₂]_{cyclohexane} = $\frac{0.001537}{15/1000}$ = 0.1025 mol dm⁻³

$$\textit{K}_{pc} = \frac{[I_2]_{cyclohexane}}{[I_2]_{water}}$$

$$93.8 = \frac{0.1025}{[l_2]_{water}}$$

 $[I_2]_{water}$ = 1.092 × 10⁻³ mol dm⁻³

Amt of I₂ in 20.0 cm³ of aqueous layer = $1.092 \times 10^{-3} \times \frac{20}{1000} = 2.184 \times 10^{-5}$ mol Mass of I₂ remaining in aqueous layer = $2.184 \times 10^{-5} \times 2(126.9) = 5.54 \times 10^{-3}$ g

[2]

(iii) The value of K_{pc} would be smaller.

Hexan-2-one is polar while cyclohexane is non-polar, so hexan-2-one forms less favourable interactions with non-polar I_2 , hence I_2 is less soluble in hexan-2-one than in cyclohexane.

- (b) The Group 1 iodides all form stable ionic lattice and are soluble in water.
 - (i) Define *enthalpy change of solution*.

[1]

Use the data in Table 2.1 to calculate the enthalpy change of solution of potassium iodide.
 Table 2.1

process	enthalpy change, $\Delta H / \text{ kJ mol}^{-1}$		
$K^+(g) + \mathrm{I}^-(g) \longrightarrow KI(s)$	-629		
$K^{+}(g) \longrightarrow K^{+}(aq)$	-322		
$I^-(g) \longrightarrow I^-(aq)$	-293		

[1]

- (iii) Suggest the trend in the magnitude of lattice energies of Group 1 iodides, LiI, NaI, KI. Explain your answer. [2]
- (i) Enthalpy change of solution is the <u>energy change</u> when <u>one mole</u> of <u>substance is</u> <u>completely dissolved</u> in a solvent / water to form an infinitely dilute solution.
- (ii) $\Delta H_{\text{solution}} = -\text{LE} + \Delta H_{\text{hydration of cation}} + \Delta H_{\text{hydration of anion}}$ = -(-629) + (-322) + (-293) = +14.0 kJ mol⁻¹
- (iii) Product of charges are similar while interionic distances increase from LiI to KI since cationic radii increases from Li⁺ to K⁺.

Given that $|L.E.| \propto \left| \frac{q_+ \times q_-}{r_+ + r_-} \right|$

Magnitudes of lattice energies decreases from LiI to KI.

(c) A solution is prepared by dissolving 35.0 g of hydrated copper(II) sulfate crystals in 1 dm³ of water. 25.0 cm³ of the resultant solution is pipetted out and reacted with an excess of I⁻(aq).

Reaction 1: $2Cu^{2+} + 4I^- \longrightarrow 2CuI + I_2$

The I_2 produced is titrated against a solution containing thiosulfate ions, $S_2O_3^{2-}(aq)$, using a suitable indicator.

Reaction 2: $2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$

The end-point of the titration is reached when 22.30 cm³ of 0.150 moldm⁻³ $S_2O_3^{2-}(aq)$ has been added.

- (i) Calculate the mass of copper in the 35.0 g sample of hydrated copper(II) sulfate. [3]
- (ii) Identify a suitable indicator for the titration.
- (i) Amt of thiosulfate = $\frac{22.30}{1000} \times 0.150 = 3.345 \times 10^{-3}$ mol Amt of I₂ produced from reaction 1 = $\frac{1}{2} \times 3.345 \times 10^{-3} = 1.673 \times 10^{-3}$ mol Amt of Cu²⁺ in 25 cm³ = 2 × 1.673 × 10⁻³ = 3.345 × 10⁻³ mol Amt of Cu²⁺ in 1 dm³ = $\frac{1000}{25} \times 3.345 \times 10^{-3} = 0.1338$ mol Mass of Cu in 35.0 g sample = 0.1338 × 63.5 = 8.496 = 8.50 g
- (ii) Starch indicator
- (d) An orange precipitate of HgI_2 forms when Hg^{2+} ions are added to KI(aq). The solubility of HgI_2 at 25 °C is 1.00×10^{-7} g dm⁻³.

Calculate the solubility product, K_{sp} , of HgI₂.

[1]

 $HgI_2(s) \implies Hg^{2+}(aq) + 2I^{-}(aq)$

Equilibrium conc/ mol dm⁻³

 $M_{\rm r}$ of HgI₂ = 454.4 Solubility of HgI₂ in mol dm⁻³ =1.00 × 10⁻⁷ ÷ 454.4 = 2.20 × 10⁻¹⁰

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$$K_{sp} = [Hg^{2+}][I^{-}]^{2}$$

= [s][2s]^{2}
= 4s^{3}
= 4 × (2.20 × 10^{-10})^{3}
= 4.26 × 10^{-29}

[Total: 16]

2s

7

3 Halogenoalkane **Q** can be made in 2 steps from benzene as shown in Fig 3.1. In step I, compound **P** is the sole organic product formed.





- (a) (i) Suggest the structure of compound P. [1]
 - (ii) Suggest the reagents and conditions for step I and II. [2]
 - (i)
 - (ii) Step I: CH₃Br, anhydrous FeBr₃

Step II: limited Cl₂, UV light (or heat)

(b) Ether can be synthesized using a halogenoalkane and phenol as shown in Fig 3.2. Phenol is first converted into phenoxide ion before reacting with halogenoalkane **Q**.



To understand the mechanism of this substitution reaction, two kinetics experiments were carried out. 1.0 mol dm⁻³ of phenoxide was reacted with 0.06 mol dm⁻³ of halogenoalkane **Q** in inert organic solvent. This experiment was then repeated with 2.0 mol dm⁻³ of phenoxide used instead.

Colorimetric method was used to monitor the concentration of compound R present in the solution in both experiments. The following graphs were obtained from the two experiments.



(i) Deduce the rate equation for the reaction.



- (ii) Hence, calculate the rate constant, for the reaction between compound **Q** and phenoxide. Give the units of the rate constant. [1]
- (iii) With reference to your answer in **b**(i), describe the mechanism of this reaction, showing curly arrows, charges, dipoles and any relevant lone pairs. [3]

(i) Doubling the concentration of phenol (or phenoxide ions) did not change the rate of reaction significantly. The order of reaction with respect to phenoxide ion is zero.

As the reaction proceeds, concentration of phenoxide ion remained relatively unchanged while concentration of \mathbf{Q} decreases. Rate of reaction (gradient of [R] over time graph) decreases with a constant half-life of 3.1 minutes. Reaction is 1st order with respect to \mathbf{Q} .

Rate = k [**Q**]

- (ii) For first order reaction, $t_{1/2} = \frac{\ln 2}{k}$ Rate constant, $k = \frac{\ln 2}{3.1} = 0.224 \text{ min}^{-1}$
- (iii) Since reaction is unimolecular, the reaction mechanism is S_{N1} nucleophilic substitution. (Only 1 reactant in the slow step)



(c) Halogenoalkane **Q** can be converted into benzoyl chloride as shown in Fig 3.3. Benzoyl chloride is a reactive precursor for synthesizing other useful molecules.



- (i) State the reagents and conditions needed to convert halogenoalkane **Q** into benzoic acid. [1]
- (ii) Three samples of phenol, benzoic acid and benzoyl chloride are added separately into 3 beakers containing equal volume of water.

Arrange the resultant solutions of phenol, benzoic acid, and benzoyl chloride in increasing order of pH values. Explain your answer. [3]

(iii) A pH 4.70 buffer solution was prepared by adding 0.1 mol dm⁻³ benzoic acid into a vessel containing 50 cm³ of 0.2 mol dm⁻³ sodium hydroxide solution.

Calculate the volume of benzoic acid needed for the preparation of this buffer solution.

 $[pK_a \text{ of benzoic acid} = 4.20]$

[3]

- (i) $KMnO_4$, $H_2SO_4(aq)$, heat
- (ii) Increasing pH: Benzoyl chloride, benzoic acid, phenol

When benzoyl chloride is dissolved in water, a strong acid, HCl, is produced which dissociates in water to give H⁺ and Cl^{-} . Hence, it has the lowest pH value.

The two electronegative O atoms in –COO⁻ can disperse the negative charge of the conjugate base of benzoic acid better compared to the benzene ring in phenoxide ions. Hence, the conjugate base of benzoic acid is more stable than phenoxide ion, favouring the acid dissociation of benzoic acid to a greater extent, resulting in benzoic acid being more acidic than phenol, lower pH than phenol.

	C ₆ H ₅ COOH(aq)	+	NaOH(aq)	\rightarrow	C ₆ H₅COO⁻ (aq)	+	$H_2O(l)$
Initial / mol	x		0.01		0		-
Change / mol	-0.01		-0.01		+0.01		-
Final / mol	x-0.01		0		0.01		-

(iii) Let the initial amount of benzoic acid used be x mol

Amt of $C_6H_5COO^-$ at equivalence pt = 0.01 mol

Let the volume of buffer solution at pH 4.70 be V dm³.

pH = pK_a + lg $\frac{[\text{conjugate acid}]}{[\text{weak acid}]}$ 4.70 = 4.20 + lg $\frac{0.01 / \text{V}}{(x - 0.01) / \text{V}}$ $\frac{0.01}{x - 0.01}$ = 10^{0.5}

0.01 = 3.162x - 0.03162x = 0.01316 mol

Volume of benzoic acid needed = $0.01316 / 0.1 = 0.1316 \text{ dm}^3 = 132 \text{ cm}^3$

(d) Resedine, a natural compound, is useful in the preparation of antiviral agents.

A plausible synthetic pathway of resedine from halogeoalkane **Q** is shown in Fig 3.4.



- (i) State the reagents and conditions for step 2.
- (ii) Suggest the structure for compound V and state the reagents and conditions required for step 4. [2]
- (iii) Suggest the type of reaction in step 5 and hence state the reagents and conditions required. [2]
- (iv) Predict the optical activity of resedine formed via the synthetic pathway proposed in (d). [2]
- (i) $K_2Cr_2O_7$, dil H_2SO_4 , heat with immediate distillation
- (ii) OH CH₂NH₂

Step 4: LiA/H₄ in dry ether / H₂(g), Pt

- (iii) Type of reaction: Condensation Step 5: anhydrous COCl₂
- (iv) Resedine obtained would be optically inactive.

The carbonyl group in compound **T** is trigonal planar in structure. Hence, nucleophile CN^- can attack the carbonyl group from top and bottom of the carbonyl group with equal probability, producing equal amount of the enantiomers of compound **U** and hence resedine (racemic mixture). The enantiomers in the racemic mixture rotate plane polarised light in opposite direction but of equal magnitude hence cancelling out its optical activity.

[Total: 24]

[1]

[Turn over

Section B

Answer one question from this section.

4 (a) Fig 4.1 shows an electrolytic cell that produces molten aluminium and carbon dioxide gas.



The overall equation for this reaction is:

 $2Al_2O_3(l) + 3C(s) \longrightarrow 4Al(l) + 3CO_2(g)$

- (i) Construct equations for the reactions that occur at the anode and cathode. Include state symbols in your equations. [1]
- (ii) A steady current of 108 A was used to produce 185 g of Al(l). Calculate the number of moles of electrons that must be transferred in the cell. Hence calculate the time needed to produce the mass of Al(l). [2]
- (iii) Calculate the volume of CO₂(g), measured at 301 K and 1.31 atm, that is produced in the process. [2]
- (iv) For the electrolytic cell to operate, Al_2O_3 must be in liquid state rather than in solid state. Explain, in terms of structure and bonding, why this is so. [2]

(i) Anode:
$$C(s) + 2O^{2-}(l) \longrightarrow CO_{2}(g) + 4e^{-}$$

(Oxidation of C in presence of O²⁻ to give CO₂, balance the half eqn)

Cathode: $Al^{3+}(l) + 3e^{-} \longrightarrow Al(l)$

(ii) No of mol of $Al = \frac{185}{27.0} = 6.852 \text{ mol}$ $Al = 3e^{-1}$

No of mol of electrons = $6.852 \times 3 = 20.56$ mol

$$n_{AI} = \frac{I \times t}{n_e \times F} \implies 6.852 = \frac{108 \times t}{3 \times 96500}$$

(iii) $CO_2 = 4e^-$ No of mol of $CO_2 = \frac{20.56}{4} = 5.14$ mol pV = nRT $(1.31 \times 101325) \times V = 5.14 \times 8.31 \times 301$

V = <u>0.0968 m³</u>

(iv) Al_2O_3 has a <u>giant ionic lattice structure</u> with strong <u>electrostatic forces of</u> <u>attraction between the oppositely charged ions</u>.

In the <u>solid state</u>, Al_2O_3 will not conduct electricity, as the ions are in a <u>fixed</u> <u>position</u> and unable to move to the electrode.

In <u>the liquid state, the ions are mobile and able to move to the electrodes</u> for electrolysis to occur.

(b) An Ellingham diagram shows how the Gibbs free energy change for a reaction varies with temperature, T.

The Ellingham diagram for **reaction 1** and **2** is shown in Fig 4.2.

Reaction 1: $2C(s) + O_2(g) \longrightarrow 2CO(g)$ $\Delta G_{1500K} = -493 \text{ kJ mol}^{-1}$

Reaction 2: $2Fe(s) + O_2(g) \longrightarrow 2FeO(s)$ $\Delta G_{1500K} = -330 \text{ kJ mol}^{-1}$



- With reference to the physical state of the reactants and products, explain clearly which graph in the Ellingham diagram represents reaction 1. [3]
- (ii) The Gibb's free energy for a given reaction can be calculated in the same way as enthalpy change of reaction, via an energy cycle.

Calculate the free energy change of the following reaction at 1500 K:

FeO (s) + C (s)
$$\rightarrow$$
 Fe (s) + CO (g)

[1]

(iii) Molten steel is stored in a vessel saturated with oxygen at 1500 K.

Such vessels are commonly lined with aluminium oxide, which has a high melting point. Despite carbon having a high melting point, it cannot be used for the same purpose.

With reference to the information provided in **(b)**, explain why carbon cannot be used to line such vessels. [1]

(i) Reaction 1: $2C(s) + O_2(g) \longrightarrow 2CO(g)$

There is an increase in the number of moles of gas after reaction so $\Delta S > 0$.

Since $\Delta G = \Delta H - T \Delta S$

 ΔG becomes more negative as T increases (or gradient of Ellingham diagram is $-\Delta S$)

Hence graph A represents reaction 1.

(ii)



$$\Delta G + \left(-\frac{330}{2}\right) = -\frac{493}{2}$$

 $\Delta G = - 81.5 \text{ kJ mol}^{-1}$

(iii) At <u>T = 1500 K</u>, Reaction 1 has $\Delta G < 0$, so it is thermodynamically feasible.

The oxygen can react with carbon to form **CO**. Thus, carbon is <u>not suitable to be</u> <u>used as a lining material at such a high temperature in the presence of</u> <u>oxygen gas</u>.

(c) Compound Q with the molecular formula ●C₈H₉NO₂ is found to be able to relief pain and reduce fever. At room temperature, Q is ②insoluble in water and dilute acids but soluble in aqueous sodium hydroxide. Q reacts with ③aqueous bromine to form R, C₈H₇NO₂Br₂.

On warming **Q** with **4** dilute hydrochloric acid, compounds **S** and **T** are formed. **S** with the molecular formula of C_6H_8NOCl is soluble in water.

T, on reaction with Slithium aluminum hydride, forms U. U reacts with G aqueous alkaline iodine to form a yellow precipitate.

Suggest possible structures for **Q**, **R**, **S**, **T** and **U**. For each reaction, state the *type of reaction* described and explain what the information tells you about the functional group present in each compound. [8]

	Type of reaction / functional group
Compound Q has molecular formula C ₈ H ₉ NO ₂	 Q has <u>comparable no. of C and H atoms</u> with <u>at least 6 C atoms</u> ⇒ Q contains a <u>benzene ring [</u>√]
Q is insoluble in water and dilute acids but soluble in aqueous sodium hydroxide.	Q undergoes <u>neutralization</u> [$$] reaction with sodium hydroxide to give a soluble salt but not with dilute acid.
	Q has <u>carboxylic acid or phenol functional</u> group [√]
Q reacts with aqueous bromine to form R, C ₈ H ₇ NO ₂ Br ₂	Q , $C_8H_9NO_2$, lost 2 H and gain 2 Br, Q undergoes <u>electrophilic substitution</u> reaction to form R , $C_8H_7NO_2Br_2$ [$$]
	Q has presence of <u>phenol group</u> . $[\sqrt]$ Only 2 Br added so either position 2 or 4 with respect to phenol is occupied by a side chain.
On warming Q with dilute hydrochloric acid , compounds S and T are formed.	Q undergoes <u>acidic hydrolysis</u> $[]$ to form an S an ammonium salt and T a carboxylic acid $[]$ with only 2 carbon atoms.
S , C ₆ H ₈ NOC/ is soluble in water	
5 T, on reaction with lithium aluminium hydride, forms U.	T undergoes <u>reduction</u> $[]$ to form U, a <u>primary alcohol</u> . $[]$
G U reacts with aqueous alkaline iodine to form a yellow precipitate.	U undergoes <u>oxidation</u> [√] and it has −CH(OH)CH ₃ group [√]



For compound Q, R and S, nitrogen group can also be at the 2-position w.r.t. phenol.

[Total : 20]

- 5 (a) (i) Write the balanced equation representing the standard enthalpy change of combustion of liquid C_4H_7Cl , given that gaseous ClO_2 is one of the products. [1]
 - (ii) The dot-and-cross diagram of ClO_2 is shown below, ClO_2 has a bond angle of 117°.

Explain, with reference to VSERP theory, why the bond angle in H_2O is smaller than that in ClO_2 . [2]

(iii) The use of the Data Booklet is relevant to this question.

Using bond energy values, calculate the standard enthalpy change of combustion of 1-chlorobut-2-ene.

(Given: Bond energy of O=Cl is 257 kJ mol⁻¹) [2]

(iv) Explain why the theoretical value for the enthalpy change of combustion is different from your answer in (iii). [1]

(i)
$$C_4H_7Cl(l) + \frac{27}{4}O_2(g) \rightarrow 4CO_2(g) + \frac{7}{2}H_2O(l) + ClO_2(g)$$

(ii) ClO_2 has 2 bond pair electrons, 1 lone pair electrons and 1 lone electron around the central Cl atom while H_2O has 2 bond pair electrons and 2 lone pair electrons around the central O atom.

However, due to the presence of the single lone electron in ClO_2 , the <u>lone</u> <u>pair-bond pair electron repulsion</u> in H_2O is <u>stronger</u> than the <u>lone</u> <u>electron-bond pair electron repulsion</u> in ClO_2 .

Hence, the bond pairs in H_2O are closer, resulting in a smaller bond angle.

(iii)

$$H \rightarrow C \rightarrow H + C \rightarrow H + C \rightarrow H + C \rightarrow H = C \rightarrow H =$$

(iv) Bond energy is defined as the energy required to break one mol of gaseous covalent bonds to form gaseous atoms. However, in the calculation in (a)(iii), the bonds in 1-chlorobut-2-ene and water are not in gaseous state but in liquid state at standard conditions. This results in the difference in the magnitude of H^e_c.

OR

= -2306 kJ mol⁻¹ ≈ -2310 kJ mol⁻¹

The **bond energy data from the** *Data Booklet* used in (a)(iii) are only averages values which does not represent the exact bond energy in this reaction. This results in the difference in the magnitude of H^{e}_{c} .

(b) The isomers *cis*-1-chlorobut-2-ene and *trans*-1-chlorobut-2-ene, C₄H₇C*l*, have different stabilities.

The standard enthalpy change for the conversion of *cis*-1-chlorobut-2-ene to *trans*-1-chlorobut-2-ene isomer is ΔH^{e}_{r} .



To find out the relative stability of the two isomers, standard enthalpy change of combustion, ΔH^{e}_{c} , of the *cis* and *trans* isomers in liquid state, (henceforth known as $\Delta H^{e}_{c}(cis)$ and $\Delta H^{e}_{c}(trans)$ respectively) will be compared.

(i) Using your answer in (a)(i), and information from Table 5.1, calculate the value of ΔH°_{c} (*cis* – C₄H₇C*l*(*l*)). Give your answer in **four** significant figures.

∆ <i>H</i> ^e _f (CO ₂ (g))	−393.5 kJ mol ⁻¹
$\Delta H^{e_{f}}(ClO_{2}(g))$	+104.6 kJ mol ⁻¹
$\Delta H^{e}_{f}(H_{2}O(\hbar))$	−285.8 kJ mol ⁻¹
ΔH^{e}_{f} (<i>cis</i> – C ₄ H ₇ C <i>l</i> (<i>l</i>))	−43.1 kJ mol ⁻¹

Table 5.1

- (ii) Given that ΔH^{e}_{c} (*trans* C₄H₇C*l*(*l*)) is -2420 kJ mol⁻¹ and using your answer in (b)(i), draw an energy level diagram to calculate ΔH^{e}_{r} . [2]
- (iii) Hence, explain how the value of K_c will change when temperature is increased.

[1]

[2]

(i)
From (a)(i),
$$C_4H_7Cl(l) + \frac{27}{4}O_2(g) \rightarrow 4CO_2(g) + \frac{7}{2}H_2O(l) + ClO_2(g)$$

Note: $\Delta H^{e_f}O_2(g) = 0$

By Hess' Law, $\Delta H^{e}_{c} (cis-C_{4}H_{7}Cl(l)) = \sum n \Delta H^{e}_{f} (products) - \sum m \Delta H^{e}_{f} (reactants)$ $= 4\Delta H^{e}_{f} (CO_{2}(g)) + \frac{7}{2} \Delta H^{e}_{f} (H_{2}O(l)) + \Delta H^{e}_{f} (ClO_{2}(g)) - \Delta H^{e}_{f} (cis-C_{4}H_{7}Cl(l))$ $= 4(-393.5) + \frac{7}{2} (-285.8) + (+104.6) - (-43.1)$ $= -2427 \text{ kJ mol}^{-1} (4 \text{ s.f.})$

(ii) Energy/kJ mol⁻¹

$$cis-C_{4}H_{7}C/(l) + \frac{27}{4}O_{2}(g)$$

$$trans-C_{4}H_{7}C/(l) + \frac{27}{4}O_{2}(g)$$

$$\Delta H_{r}^{\theta} = ?$$

$$\Delta H_{c}^{\theta}(trans)$$

$$= -2420$$

$$4CO_{2}(g) + \frac{7}{2}H_{2}O(l) + ClO_{2}(g)$$

correct energy level diagram.

- correct stoichiometry of reactants and products,
- correct state symbols,
- correct relative size of arrows,
- correct direction of arrows,
- correct axis

 $\Delta H_r = -2427 + 2420 = -7.00 \text{ kJ mol}^{-1}$

(iii) By Le Chatelier's principle, when <u>temperature increases</u>, the <u>equilibrium</u> <u>position shifts to the left</u> towards the <u>endothermic reaction to absorb heat</u>.

Hence, this results in the formation of more cis-1-chlorobut-2-ene isomer.

K_c value will <u>decrease.</u>

(c) Besides alkenes, cycloalkanes can also exist as *cis*-*trans* isomers.

One example is 1,2-dimethylcyclobutane.

- (i) State two characteristics of cycloalkanes that allow *cis-trans* isomerism to exist for 1,2-dimethylcyclobutane. [1]
- (ii) Draw the structures of the *cis* and *trans* isomers of 1,2-dimethylcyclobutane.
- (i) There is a <u>restriction of bond rotation about the C-C bond in the ring</u> of 1,2-dimethylcyclobutane.

There are two different groups bonded to each carbon of the ring.



(d) The ruthenium(II) based catalyst $RuH_2(PPh_3)_4$, where PPh_3 represents $P(C_6H_5)_3$, is able to catalyse the formation of an amide from amine and alcohol, as shown in Fig 5.1.



(i) Fig 5.2 shows the formation of an amide using $RuH_2(PPh_3)_4$ catalyst.



Fig 5.2

Draw the structures of compounds **A** and **B**.

(ii) Hence, propose a synthetic route for the formation of compounds **A** and **B** respectively, using only methylbenzene as the starting compound in each case.

[3]

[2]

[2]

(iii) Draw the structure of the product for the reaction below.



[Turn over



A and B are interchangeable

(ii) Synthesis of A:



[Total : 20]