VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME .....

CT GROUP .....

CHEMISTRY **9729/03**

Paper 3 Free Response **21 September 2020**

Candidates answer on the Question Paper. **2 hours**
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and CT group 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** the questions.

Section B
Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use		
Section A	1	/ 20
	2	/ 21
	3	/ 19
Section B	4 OR 5	/ 20
Total		/ 80

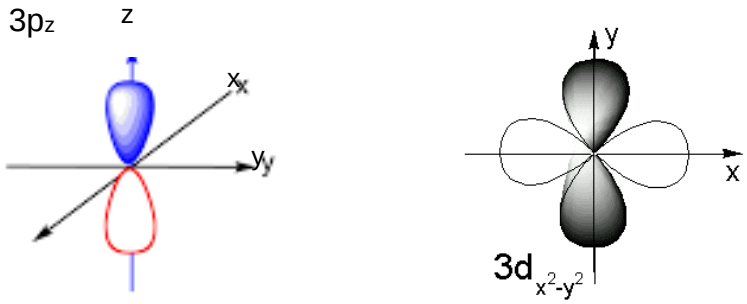
This document consists of **24** printed pages and **0** blank page.

Section A

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

1 Chlorine is in Group 17 and undergoes many reactions.

(a) Sketch and label, separately, the $3p_z$ and $3d_{x^2-y^2}$ orbitals present in chlorine.
[2]



(b) An element **A** reacts with chlorine to form **A**C*l*$_2$. The electronic configuration of $\mathbf{A}^{2+}$ is [Kr]$4d^{10}$. Identify the element **A**.
[1]

Cadmium / Cd

(c) The following reaction occurs when chlorine dissolves in water.

$$Cl_2(g) + H_2O(l) \rightleftharpoons HClO(aq) + HCl(aq)$$

When solutions of chlorine are used for water purification, the pH of these solutions are kept near to pH 7 by the addition of a base.

Chlorine is dissolved in water to produce 1000 cm^3 of a solution containing 0.170 mol of HC*l*O and 0.170 mol of HC*l*.

A buffer solution is then prepared by adding 0.200 mol of NaOH(s) to this solution. The NaOH reacts initially with the HC*l*. The remaining NaOH then reacts with HC*l*O.

(i) Write two equations to explain how this buffer is able to maintain a relatively constant pH when a few drops of $H^+(aq)$ or $OH^-(aq)$ are added to it.
[1]

$HClO + OH^- \rightleftharpoons ClO^- + H_2O$
$ClO^- + H^+ \rightarrow HClO$

(ii) Calculate the pH of the buffer solution.
[K_a of HC*l*O is $2.9 \cdot 10^{-8}$ mol dm^{-3}.]
[1]

Amount of NaOH left after reacting with HC*l*
= 0.200 – 0.170 = 0.030 mol

Amount of NaC*l*O formed when NaOH reacts with HC*l*O
= 0.030 mol

Amount of HC*l*O left
= 0.170 – 0.030 = 0.140 mol

- $K_a = \frac{[□^+][□□□^-]}{[□□□□]}$

  $2.9 \cdot 10^{-8} = \frac{[□^+](0.0301)}{(0.1401)}$

  $[H^+] = 1.35 \cdot 10^{-7}$ mol dm^{-3}
- □ **pH = –lg(1.35 · 10^{-7}) = 6.87**

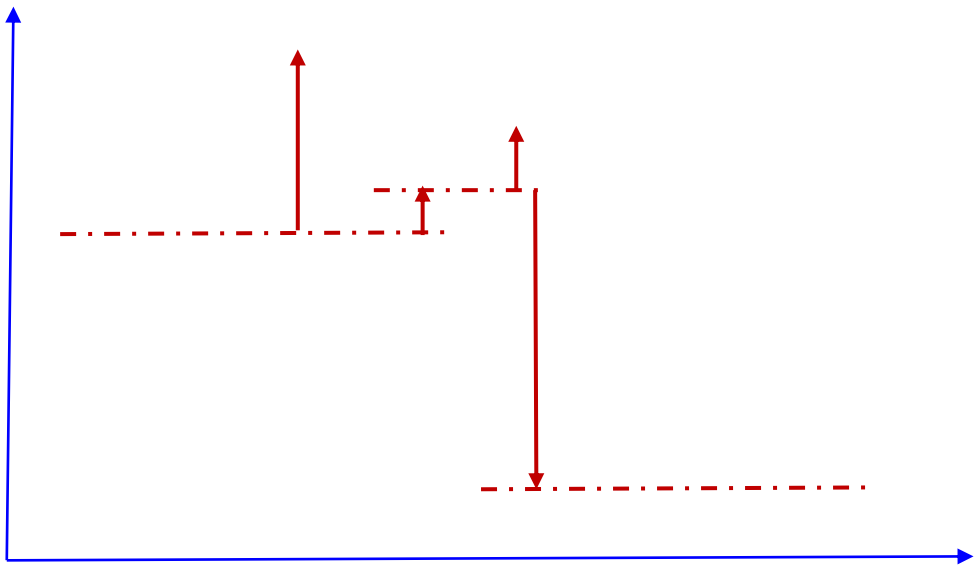
(d) A sample of an alkane, RH, and limited amount of chlorine are mixed together and irradiated with ultraviolet light. The mechanism involved two propagation steps.

Propagation step 1: RH + C*l*□ □ R□ + HC*l*
Propagation step 2: R□ + C*l*$_2$ □ RC*l* + C*l*□

Some data for the enthalpy change of reaction and the activation energy of the two propagation steps of an alkane, RH, are given below.

Step	⊗*H* / kJ mol□1	E_a / kJ mol□1
Propagation step 1	+4	17
Propagation step 2	□109	4

Use the data provided to sketch the energy profile diagram of the two propagation steps of the chlorination of RH. Indicate all the given energy changes, reactants, intermediates and products on the diagram. [3]



Energy / kJ mol□1
RH + C*l*□ + C*l*$_2$

***E*$_{a1}$ = 17 kJ mol□1**

+4 kJ mol□1

R□ +
HC*l* +

Cl_2

E_{a2} = 4 kJ mol^{-1}
–109 kJ mol^{-1}

RC*l* + HC*l* + C*l*•

Progress of reaction / Reaction coordinate

(e) In the laboratory, there are three bottles labelled **B**, **C** and **D**. Each bottle contains one of the following chemicals, Cl_2(aq), NaI(aq) and KBr(aq).

Three tests were carried out using the chemicals in the bottles. The results are summarised in the table below.

test	procedure	observation
1	mix chemical in bottle **B** with chemical in bottle **C**	colourless solution obtained
2	mix chemical in bottle **B** with chemical in bottle **D**	yellow solution obtained
3	mix chemical in bottle **C** with chemical in bottle **D**	yellow solution obtained

(i) Deduce which bottle contains Cl_2(aq). Write equations to support your reasoning.
[2]

• **Bottle D contains Cl_2(aq) which oxidised Br^-(aq) to Br_2(aq) and I^-(aq) to I_2(aq) and accounts for the brown mixture obtained.**

Cl_2(aq) + 2Br^-(aq) • 2C*l*$^-$(aq) + Br_2(aq)
Cl_2(aq) + 2I^-(aq) • 2C*l*$^-$(aq) + I_2(aq)

(ii) Suggest a reagent that could be added separately after performing test 2 and test 3 to confirm the identities of the chemicals in the bottles. State the observations clearly.
[2]

• **The reagent is hexane.**
The bottle with orange-red organic layer contains KBr(aq) initially.
The bottle with violet / purple organic layer contains NaI(aq) initially.

(f) Solid aluminium chloride sublimes at 180 °C. In the vapour phase, an equilibrium is established between aluminium chloride and its dimer.

$$Al_2Cl_6(g) \rightleftharpoons 2AlCl_3(g)$$

At 400 ºC and 1 atm, 0.84 g of the equilibrium gaseous mixture occupies 268 cm^3.

(i) Calculate the average relative molecular mass of the gaseous mixture.
[2]

pV = nRT

• **$101325 \cdot 268 \cdot 10^{-6} = \frac{0.84}{M_r} \cdot 8.31 \cdot 673$**

• **M_r = 173**

(ii) Use your answer in **(f)(i)** to determine the degree of dissociation, α, of Al_2Cl_6.
[1]

Let initial amount of $Al_2Cl_6(g)$ be x mol.

	$Al_2Cl_6(g)$	$\rightleftharpoons$	$2AlCl_3(g)$	
Initial / mol	x		0	
Change / mol	$-x\alpha$		$+2x\alpha$	
Equilibrium / mol	$x - x\alpha$		$2x\alpha$	**Total = $x + x\alpha$**

Average M_r = $\frac{(1-\alpha)(267) + 2\alpha(133.5)}{1+\alpha}$

$173 = \frac{267}{1+\alpha}$

α = 0.543

(iii) Write an expression for the equilibrium constant, K_p, for the dissociation of Al_2Cl_6. [1]

- **$K_p = \frac{(p_{AlCl_3})^2}{p_{Al_2Cl_6}}$**

(iv) Hence, calculate the equilibrium constant, K_p, for the dissociation of Al_2Cl_6 at 400 ºC, including its units.

If you were unable to calculate the degree of dissociation of Al_2Cl_6 in **(f)(ii)**, assume α = 0.456. This is not the correct value of α.
[2]

Total amount = $x + x\alpha$ = 1.543x mol
Partial pressure of Al_2Cl_6 = $\frac{0.457}{1.543} \cdot 1$ = 0.296 tm
Partial pressure of $AlCl_3$ = 1 – 0.296 = 0.704 atm

$K_p = \frac{(0.704)^2}{0.296}$
= 1.67 atm

Alternative answer using α = 0.456:
Total amount = $x + x\alpha$ = 1.456x mol
Partial pressure of Al_2Cl_6 = $\frac{0.544}{1.456} \cdot 1$ = 0.374 atm
Partial pressure of $AlCl_3$ = 1 – 0.374 = 0.626 atm

$K_p = \frac{(0.626)^2}{0.374}$
= 1.05 atm

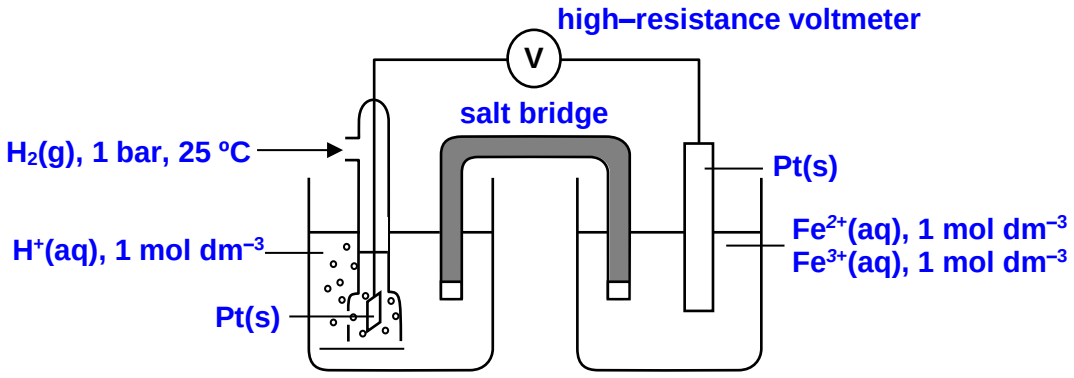
(v) State and explain the effect of increasing the temperature on the average M_r of the equilibrium mixture.
[2]

The dissociation of Al_2Cl_6 is an endothermic process as it involves the breaking of two covalent / dative bonds. According to Le Chatelier's principle, increasing the temperature favours an endothermic reaction to remove excess heat.

- **Thus, position of equilibrium shifts to the right. There will be a greater proportion of $AlCl_3$ in the reaction mixture, causing the average M_r of the reaction mixture to decrease.**

[Total: 20]

2 **(a)** By means of a fully labelled diagram, show how the standard electrode potential of the Fe^{3+}/Fe^{2+} system can be measured by using a standard hydrogen electrode.
[3]



(b) **(i)** When solid Fe and H_2O_2 are mixed together, the following reaction may occur.

$Fe + H_2O_2 + 2H^+ \rightarrow Fe^{2+} + 2H_2O$ $\quad \ominus G^\ominus = -427$ kJ mol^{-1}

Using data from the *Data Booklet*, write the equation for another possible reaction that might occur between solid Fe and H_2O_2. Calculate the $\ominus G^\ominus$ per mole of Fe for this reaction. Hence, deduce which oxidation state of Fe is more likely to be formed with H_2O_2.
[4]

- **$2Fe + 3H_2O_2 + 6H^+ \rightarrow 2Fe^{3+} + 6H_2O$**
- **$E_{cell}^\ominus = +1.77 - (-0.04) = +1.81$ V**

For oxidation of 1 mol of Fe to Fe^{3+},

- **$\Delta G^\ominus = -nFE_{cell}^\ominus = -3 \cdot 96500 \cdot (+1.81) = -524$ kJ mol^{-1}**

- **Since $\Delta G^\ominus$ of oxidation of 1 mol of Fe to Fe^{3+} is more negative, Fe is preferentially oxidised to Fe^{3+} (OR +3 oxidation state) by H_2O_2.**

(ii) Tartrate ions, $(CH(OH)CO_2^-)_2$ can be oxidised by hydrogen peroxide to carbon dioxide and water using pink $Co^{2+}(aq)$ ions as catalyst. During the reaction, the solution turns green due to formation of $Co^{3+}(aq)$ before changing back to pink at the end of the reaction.

The two half-equations for the redox reaction between tartrate ions and hydrogen peroxide are shown below.

$(CH(OH)CO_2^-)_2(aq) + 2H_2O(l) \rightleftharpoons 4CO_2(g) + 8H^+(aq) + 10e^-$
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$

State the type of catalysis that has taken place and suggest a two-step mechanism to show the role of $Co^{2+}(aq)$ ions in this reaction.
[2]

- **Homogeneous catalysis**

- **Step 1: $H_2O_2 + 2H^+ + 2Co^{2+} \rightarrow 2H_2O + 2Co^{3+}$**
- **Step 2: $(CH(OH)CO_2^-)_2 + 2H_2O + 10Co^{3+} \rightarrow 4CO_2 + 8H^+ + 10Co^{2+}$**

(c) At a concentration of 10 mol dm^{-3}, sulfuric acid ionises in two stages. The first stage of ionisation is complete while the second stage of ionisation exists as an equilibrium.

(i) Write two equations to show the two stages of ionisation.
[1]

H_2SO_4 → $H^+ + HSO_4^-$

$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$

(ii) The acid dissociation constant, K_a, for the second stage of ionisation in **(c)(i)** is $1.0 \cdot 10^{-2}$ mol dm^{-3}. Determine the percentage of ionisation in the second stage.
[2]

	HSO_4^-	$\rightleftharpoons$	H^+	+	SO_4^{2-}
Initial / mol dm^{-3}	**10**		**10**		**0**
Change / mol dm^{-3}	**–x**		**+x**		**+x**
Equilibrium / mol dm^{-3}	**10 – x**		**10 + x**		**x**

$K_a = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$

→ **$1.0 \cdot 10^{-2} = \frac{(10 + x)(x)}{10 - x}$**

Assuming x << 10, 10+x ≈ 10 and 10–x ≈ 10

x = 0.01 mol dm^{-3}

→ **Percentage of ionisation = $\frac{0.01}{10} \cdot 100\% = 0.1\%$**

(d) In an experiment, water is added to a test tube containing the solid remaining after magnesium carbonate has been heated. Dilute sulfuric acid is then added to the test tube.

The above procedure is repeated to the solid remaining after barium carbonate has been heated.

Describe all the observations made in both the experiments and give the formulae of all the species formed. [3]

The solid remaining after $MgCO_3$ is heated is MgO.

→ **MgO is only slightly soluble / insoluble in water but it dissolves in dilute sulfuric acid to form a colourless solution of $MgSO_4$.**

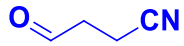
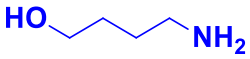
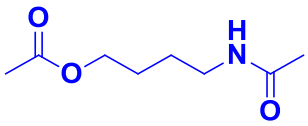
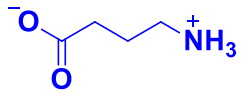
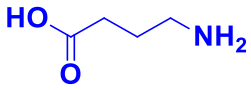
The solid remaining after $BaCO_3$ is heated is BaO.

→ **BaO solid dissolves in water to form a colourless solution of $Ba(OH)_2$. When dilute sulfuric acid is added, a white ppt. of $BaSO_4$ is formed.**

(e) Compound **E**, C_4H_5NO is non-chiral and insoluble in either acid or base. When reacted with lithium aluminium hydride, **E** forms compound **F**, $C_4H_{11}NO$. **F** reacts with ethanoyl chloride to form compound **G**, $C_8H_{15}NO_3$. When **G** is heated with acidified potassium dichromate, it forms compound **H**, which is soluble in both dilute hydrochloric acid and aqueous sodium hydroxide.

Deduce the structures of compounds **E**, **F**, **G** and **H**, explaining the reactions described. [6]

- **Since E is insoluble in acid or base, it does not undergo acid-base reaction with acid or base. E could contain either nitrile or amide.**
- **After E undergoes reduction when reacted with $LiAlH_4$ to give F, 1 mol of F undergoes condensation with 2 mol of ethanoyl chloride. F should contain amine and alcohol groups (OR G contains amide and ester groups).**
- **As there is only one O atom in E, it cannot be an amide. Otherwise, it cannot give alcohol on reduction. Hence, E should contain a nitrile group. By considering the number of C and H atoms in E, it should contain either aldehyde or ketone.**
- **Ester group in G is hydrolysed and then oxidised by acidified $K_2Cr_2O_7$ to form carboxylic acid in H. Amide group in G is hydrolysed by the acid to form amine in H.**
- **Since H is soluble in both acid and base, it contains amine and carboxylic acid. Thus, F should contain a primary alcohol and E should contain an aldehyde.**

- **E:** 
- **F:** 
- **G:** 
- **H:**  **OR** 

[Total: 21]

3 This question is about silicon and its compounds.

(a) Elemental silicon adopts a structure analogous to diamond. Describe this structure, including the type of bonding and shape around each Si atom.
[2]

- **Silicon has a giant molecular structure with a 3-dimensional network of strong covalent bonds.**
- **Each Si atom is bonded to four other Si atoms in a tetrahedral shape by covalent bonds.**

(b) Explain why the first ionisation energy of silicon is smaller than that of phosphorus but the first electron affinity of silicon is numerically greater than that of phosphorus.
[2]

- **Si has one less proton than P, leading to a smaller nuclear charge of Si.**
  Si and P have the same number of inner electrons, thus they experience similar shielding effect.
  Hence, effective nuclear charge of Si is smaller than that of P. The valence electron of Si experiences weaker nuclear attraction and requires less energy to remove, leading to a smaller first ionisation energy.

- **When an electron is added to P, it enters a 3p orbital that is already occupied by another electron.**
  When an electron is added to Si, it enters an empty 3p orbital.
  For P, the incoming electron experiences inter-electronic repulsion which outweighs its higher effective nuclear charge, leading to a numerically smaller first electron affinity.

(c) Silicides are compounds of silicon formed with more electropositive elements. The structures in silicides range from conductive metal-like structures to covalent or ionic. In the laboratory,

Group 2 silicides, M_xSi_y, are mixed with acids to form monosilanes according to the equation below.

$$M_xSi_y(s) + 4yH^+(aq) \rightarrow xM^{y+}(aq) + ySiH_4(g)$$

(i) In one particular experiment, 120 cm^3 of SiH_4, measured at r.t.p., was obtained when 0.384 g of M_xSi_y was added to 100 cm^3 of an acid which was in excess. Analysis of the resultant solution found that the concentration of M^{y+} is 0.100 mol dm^{-3}.

Find the A_r of M and hence deduce the identity of M.
[3]

Amount of SiH_4 = 120 | 24000 = $5.00 \cdot 10^{-3}$ mol

Amount of M^{y+} = $0.100 \cdot \frac{100}{1000}$ = 0.0100 mol

$\frac{x}{y} = \frac{0.0100}{5.00\ 10^{-3}} = 2$

$y = 0.5x$

Amount of M_xSi_y = $\frac{0.384}{x(A_r + 28.1)}$

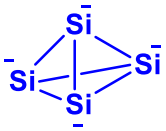
Comparing the mole ratio of M_xSi_y and M^{y+},

$0.0100 = \frac{0.384x}{x(A_r + 28.1(0.5x))}$

$0.0100\ (A_r + 14.05) = 0.384$

- $A_r = 38.4 - 14.05 = 24.4$
- **M is magnesium.**

(ii) The structure of silicide ion is thought to be a tetrahedron with four silicon atoms. Each Si atom forms single covalent bonds with the other three Si atoms. All the Si atoms achieve octet configuration. Draw the structural formula of this silicide ion, indicating clearly the bond between the atoms and its overall charge.
[1]

- 

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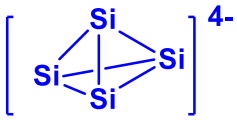


(d) By controlling the reaction conditions, the reaction of metal silicides described in **(c)** can also produce longer-chain silanes. The physical data of some silanes are given in **Table 3.1** below.

Table 3.1

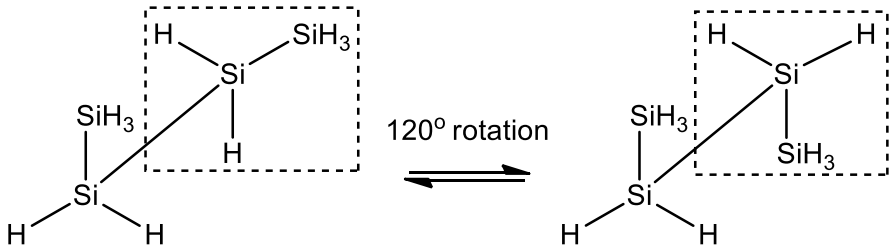
silane	formula	M_r	boiling point / °C	melting point / °C	density at 25 °C / g cm^{-3}
monosilane	SiH_4	32.1	–112	–185	gas
disilane	Si_2H_6	62.2	–14	–132	gas
trisilane	Si_3H_8	92.3	53	–117	0.743
tetrasilane	Si_4H_{10}	122.4	108	–90	0.793
n-pentasilane	Si_5H_{12}	152.5	153	–72.8	0.827
cyclopentasilane	Si_5H_{10}	150.5	194	–10.5	0.963

(i) Unlike alkanes, the formation of silanes larger than heptasilane has proven difficult due to their instability. With reference to the *Data Booklet*, suggest why silanes (Si_nH_{2n+2}) are less stable than alkanes (C_nH_{2n+2}).
[1]

- **Si–Si bond with smaller bond energy of 222 kJ mol^{-1} is easier to break than C–C bond with greater bond energy of 350 kJ mol^{-1} leading to a lower stability for silanes. The weaker bond is due to larger atomic radius of Si compared with that of C.**

(ii) The Si–Si single bond in silanes can be rotated through different angles, resulting in the formation of different conformational isomers.

Two of the conformational isomers of disilane are shown below.



conformation 1 conformation 2

Straight-chain silanes have more conformational isomers compared to cyclic silanes with the same number of Si atoms.

Use the given information on conformational isomers to explain why cyclopentasilane has an unexpectedly higher boiling point than n-pentasilane. Support your answer with an additional data from **Table 3.1**.
[2]

- **As a cyclic silane, cyclopentasilane has fewer conformational isomers than straight-chain n-pentasilane. Hence, their molecules can approach each other more orderly and effectively, resulting in a larger surface area of interaction and stronger intermolecular forces of attraction. More energy is required to overcome these forces of attraction leading to a higher boiling point.**

- **Density data showed that cyclopentasilane is denser than n-pentasilane. This implies that cyclopentasilane molecules occupy a smaller volume and are closer to one another, leading to stronger intermolecular forces of attraction. More energy is required to overcome these forces of attraction leading to a higher boiling point.**

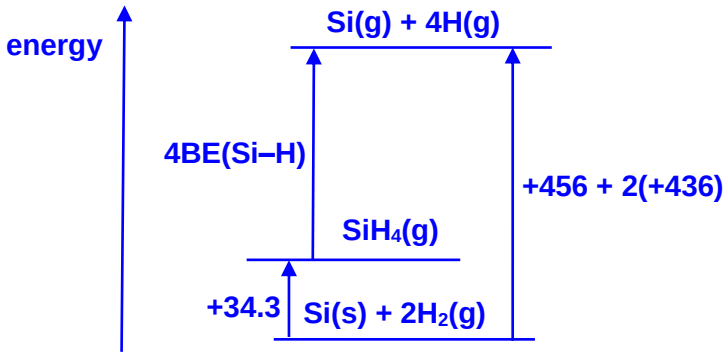
(e) The element, silicon, is used extensively as a semiconductor in the computer and microelectronics industries. One of the methods to make silicon involves thermal decomposition of monosilane, SiH_4, at high temperatures of at least 500 ^oC to deposit silicon on the computer chips.

$$SiH_4(g) \rightarrow Si(s) + 2H_2(g)$$

(i) Using the following data and data from the *Data Booklet*, construct an energy level diagram to determine the average bond energy of Si–H in monosilane.

	$\ominus H$ / kJ mol^{-1}
enthalpy change of atomisation of Si	+456
standard enthalpy change of formation of $SiH_4(g)$	+34.3

[3]



By Hess's Law,

- **4BE(Si–H) = –34.3 + 456 + 2(+436)**
  BE(Si–H) = +323 kJ mol^{-1}

(ii) Suggest and explain the sign of the standard entropy change of decomposition of monosilane, $\otimes S^{\ominus}$.
[1]

- **The system becomes more disorderly due to an increased amount of gaseous particles formed. Hence, $\otimes S^{\ominus}$ will have a positive sign.**

(iii) Calculate the standard Gibbs free energy change, $\otimes G^{\ominus}$, for the decomposition of monosilane. Hence, suggest why high temperatures are needed for this decomposition.

[2]

$\otimes H_{decomposition} = -\otimes H_{formation} = -34.3$ kJ mol^{-1}
$\otimes G^{\ominus} = \otimes H - T\otimes S$
$= -34.3 \cdot 10^3 - 298(+75.5)$
$= -56800$ J mol^{-1}

High temperatures are needed as the activation energy for the decomposition is very high due to breaking of strong covalent bonds.

(f) Silicon tetrafluoride, SiF_4, a *Lewis acid*, reacts readily with fluoride ion to form species such as SiF_5^- and SiF_6^{2-}.

(i) What is meant by the term *Lewis acid*?
[1]

- **A Lewis acid is an electron-pair acceptor.**

(ii) Suggest why $Si(CH_3)_4$ does not react similarly with fluoride.
[1]

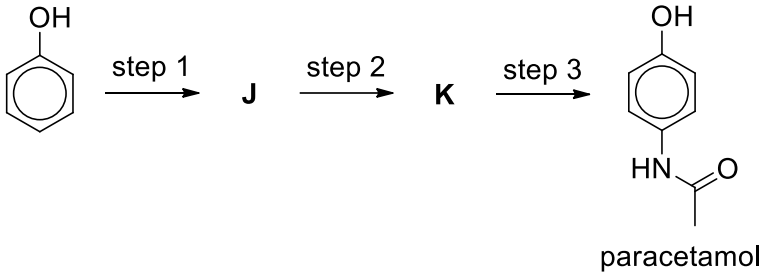
- **The steric hindrance caused by the more bulky methyl groups in $Si(CH_3)_4$ prevents the attack of Si by fluoride ions.**

[Total: 19]

Section B

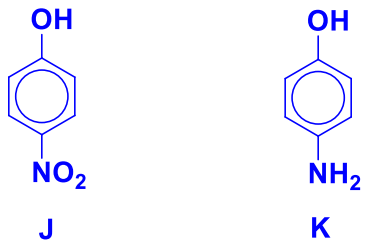
Answer **one** question from this section.

4 (a) Phenol is a valuable industrial commodity for the synthesis of various useful materials and compounds. For example, paracetamol, a medication used to treat pain and fever, can be prepared from phenol via a three-step synthesis as shown below.

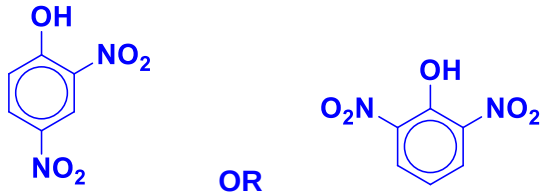


(i) Suggest the structures of compounds **J** and **K**, and the reagents and conditions for steps 1, 2 and 3. [4]

- **step 1: dilute nitric acid**
- **step 2: Sn and concentrated HC*l*, heat (followed by NaOH(aq))**
- **step 3: CH_3COCl**

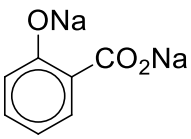


(ii) Identify one possible organic side product with the molecular formula, $C_6H_4N_2O_5$, formed in step 1. Suggest one way to minimise its formation. [2]



- **Use excess phenol or limited HNO_3 to minimise its formation.**

(b) Phenol is also used to make aspirin with compound **L** as an intermediate in the synthesis. Compound **L** is formed by heating phenol with CO_2 and NaOH strongly under pressure.

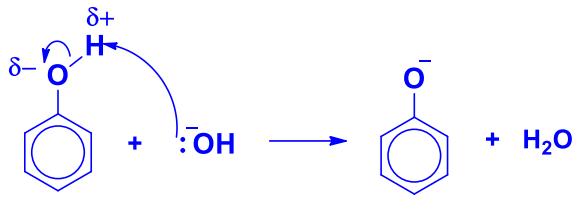


L

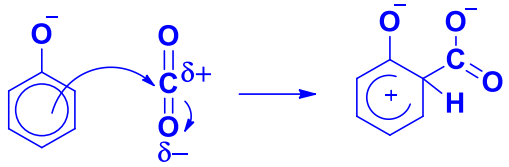
This reaction occurs in the following three steps.
Step 1: Phenol undergoes acid-base reaction with hydroxide ion.
Step 2: CO_2 functions as an electrophile.
Step 3: The anion of **L** is formed.

(i) Suggest the mechanism for this reaction, showing all charges and using curly arrows to show the movement of electron pairs in each step. [3]

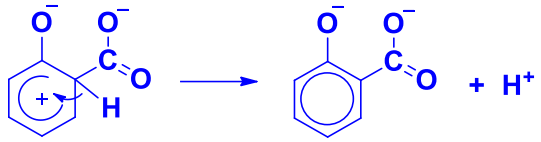
□ **Step 1:**



□ **Step 2:**



□ **Step 3:**



(ii) Explain why hydroxide ion is needed in this reaction so that the second step can occur more readily. [1]

□ **Hydroxide ion is needed to generate the phenoxide ion which is a stronger nucleophile than phenol since it is negatively charged.**

□ **The lone pair of electrons on oxygen atom is more easily delocalised into the benzene ring (through the overlap of p-orbital of oxygen with □ orbitals of carbon) to make it richer in electrons. Hence, the ring can attract electrophiles more easily.**

(c) In an experiment to determine the enthalpy change of combustion of phenol, ⊗H_c, a quantity of the fuel was burned underneath a copper can containing 200 g of water. It was found that the temperature of the water rose by 30.0 °C after 1.50 g of phenol was burned.

(i) Define the term *standard enthalpy change of combustion*. [1]

□ **The energy evolved when 1 mol of substance is burnt completely in excess oxygen under standard conditions of 298 K and 1 bar.**

(ii) Calculate the ⊗H_c of phenol using the data given. Ignore the heat capacity of the copper can. [2]

□ **Heat evolved = mc⊗T = 200 · 4.18 · 30.0 = 25080 J = 25.1 kJ**

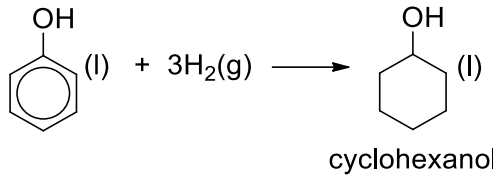
Amount of phenol burned = 1.50 ÷ (12.0 · 6 + 1.0 · 6 + 16.0) = 0.0160 mol

□ **⊗H_c = –25.1 ÷ 0.0160 = –1570 kJ mol^{-1}**

(iii) When phenol was burned in air, some black soot was observed. Explain how the actual ⊗H_c could be different from the one calculated in **(c)(ii)**. [1]

Black soot is carbon. The formation of black soot showed that phenol was not burned completely to CO_2. Thus, the actual heat evolved should be higher and the actual $\ominus H_c$ should be more exothermic than the one calculated in (c)(ii).

(iv) Phenol can be reduced by hydrogen gas under high temperature and pressure to give cyclohexanol as shown below.



Given that the above enthalpy change of reaction is –210 kJ mol^{-1} and the enthalpy change of combustion of cyclohexanol is –2215 kJ mol^{-1}, calculate the enthalpy change of combustion of hydrogen. [1]

$\ominus H_r = \Sigma\ominus H_c$(reactant) – $\Sigma\ominus H_c$(product)

$-210 = (-1570) + 3\ominus H_c(H_2) - (-2215)$

$3\ominus H_c(H_2) = -210 + 1570 - 2215 = -855$

$\ominus H_c(H_2) = -855 \div 3 = -285$ kJ mol^{-1}

(d) The pH values of 0.10 mol dm^{-3} of the following salt solutions are shown in the table below.

salt	pH
$CH_3CH_2NH_3Cl$	5.82
NH_4Cl	5.13
$C_6H_5NH_3Cl$	2.81

(i) Suggest an explanation for the different pH values of the three solutions. [3]

The salt solutions are acidic because they undergo hydrolysis in water as shown. A stronger base forms a weaker conjugate acid and hence the higher would be the pH of the solution.

$RNH_3^+ + H_2O \rightleftharpoons RNH_2 + H_3O^+$

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

$CH_3CH_2NH_2$ is more basic than NH_3 as the alkyl group exerts electron donating inductive effect causing the lone pair of electrons on N to be more available for donation.

$C_6H_5NH_2$ is less basic than NH_3 as the lone pair of electrons on N is delocalised into the benzene ring causing the lone pair of electrons on N to be less available for donation.

Thus, $CH_3CH_2NH_3^+$ is the weakest acid and produces the highest pH while $C_6H_5NH_3^+$ is the strongest acid and produces the lowest pH, since all of them have the same initial concentration.

(ii) Use the data provided in the table to calculate the pK_a of $C_6H_5NH_3^+$. [2]

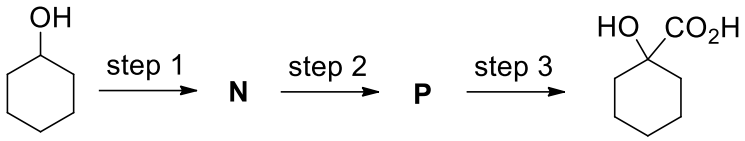
$[H^+] = [C_6H_5NH_2] = 10^{-2.81}$

K_a of $C_6H_5NH_3^+ = (10^{-2.81})^2 \div 0.10 = 10^{-4.62}$

pK_a of $C_6H_5NH_3^+ = -\lg K_a = 4.62$

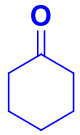
[Total: 20]

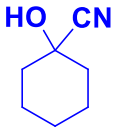
5 (a) A 3-step synthesis is shown below.



Suggest the structures of compounds **N** and **P**, and the reagents and conditions for the three steps. [4]

- **step 1: $KMnO_4$, H_2SO_4(aq), heat OR $K_2Cr_2O_7$, H_2SO_4(aq), heat**
- **step 2: HCN, with trace amount of KCN catalyst or KOH**
- **step 3: H_2SO_4(aq), heat**

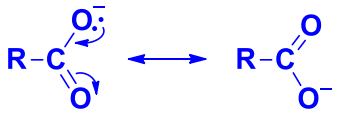
N: 

P: 

(b) The pK_b values for sodium ethanoate, CH_3CO_2Na, and sodium phenoxide, C_6H_5ONa, are 9.24 and 4.10 respectively.

(i) Suggest an explanation for the different pK_b values of sodium ethanoate and sodium phenoxide. [2]

Ethanoate ion is less basic as the lone pair electrons can delocalise to form a resonance structure shown below.



- **Since O atom is more electronegative than C atom, the decalisation of lone pair electrons in ethanoate is more effective than the delocalisation of lone pair electrons into the benzene ring in phenoxide.**
- **Thus, the lone pair electrons on the ethanoate ion is less available for donation, leading to a weaker base and larger pK_b value.**

(ii) Buffer solutions can be prepared by adding appropriate amounts of HC*l*(aq) into separate solutions of CH_3CO_2Na and C_6H_5ONa. Suggest and explain which of the two solutions can be used to make a buffer solution with a buffer pH of less than 7 when an appropriate amount of HC*l*(aq) is added to it. [1]

$\underline{CH_3CO_2Na}$ can be used to make a buffer solution with a buffer pH of less than 7 when an appropriate amount of HC*l*(aq) is added to it.

At maximum buffer capacity,
pH = pK_a
= 14 – pK_b
= 14 – 9.24
= $\underline{4.76}$ < 7

(iii) When 0.1 mol of sodium ethoxide, CH_3CH_2ONa, is dissolved in 1.0 dm^3 of water, it gives a solution of pH 13. Use the given data to determine the percentage of ethoxide ion that is hydrolysed. [2]

$CH_3CH_2O^- + H_2O \rightleftharpoons CH_3CH_2OH + OH^-$

pOH = 14 – 13 = 1
$[OH^-] = 10^{-1} = 0.1$ mol dm^{-3}
- **Hence, $[OH^-] = [CH_3CH_2O^-]$**
- **100% of ethoxide ion is hydrolysed.**

(c) Phenylamine, $C_6H_5NH_2$, is an important substance used in many industrial processes. It can react with dilute nitrous acid, HNO_2, at room temperature to give a diazonium salt, $C_6H_5N_2^+$, as shown in step 1.

step 1: $C_6H_5NH_2 + HNO_2 + H^+ \rightarrow C_6H_5N_2^+ + 2H_2O$

The diazonium salt formed is not stable and it can decompose on heating as shown in step 2.

step 2: $C_6H_5N_2^+ + H_2O \rightarrow C_6H_5OH + N_2 + H^+$

(i) Write a balanced equation for the overall reaction when phenylamine is heated with aqueous HNO_2. [1]

- **$C_6H_5NH_2 + HNO_2 \rightarrow C_6H_5OH + N_2 + H_2O$**

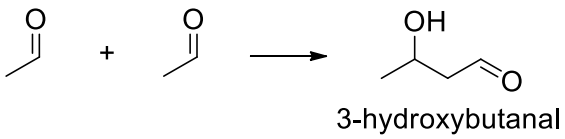
(ii) Outline briefly how the initial rate of the reaction in **(c)(i)** could be measured. [2]

- **Measure the volume of N_2 gas formed at room temperature and pressure with time.**
- **Plot the graph of volume of N_2 gas formed against time. Draw the tangent at t = 0 and determine the gradient of the tangent. The gradient gives the initial rate.**

(iii) A student conducted an experiment and determined that the rate equation for the reaction in **(c)(i)** is rate = $k[C_6H_5NH_2][HNO_2][H^+]$. Assuming that both steps are elementary steps, deduce if the rate equation can be used to determine which step is the slow step. [2]

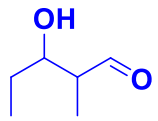
- **When step 1 or step 2 is the slow step, the same rate equation will be obtained as water is the solvent and its concentration remains constant.**
- **Hence, the rate equation cannot be used to determine which step is the slow step.**

(d) Aldol reaction is commonly used to lengthen a carbon chain. It is based on the property that the C–H group next to a C=O group is often acidic and can be cleaved heterolytically in the presence of a base, such as sodium hydroxide. For example, ethanal can react with itself to give 3-hydroxybutanal as shown below.

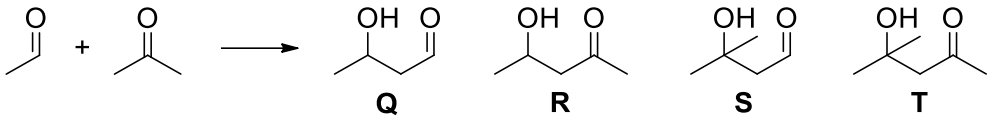


3-hydroxybutanal

(i) Draw the skeletal formula of the product formed when propanal undergoes aldol reaction in the presence of a base. [1]



An aldol reaction that starts with two different carbonyl compounds are of little synthetic importance because this reaction gives a mixture of products. For example, when ethanal and propanone undergo aldol reaction in the presence of sodium hydroxide, a mixture of four different products is formed as shown below.



(ii) The product mixture obtained in the above reaction was separated. Suggest how you could distinguish these products using not more than three simple chemical tests. You are allowed to use negative results to identify the products. [3]

Heat each product with $K_2Cr_2O_7$(aq), H_2SO_4(aq).
Q, R and S will cause the colour to change from orange to green but T does not.
Hence, T can be identified.

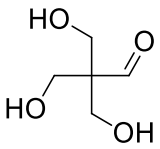
Warm Q, R and S with I_2(aq), NaOH(aq).
Q and R will give pale yellow ppt. but S does not.
Hence, S can be identified.

Heat Q and R with Tollens' reagent.
Q will give a silver mirror but R does not.
Hence, both Q and R can be identified.

(iii) Suggest how many different organic products are formed when propanone and butanone undergo aldol reaction in the presence of sodium hydroxide. [1]

6

(iv) Suggest the two carbonyl compounds with no more than 2 carbon atoms in each of them that can be used to prepare the following compound using the aldol reaction.



[1]

CH_3CHO and HCHO

[Total: 20]