H

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE NAME								
CT GROUP	1	3				INDEX NUMBER		

CHEMISTRY 9647/02

Paper 2 Structured **23 September 2014**

2 hours

Candidates answer on Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, CT group and index number on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.
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			
Paper 2			
1	/ 12	5	/ 12
2	/ 15		
3	/ 10	Penalty	sf units
4	/ 23	Total	/ 72

Answer **all** the questions in the spaces provided.

1 Planning

The label of a bottle of an aqueous acid, represented by H_xA, had been damaged. Only the concentration of the acid, 0.50 mol dm^{-3} was known.

A student was tasked to determine (1) if the acid is monobasic or dibasic, and (2) if the acid is a strong acid or a weak acid.

(a) The student was given a 0.50 mol dm^{-3} sodium hydroxide solution. She proposed to first determine the basicity of the acid in the bottle by mixing different volumes of the acid and sodium hydroxide and measure the maximum temperature change, ΔT, for each of the constant volume mixtures.

The following experiments were performed:

Experiment 1: 50 cm^3 of $H_xA(aq)$ was added to 100 cm^3 of NaOH(aq)
Experiment 2: 100 cm^3 of $H_xA(aq)$ was added to 50 cm^3 of NaOH(aq)

The changes in temperature of the mixture were measured for Experiment 1 and Experiment 2 as ΔT_1 and ΔT_2 respectively.

(i) Write an equation to represent the standard enthalpy change of neutralisation between sodium hydroxide and H_xA.

$$\frac{1}{x}H_xA(aq) + NaOH(aq) \rightarrow \frac{1}{x}Na_xA(aq) + H_2O(l)$$

(ii) Explain how the basicity of the acid can be determined by comparing the ΔT_1 and ΔT_2 values.

The basicity of the unknown acid can be determined by finding out the number of moles of water formed during neutralisation. Since heat evolved = $n\Delta H_{neu}^{\theta} = mc\Delta T$, by keeping the total volume of the mixture constant, the value of n is directly proportional to the value of the ΔT.

If x = 1
$HA + NaOH \rightarrow NaA + H_2O$

Experiment	H_xA	NaOH	n_{H2O}
1	50 (limiting)	100 (excess)	y
2	100 (excess)	50 (limiting)	y

Both experiments will produce same amount of water.
Hence $\Delta T_1 = \Delta T_2$ will be observed if H_xA is monobasic (since total volume of mixture is fixed).

If x = 2
$H_2A + 2NaOH \rightarrow Na_2A + 2H_2O$

Experiment	H_xA	NaOH	n_{H2O}
1	50 (limiting)	100 (limiting)	$2y$
2	100 (excess)	50 (limiting)	y

Experiment 1 will produce twice the amount of H_2O.
Hence $\Delta T_1 = 2\Delta T_2$ will be observed if H_xA *is dibasic* (as total volume of mixture kept constant).

[4]

(b) It was determined that the acid in the bottle is a monobasic acid, HA.

The student proceeded to determine if HA is a strong or weak acid using the following:

- **FA 1**, a solution of 0.50 mol dm^{-3} sodium hydroxide.
- **FA 2**, a solution of 0.50 mol dm^{-3} HA.
- Thermometers
- Styrofoam cups
- Apparatus normally found in a college laboratory

She performed a series of experiments by mixing different volumes of **FA 1** with **FA 2** and measuring the temperature changes of each of these mixtures.

(i) Write a plan to determine the temperature changes, ΔT, for the following series of reactions between **FA 1** and **FA 2**:

Mixture	Volume of **FA 1** / cm^3	Volume of **FA 2** / cm^3
1	15	45
2	25	35
3	35	25
4	45	15
5	50	10

Your plan should include the apparatus for measurement of volume. Indicate clearly the measurements that will be made during the experiment and show how these measurements can be used to obtain the temperature change, ΔT.

1. Use a burette / measuring cylinder to transfer 15 cm^3 of **FA 1** into the Styrofoam cup labelled **FA 1**. Place the cup in a 250 cm^3 beaker to prevent it from tipping over.

2. Use another burette / measuring cylinder to transfer 45 cm^3 of **FA 2** into the Styrofoam cup labelled **FA 2**.

3. Use thermometer to stir and measure the temperature of the **FA 1** and **FA 2** solution, T_{FA1} and T_{FA2} respectively.

4. Calculate the average temperature, $T_{average}$ of the solutions by $T_{average}$ = $[(T_{FA1} \times V_{FA1}) + (T_{FA2} \times V_{FA2})] / V_{total}$.

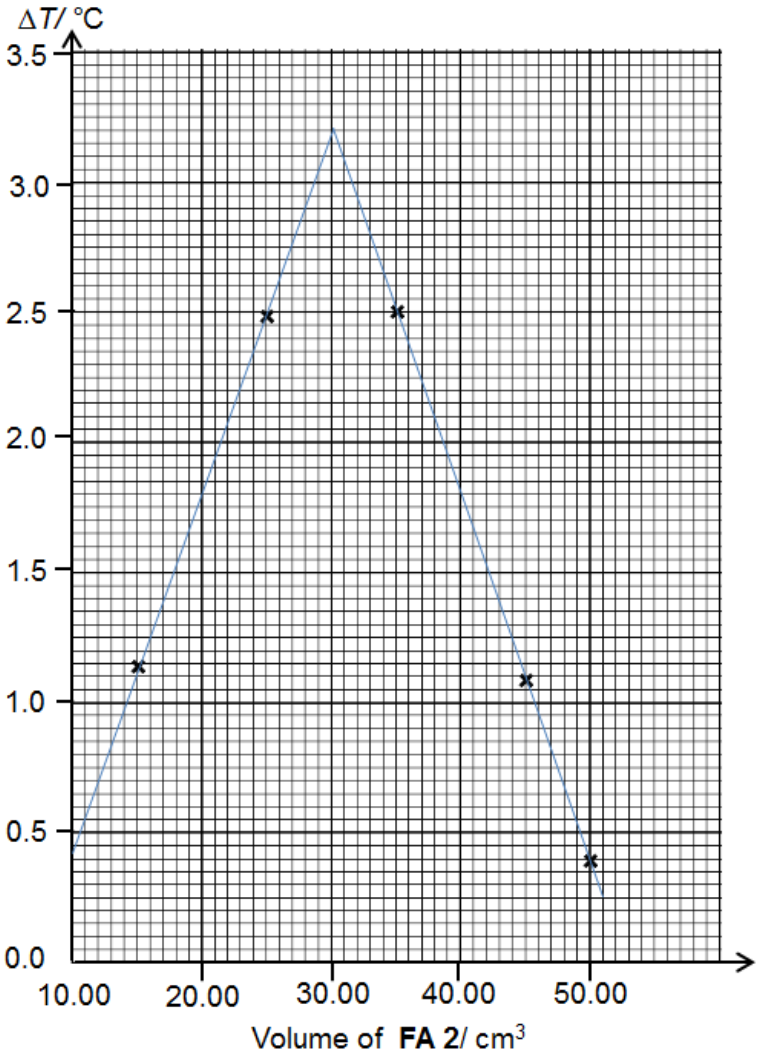
5. Add the contents of **FA 2** cup to the **FA 1** cup. Use the thermometer to stir the mixture and measure the maximum temperature, T_{max} of the mixture.

6. Calculate the temperature change, ΔT, by taking $\Delta T = T_{max} - T_{average}$

7. Wash and carefully dry both the **FA 1** and **FA 2** styrofoam cups.

8. Repeat steps 1 to 7 for Mixtures 2 to 5.

(ii) The student performed the experiment for the series of reactions between **FA 1** and **FA 2** and the temperature changes were plotted as shown below.



By means of two straight lines, determine the ΔT_{max} for the series of experiments.

Draw 2 straight lines for each side of each graph.

From the graph, ΔT_{max} = 3.2 °C.

(iii) Using your graph in **(b)(ii)**, calculate the enthalpy change of neutralisation for the reaction between HA and NaOH. [Assume that the heat capacity of the solution = 4.2 J K^{-1} cm^{-3}.]

Heat evolved = $m_{solution} c \Delta T_{max}$
= 60 cm^3 × 4.2 J K^{-1} cm^{-3} × 3.2 K
= 806.4 J

$HA + NaOH \rightarrow NaA + H_2O$

ΔT_{max} occurs at end-point, when 30 cm^3 of **FA 2** is added.

Since 1 mol of HA ≡ 1 mol of H_2O
Therefore, (0.50)(0.030) mol of HA ≡ (0.50)(0.030) mol of H_2O
≡ 0.015 mol of H_2O

$n_{H2O} \times \Delta H_{neu} = -806.4$ J

0.015 mol × ΔH_{neu} = –806.4 J

ΔH_{neu} = –53760 J mol^{-1} ≈ –53.8 kJ mol^{-1}

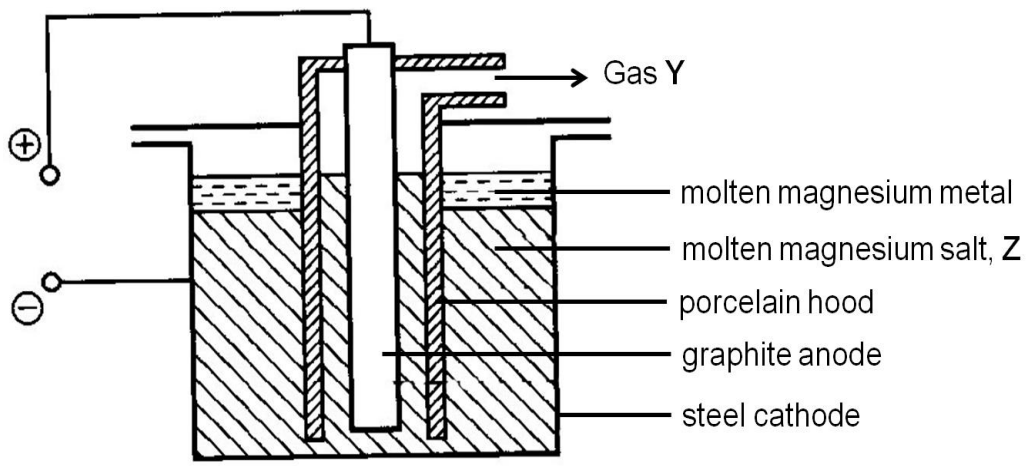
(iv) Given that the enthalpy change of neutralisation for reaction between HC*l* and NaOH is –57.3 kJ mol^{-1}, deduce whether the unknown acid HA is a strong acid or a weak acid. Explain your answer.

ΔH_{neu} is much less exothermic than ΔH_{neu} involving a strong acid and strong base. This means that some of the energy must have been absorbed to fully dissociate the acid HA. Hence HA must be a weak acid which does not dissociate completely in water.

[8]

[Total: 12]

2 Magnesium metal can be manufactured by the electrolysis of molten magnesium salt, **Z** using the setup shown below. During the electrolysis process, 0.912 g of unknown gas **Y** was produced which occupied 500 cm^3 volume at 200 °C and 1 atm.



(a) **(i)** Determine the M_r of gas **Y** and hence identify it.

$pV = nRT$

$M_r = \dfrac{(0.912)(8.31)(273+200)}{(101000)(500\times10^{6})}$

$= 71.0$

Therefore, the gas produced is chlorine gas.

(ii) Explain why you would expect the behaviour of gas **Y** to be less ideal at low temperature.

At low temperature, the gas molecules do not sufficient energy to overcome intermolecular forces of attraction and hence it is less ideal.

(iii) Write ion-electron equations for the reaction occurring at the cathode and anode.

Cathode: $Mg^{2+}(l) + 2e^{-} \rightarrow Mg(l)$
Anode: $2Cl^{-}(l) \rightarrow Cl_2(g) + 2e^{-}$

(iv) Given that the electrolysis took place for 40 minutes, calculate the current used for the process.

Amount of Cl_2 produced = $\dfrac{0.912}{71.0}$ = 0.1285 mol

$0.1285 = \dfrac{I\times(40\times60)}{2\times96500}$

I = 1.03 A

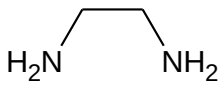
(v) Using relevant $E^{\ominus}$ data from the *Data Booklet*, explain why magnesium metal cannot be obtained by the electrolysis of aqueous magnesium salt.

$Mg^{2+} + 2e^{-} \rightleftharpoons Mg$ $\quad E^{\theta}_{red} = -2.38V$
$2H_2O + 2e^{-} \rightleftharpoons H_2 + 2OH^{-}$ $\quad E^{\theta}_{red} = -0.83V$

The E^{θ}_{red} value for reduction of water is less negative than that for magnesium ions, water will be preferentially reduced. Hence hydrogen gas is produced instead of magnesium metal.

[8]

(b) Ethylenediamine (*en*) can act as a bidentate ligand. The structure of *en* is shown below.



ethylenediamine

$[Ni(NH_3)_6]^{2+}(aq)$ and $[Ni(en)_3]^{2+}(aq)$ can be prepared from ligand exchange reaction of 1 mol dm^{-3} $[Ni(H_2O)_6]^{2+}(aq)$ with NH_3 and *en* ligands respectively.

(1): $[Ni(H_2O)_6]^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq) + 6H_2O(l)$
(2): $[Ni(H_2O)_6]^{2+}(aq) + 3en(aq) \rightleftharpoons [Ni(en)_3]^{2+}(aq) + 6H_2O(l)$

The standard enthalpy change of reaction, $\Delta H^{\ominus}_r$, and standard entropy change of reaction, $\Delta S^{\ominus}_r$, for the ligand exchange reactions **(1)** and **(2)** are as follows.

Reaction	$\Delta H^{\ominus}_r$ / kJ mol^{-1}	$\Delta S^{\ominus}_r$ / J mol^{-1}
(1)	–27.5	+4.5
(2)	–35.0	+34.0

The $\Delta H^{\ominus}_r$ for both reactions **(1)** and **(2)** are similar as the Ni-O bonds broken and Ni-N bonds formed are similar.

Chelate effect refers to the greater stability of complexes formed by polydentate ligands (e.g. *en*) than those formed by monodentate ligands (e.g. NH_3).

(i) Explain why the ΔS^{θ}_r for reaction **(1)** is so different from that of reaction **(2)**.

In reaction **(1)**, 7 particles react to form 7 particles and there is no net increase in the number of particles in the aqueous solution. In contrast, 4 particles of reaction **(2)** react to form 7 particles and there is a large increase in the number of particles in the aqueous solution. Hence there is an increase in the disorderliness and ΔS^{θ}_r for reaction **(1)** is much larger than that of reaction **(2)**.

(ii) Calculate the standard Gibbs free energy change, $\Delta G^{\ominus}_r$ for reactions **(1)** and **(2)** to show why $[Ni(en)_3]^{2+}(aq)$ exhibit the *chelate effect*.

ΔG^{θ}_r for reaction **(1)** = (–27.5) – (298)(4.5/1000) = –28.8 kJ mol^{-1}
ΔG^{θ}_r for reaction **(2)** = (–35.0) – (298)(34.0/1000) = –45.1 kJ mol^{-1}

ΔG^{θ}_r for reaction **(2)** is more negative due to formation of more stable $[Ni(en)_3]^{2+}(aq)$ and hence it exhibit *chelate effect*.

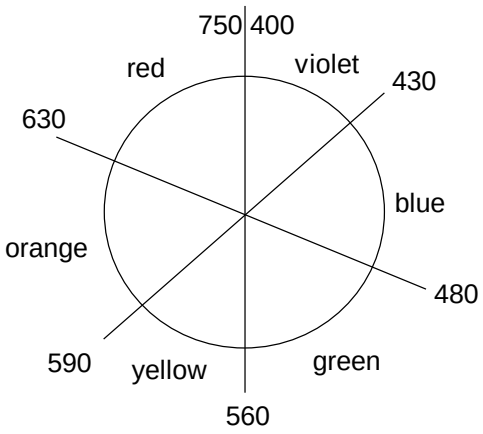
(iii) Using your answers from **(b)(i)** and **(b)(ii)**, comment qualitatively on the statement: "*The chelate effect is an entropy effect.*"

$\Delta G^{\theta}_r = \Delta H^{\theta}_r - T\Delta S^{\theta}_r$

For both ligand exchange reactions with monodentate and polydentate ligands for **(1)** and **(2)** respectively, the ΔH^{θ}_r is similar and hence enthalpy does not contribute significantly to the difference in ΔG^{θ}_r. Instead, there is a big increase in the ΔS^{θ}_r from reaction **(1)** and **(2)** and hence entropy contributes greatly to the overall difference in ΔG^{θ}_r. Therefore chelate effect is an entropy effect.

(iv) Stronger field ligands are known to give rise to a larger energy gap between the two sets of d-orbitals in a transition metal complex.

The figure below shows a colour wheel with approximate wavelength values (in nm) for different colour light. As wavelength decreases, the energy of the light increases.



Various complexes of Ni have different colours. The colours of $[Ni(CN)_6]^{3-}(aq)$ and $[Ni(en)_3]^{2+}(aq)$ are as follow.

Complex	Colour
$[Ni(CN)_6]^{3-}(aq)$	red
$[Ni(en)_3]^{2+}(aq)$	violet

State whether CN^- or *en* is a stronger field ligand. Explain your answer.

CN^- is the stronger field ligand. $[Ni(CN)_6]^{3-}(aq)$ appears red because it absorbs green light. $[Ni(en)_3]^{2+}(aq)$ appears violet because it absorbs yellow light. Green light has higher energy than yellow light, the energy gap between the d orbitals of $[Ni(CN)_6]^{3-}$ (aq) is larger than that of $[Ni(en)_3]^{2+}(aq)$.

[7]

[Total: 15]

3 This question is about Group II elements and their compounds.

(a) (i) All Group II carbonates and nitrates undergo thermal decomposition.

Write a general equation for the thermal decomposition of Group II nitrates.

$M(NO_3)_2(s) \rightarrow MO(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$

(ii) Magnesium nitrate dissolves in water to give a solution of pH ≈ 6.5.

Write equations to show why the solution formed is slightly acidic.

$Mg(NO_3)_2(s) + 6H_2O(l) \rightarrow [Mg(H_2O)_6]^{2+}(aq) + 2NO_3^-(aq)$
$[Mg(H_2O)_6]^{2+}(aq) \rightleftharpoons [Mg(H_2O)_5(OH)]^+(aq) + H^+(aq)$

(iii) In an experiment, water is added separately to two test tubes containing residues obtained from the thermal decomposition of magnesium carbonate and barium carbonate. This is followed by the addition of dilute sulfuric acid.

Describe and account for what you would see in both test tubes.

The white residue of MgO will not dissolve in water. However, when sulfuric acid is added, the white solid dissolves to give colourless solution of $MgSO_4$.

White residue of BaO dissolves in water to form an colourless solution of $Ba(OH)_2$. When dilute sulfuric acid is added, white precipitate of $BaSO_4$ forms.

[5]

(b) (i) Given that the solubility product for magnesium hydroxide in water at 25 ºC is 1.10×10^{-11} mol^3 dm^{-9}, calculate the mass of solid magnesium nitrate to be added to 30 cm^3 of sodium hydroxide solution of pH 9.0 to form a saturated solution of magnesium hydroxide.

pOH = 14 – 9.0 = 5.0
$[OH^-] = 10^{-5.0} = 1.0 \times 10^{-5}$ mol dm^{-3}

At saturation, ionic product = K_{sp}
$[Mg^{2+}][OH^-]^2 = 1.10 \times 10^{-11}$
$[Mg^{2+}] = 1.10 \times 10^{-11} / (1.0 \times 10^{-5})^2$
$= 0.110$ mol dm^{-3}

Mass of $Mg(NO_3)_2$ = 0.110 x 0.0300 x 148.3
= 0.489 g

(ii) Explain, with the aid of equations, how the solubility of magnesium hydroxide in aqueous sodium hydroxide would differ from that in water.

$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$ ------ (1)
$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$ ------ (2)

NaOH(aq) dissociates to give OH^- ions which increases $[OH^-]$. Due to Common Ion Effect, position of equilibrium (1) shifts to the left as according to Le Chatelier's principle. Hence, solubility in aqueous sodium hydroxide is lower than that in water.

[5]

[Total: 10]

4 Alkenes and alkynes are useful starting materials for the synthesis of many organic intermediates.

(a) The "OXO" reaction is industrially important for making alcohols, aldehydes and carboxylic acids from alkenes. For example, ethene can be converted into propanal as follows:

$$CH_2{=}CH_2(g) + CO(g) + H_2(g) \rightleftharpoons CH_3CH_2CHO(g)$$

(i) Write an expression for K_p for the "OXO" reaction.

$$K_p = \frac{P_{propanal}}{(P_{ethene})(P_{H_2})(P_{CO})}$$

(ii) When equimolar mixture of ethene, CO and hydrogen gas at an initial total pressure of 150 atm is allowed to reach equilibrium, the partial pressure of propanal is found to be 49.4 atm.

Calculate the value of K_p and state the units

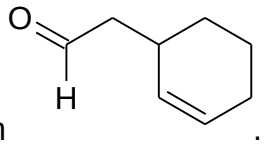
$P_{ethene} = P_{hydrogen} = P_{carbon\ monoxide} = (150 / 3) – 49.4 = 0.60$ atm

$K_p = \frac{49.4}{(0.600)^3} = 229\ atm^{-2}$

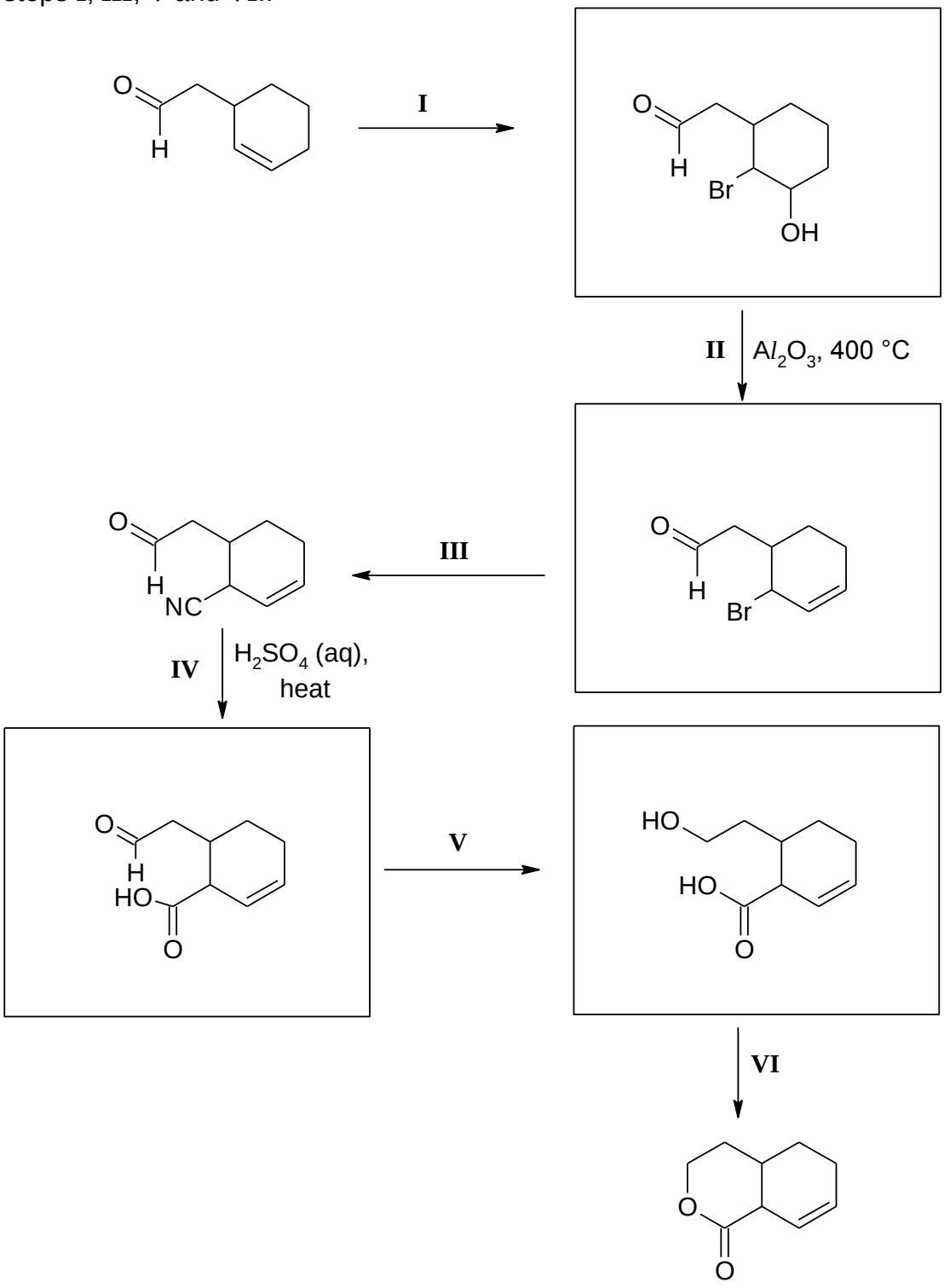
(iii) Suggest why this reaction is carried out at 150 atm.

At high pressure, the equilibrium position lies more to the right to reduce the number of moles of gaseous molecules, thus increases the yield of propanal.

[5]

(b) The reaction scheme below shows how an ester is synthesised from  .

Complete the reaction scheme below by giving the structural formulae of the organic products in the spaces provided and state the reagents and conditions for steps **I**, **III**, **V** and **VI**..



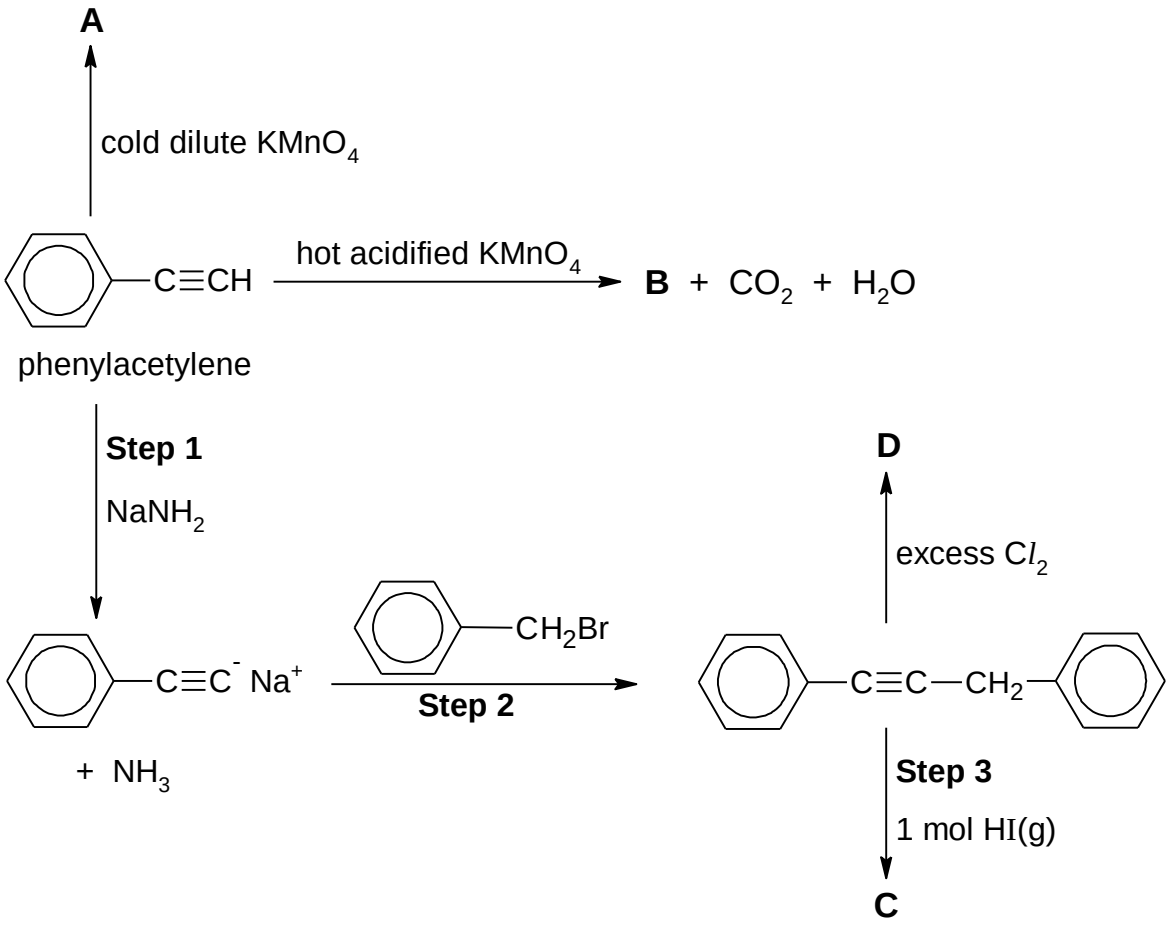
Step	Reagents and conditions
I	Br_2(aq)
III	Ethanolic KCN, heat
V	$NaBH_4$ in methanol
VI	concentrated H_2SO_4, heat

[8]

(c) Alkynes are hydrocarbons containing a C≡C triple bond. Reactions involving alkynes resemble that of corresponding alkenes.

For example, alkynes react with bromine in tetrachloromethane to give dibromoalkenes. In the mild oxidation of alkynes, the π bonds are broken and a dicarbonyl compound is formed, while oxidation with powerful oxidising agents such as potassium manganate(VII) cleaves the C≡C triple bond.

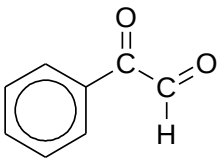
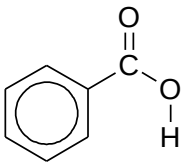
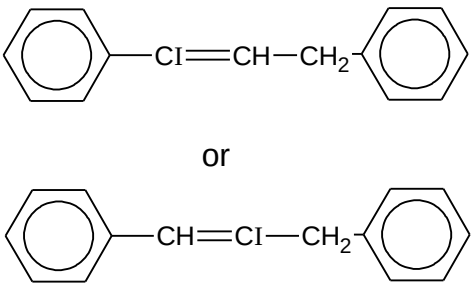
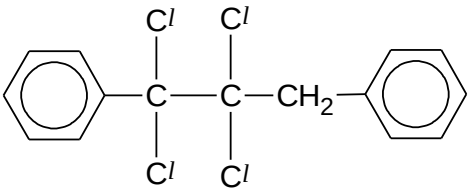
The following reaction scheme shows some reactions involving phenylacetylene, an alkyne that is useful in organic synthesis.



(i) State the types of reaction that occur in steps **1** and **2**.

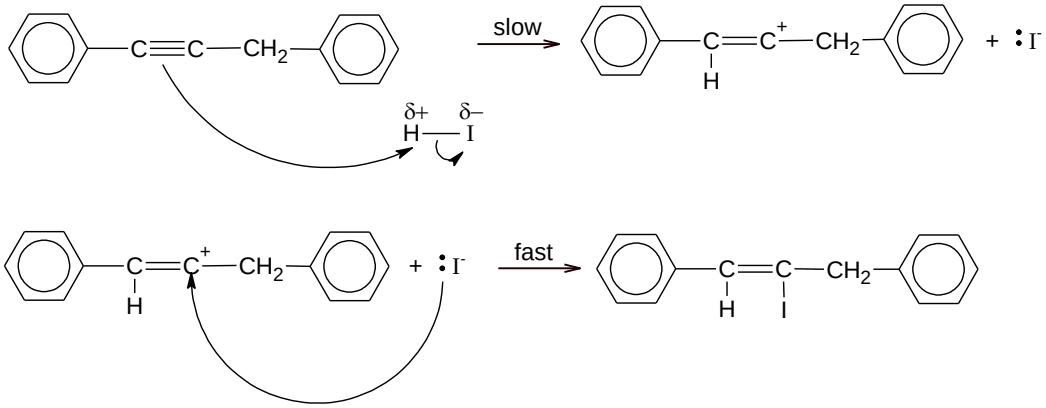
Step **1**: acid-base
Step **2**: nucleophilic substitution

(ii) Draw the structures for the organic products **A** to **D** from the reaction scheme.

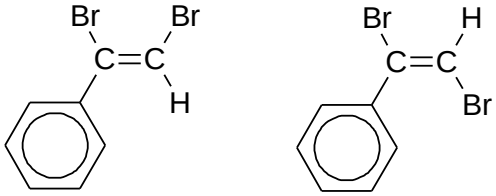
A 	**B** 
C 	**D** 

(iii) Name and outline the mechanism for step **3**.

Electrophilic addition



(iv) Phenylacetylene reacts with Br_2 in tetrachloromethane to give a product with molecular formula $C_8H_6Br_2$. Draw the isomers of the product and state the type of isomerism displayed.

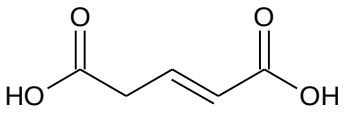


Type of isomerism: Geometric / cis-trans isomerism

[10]

[Total: 23]

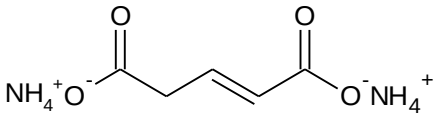
5 (a) Glutaconic acid is a dicarboxylic acid that is being investigated as a monomer for the production of biodegradable polymers.



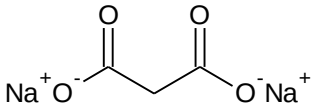
glutaconic acid

Draw the organic product formed when glutaconic acid is treated with:

(i) $NH_3(g)$,



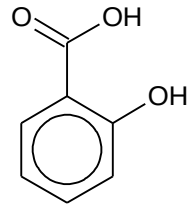
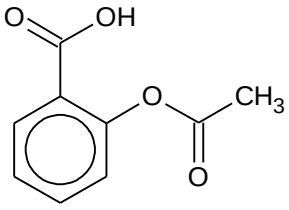
(ii) $KMnO_4(aq)$, NaOH(aq) and heated under reflux.



[2]

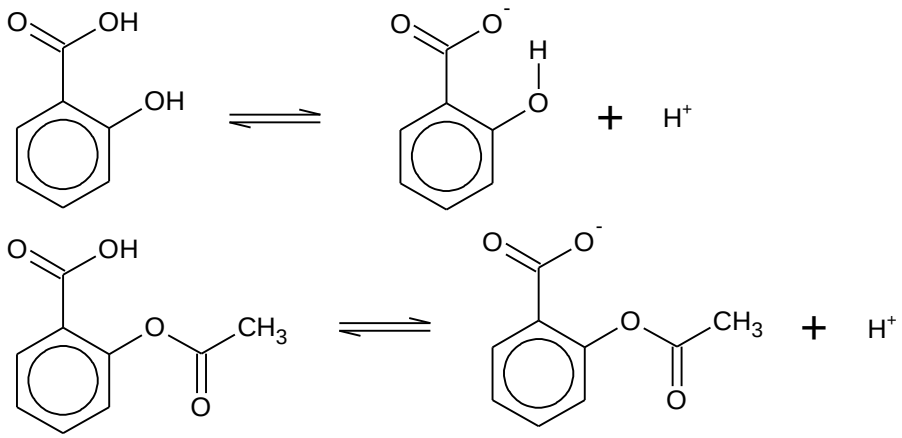
(b) Salicylic acid is a naturally occurring carboxylic acid found in many plants. It has been used by many native American tribes as a pain reliever. Salicylic acid is also used to produce acetylsalicylic acid.

The following table compares the pK_a values of the two acids.

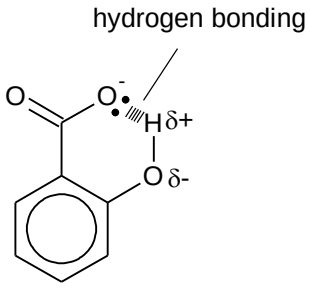
acid	pK_1	pK_2
 Salicylic acid	2.97	13.8
 Acetylsalicylic acid	3.40	–

With the aid of a diagram, explain why the pK_1 of the salicylic acid is lower than that of acetylsalicylic acid.

[4]



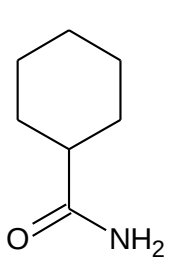
The salicylate anion is more stable than the acetylsalicylate anion as it can form an energetically favourable by forming intramolecular hydrogen bonding between $–CO_2^-$ and the electron deficient H atom of the phenol.



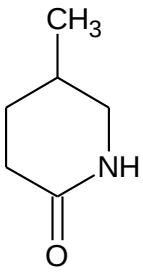
The extent of dissociation is greater in salicylic acid. Thus, it is a stronger acid.

(c) For each of the following pairs of compounds, describe one simple chemical test which would enable you to distinguish between them. State clearly how each compound behaves in the test and write balanced equations for the reactions occurred.

(i)

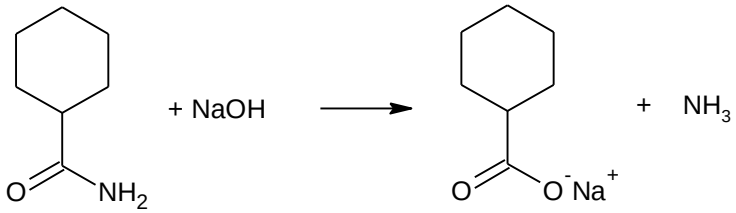


A

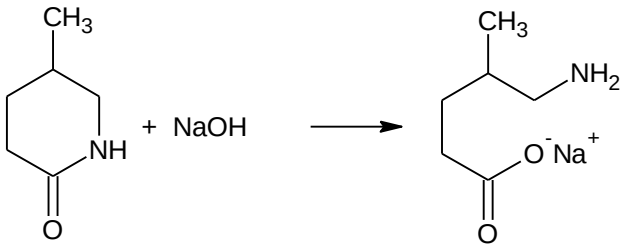


B

To each compound in separate test tubes, add NaOH(aq), heat. Test for any gas evolved using a piece of moist red litmus paper.

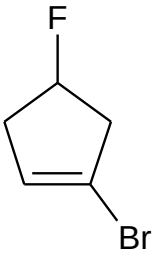


Gas (NH_3) evolved turns moist red litmus blue. Gas is NH_3.

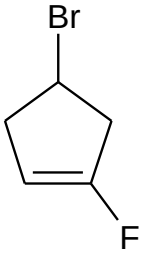


No gas evolved / moist red litmus paper remains.

(ii)



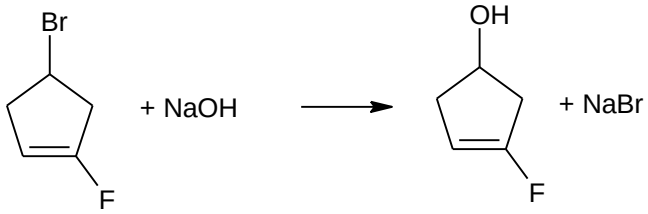
C



D

To each compound in separate test tubes, add NaOH(aq), heat. Cool the mixture. Acidify with HNO_3(aq). Add $AgNO_3$(aq).

Compound **C** does not produce any precipitate.



$Ag^+(aq) + Br^-(aq) \longrightarrow AgBr(s)$

Compound **D** forms a cream precipitate of AgBr.

[6]

[Total: 12]

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