NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME

SUBJECT CLASS

REGISTRATION NUMBER

CHEMISTRY

9729/03

Paper 3 Free Response

17 September 2024
2 hours

Candidates answer on Question Paper.
Additional Materials: Data Booklet

READ THE INSTRUCTIONS FIRST

Write your subject class, registration number and name on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

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

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

For Examiner's Use	
Section A	
1	**/20**
2	**/20**
3	**/20**
Section B (*circle the question you attempted)	
4	**/20**
5	**/20**
Paper 3 Total	**/80**

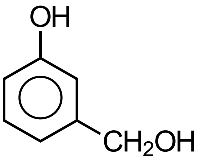
This document consists of **32** printed pages.

Section A

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

1 **(a)** Chlorinated phenols have seen growing applications as fungicides, herbicides, insecticides, and as starting materials in the production of various pesticides since the 1930s.

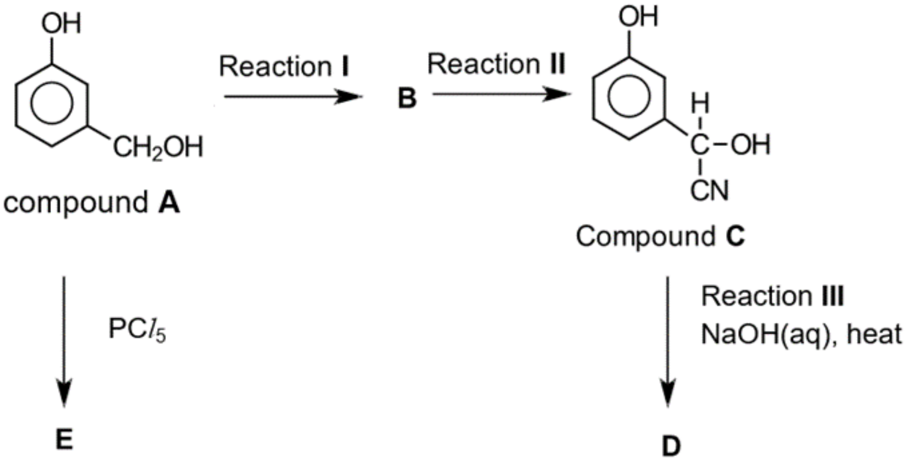
It can be readily produced from compound **A** using chlorine in water.



compound **A**

(i) Write a balanced equation for the reaction between compound **A** and excess aqueous chlorine. [1]

(ii) Compound **A** undergoes a series of reactions shown in the reaction scheme below.



State the reagent and condition for Reaction **I** and **II**, and hence draw the structures of **B** and **E**. [4]

(iii) Write a balanced equation for reaction **III**. [1]

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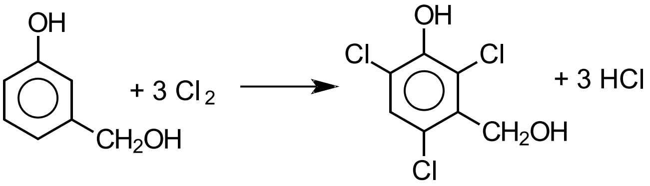
1(a)(i)

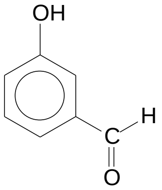


Note: Similar to reaction of phenol with Br_2(aq). Electrophilic substitution at 2,4,6 position w.r.t. phenol.

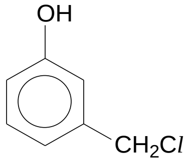
1(a)(ii)

- Reaction I: $K_2Cr_2O_7$, H_2SO_4(aq), heat with distillation
- Reaction II: HCN, trace amount of NaCN, Cold

● B:



● E:

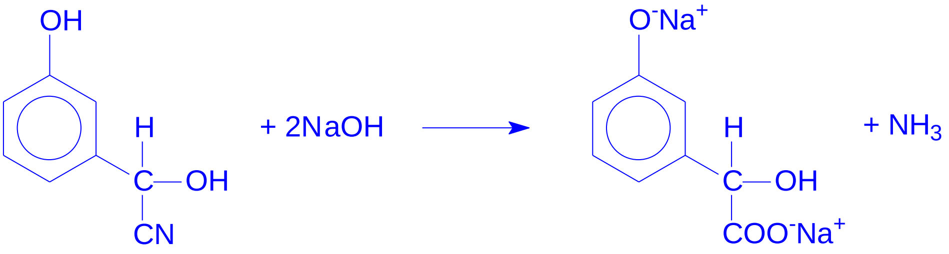


Note:

For reaction of C to give D, NaOH causes alkaline hydrolysis of −CN and neutralisation of the acidic phenol −OH. Alcohol group is neutral and remains unchanged.

For reaction of A to give E, alcohol −OH undergoes substitution by −C*l*, phenol −OH does not undergo substitution due to partial double bond of C−O

1(a)(iii)



(b) Vanadium is a transition element that exhibits variable oxidation states.

(i) Explain why vanadium can form stable ions with varying oxidation states. [1]

(ii) Write the full electronic configuration for V^{3+}. [1]

(iii) Draw a fully labelled diagram of the experimental set-up used to measure the standard electrode potential of the $VO^{2+}(aq)/V^{3+}(aq)$ half-cell. [3]

A Latimer diagram below summarises the standard electrode potential data of vanadium complexes in acidic medium.

$$\begin{tikzcd}
VO_3^- \arrow[r, "+1.00\text{ V}"] \arrow[rr, bend left, "x"] & VO^{2+} \arrow[r, "+0.34\text{ V}"] & V^{3+}
\end{tikzcd}$$

The standard electrode potential x for converting VO_3^- to V^{3+}, is **not** the sum of +1.00 V and +0.34 V. Instead, it can be calculated from $\Delta G^\ominus$.

(iv) Write the half-equation for the conversion of VO_3^- to V^{3+}. [1]

(v) Calculate the standard electrode potential x, given that $\Delta G^\ominus$ for the conversion of VO_3^- to V^{3+} is −129 kJ mol^{-1}. [1]

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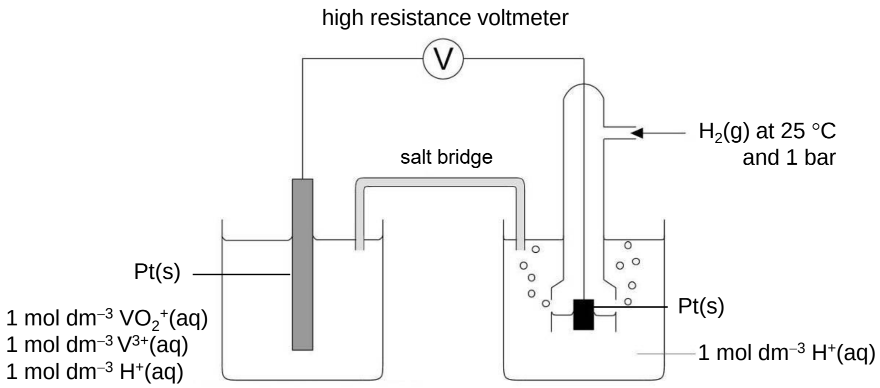
1(b)(i) Vanadium can exhibit a variety of oxidation states due to close similarity in energy of the 3d and 4s electrons. Both 3d and 4s electrons can be removed to form stable ions of different oxidation states.

1(b)(ii) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2$

1(b)(iii)



Note: For VO^{2+}/V^{3+} half-cell, H^+ is required in the electrolyte.
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$
Minus 0.5m for each missing details

1(b)(iv) $VO_3^- + 6H^+ + 2e^- \rightarrow V^{3+} + 3H_2O$

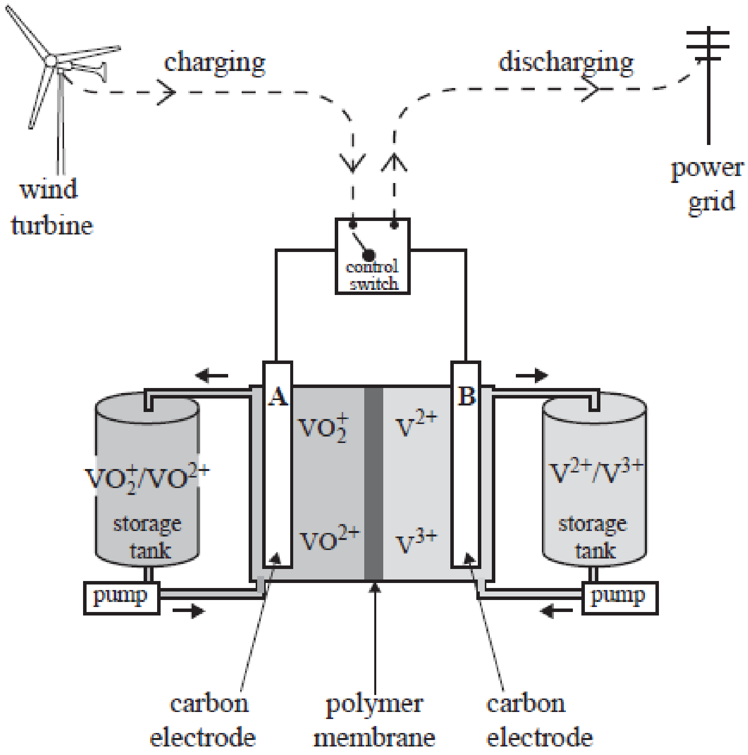
1(b)(v)$\Delta G^\ominus = -nFE^\ominus$, where n = 2 for this equation.

$E^\ominus = (-129 \times 10^3) / (-2 \times 96500) = +0.67$ V
Note: ΔG has to be in J mol^{-1}

(c) A vanadium redox battery is employed to store electrical energy produced at a wind farm in Tasmania.

The diagram below illustrates the configuration of a cell in a vanadium redox battery. The reactants are dissolved in an acidic solution, stored in large tanks, and circulated through the cell. A polymer membrane facilitates the movement of specific ions.

When discharging, the battery supplies electricity to the power grid on demand through a control switch. During charging, the battery uses electricity from the wind turbines to reverse the chemical reaction.



(i) State the polarity of electrode **A** when the cell is **discharging.** Explain your answer. [2]

(ii) Write an equation for the reaction that occurs when the cell is being **charged**. [1]

1(c)(i) $VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$ $E^\ominus = +1.00$ V

$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$ $E^\ominus = -0.26$ V

When the cell is discharging, it is an electrochemical cell. Since $E^\ominus(VO_2^+/VO^{2+})$ is more positive than $E^\ominus(V^{3+}/V^{2+})$, VO_2^+ will undergo reduction.

Therefore, electrode A is the cathode and is positive.

1(c)(ii) $VO^{2+} + H_2O + V^{3+} \rightarrow VO_2^+ + V^{2+} + 2H^+$

Note: During charging, the reverse reaction occurs.

E.g. VO^{2+} is oxidised to VO_2^+ and V^{3+} is reduced to V^{2+}.

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(d) The exhaust from heavy-duty diesel engines emits considerable particulate matter (PM) and pollutant gases like nitrogen oxides. A Continuous Regenerating Trap (CRT) is a device intended for use in the exhaust systems of diesel-powered buses and trucks to eliminate PM and pollutant gases.

(i) Explain, with the aid of an equation, why oxides of nitrogen are present in the engine exhaust. [1]

(ii) State one harmful effect of nitrogen oxides. [1]

(iii) Identify one other pollutant gas present in engine exhaust. Provide a chemical equation to illustrate its removal in the catalytic chamber of a CRT. [2]

1(d)(i) Under the high temperature condition of the internal combustion engine, atmospheric nitrogen reacts with oxygen to from oxides of nitrogen.

$N_2(g) + O_2(g) \rightarrow 2NO(g)$ or $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$

1(d)(ii) It leads to the formation of ozone at ground level,
Leads to the formation of acid rain OR photochemical smog

1(d)(iii) CO or hydrocarbons [1]

$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$
$C_xH_y(g) + (x + y/4)\, O_2(g) \rightarrow xCO_2(g) + y/2\, H_2O(l)$
1m for equation.

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[Total: 20]

2 **(a)** 4-nitrobenzoyl chloride can be synthesized from benzene in four steps as shown in Fig 2.1.

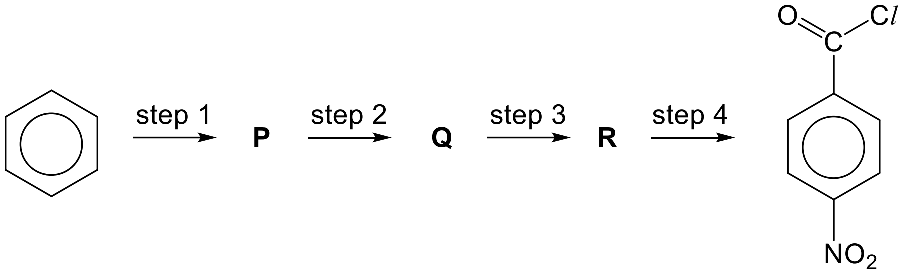


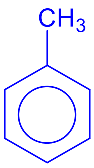
Fig 2.1

(i) Suggest the structures for compounds **P**, **Q** and **R**. [3]

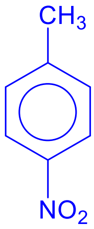
(ii) Suggest reagents and conditions for each of the steps 1, 2, 3 and 4. [2]

2(a)(i)

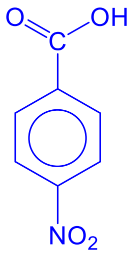
P



Q



R



1m each

2(a)(ii)

Step 1: CH_3X, anhydrous FeX_3 (X = C*l*, Br) [0.5]

Step 2: Conc H_2SO_4, Conc HNO_3, 30°C [0.5]

Step 3: $KMnO_4$, H_2SO_4(aq), heat [0.5]

Step 4: anhydrous $SOCl_2$, PCl_3, PCl_5 [0.5]

(b) Procainamide is used for treating heart ventricular issues. Procainamide can be synthesized from 4-nitrobenzoyl chloride in 2 steps as shown in Fig 2.2.

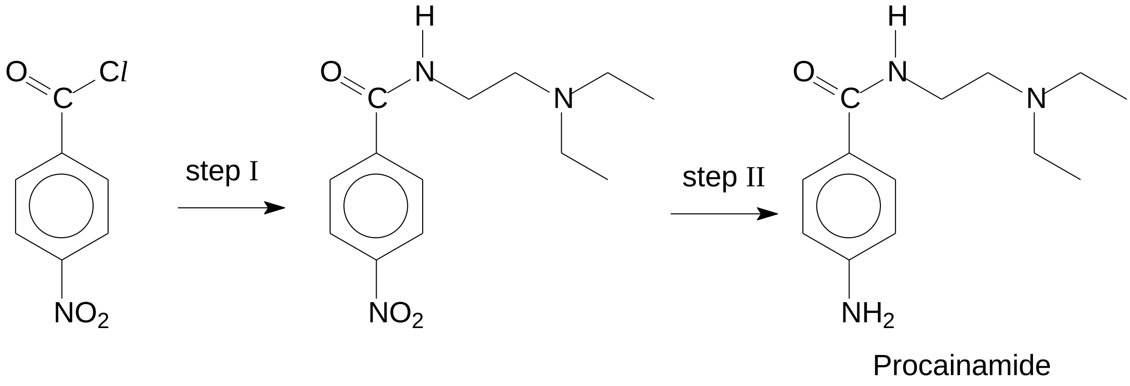


Fig 2.2

(i) State the reagents and conditions needed for step I and II. [2]

(ii) An alternative synthesis pathway for procainamide is shown in Fig 2.3.

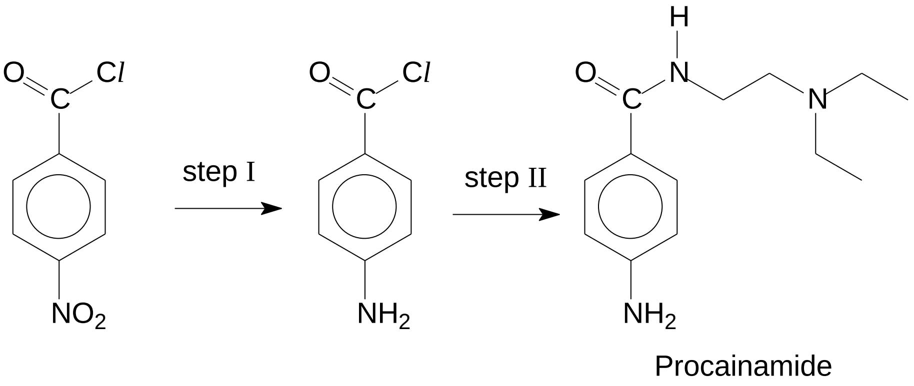


Fig 2.3

Suggest why the yield of procainamide obtained from Fig 2.3 would be lower compared to that from Fig 2.2. [1]

2(b)(i) Step **I**: $H_2NCH_2CH_2N(CH_2CH_3)_2$
Step **II**: (1) Sn, Conc. HCl, heat, (2) Excess NaOH

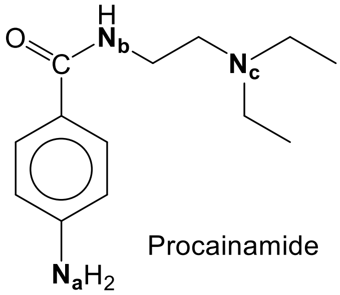
2(b)(ii) For Fig 2.3, step I reagent (Sn, conc. HCl, heat, followed by excess NaOH) would also react with the –COCl group via hydrolysis and a $-COO^-$ group is obtained. $-COO^-$ cannot react to give the amide group.

OR

For Fig 2.3, step II would give another side product. The $-NH_2$ group on 4-aminobenzoyl chloride is nucleophilic in nature and will also react with the -CO*Cl* group of another 4-aminobenzoyl chloride molecule and form another amide instead. **[1]**

(c) Nitrogen atoms in organic compounds are potential Brønsted-Lowry base.

The 3 nitrogen atoms on procainamide have different basicity.



Procainamide

Rank the three nitrogen atoms in order of increasing basicity. Explain your answer. [3]

$N_b < N_a < N_c$ **[1]**

Amide is neutral (the least basic), as the lone pair electrons on **N_b** is delocalised significantly into the electronegative O atom in the C=O bond, making the lone pair electrons on **N_b** not available to accept H^+. **[0.5]**

Phenylamine is less basic than tertiary amine as the lone pair electron on **N_a** is delocalised into the π electron cloud of the benzene ring, making the lone pair electrons on **N_a** to be less available to accept H^+. **[0.5]**

Tertiary amine is the most basic, as the electron donating alkyl groups increases the electron density of the lone pair electrons on **N_c**, making the lone pair electrons on **N_c** atom to be more available to accept H^+ as compared amide and phenylamine. **[0.5]**

0.5 "to accept H^+ (bronsted base definition)"

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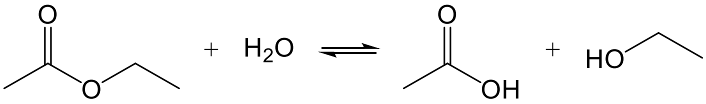
(d) Ethyl ethanoate can undergo the following hydrolysis.



(i) The standard entropy change in a chemical reaction can be defined as shown in Equation 2.1.

Equation 2.1 : $\Delta S^{\ominus}_{\text{reaction}} = \sum S^{\ominus}\text{(products)} - \sum S^{\ominus}\text{(reactants)}$

Table 2.1

Species	Standard enthalpy change of formation / kJ mol^{-1}	Standard Molar Entropy ($S^{\ominus}$) / J K^{-1}mol^{-1}
$CH_3COOCH_2CH_3$	– 479	258
CH_3COOH	– 484	160
CH_3CH_2OH	– 287	161
H_2O	– 286	70

Use the data in Table 2.1 and Equation 2.1, calculate the standard Gibb's free energy change for the hydrolysis of ethyl ethanoate. [2]

(ii) With reference to the *Data Booklet*, calculate the enthalpy change of reaction for the hydrolysis of Ethyl ethanoate. Explain why this value is different from the answer in **(i)**. [2]

2(d)(i) $\Delta H^{\ominus} = (-484 - 283) - (-479 - 286) = -767 + 765 = -2$ kJ mol^{-1} **[0.5]**
$\Delta S^{\ominus} = (160 + 161) - (258 + 70) = -7$ J K^{-1}mol^{-1} **[0.5]**
$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus} = -2 - (298 \times 0.007) = -4.09$ kJ mol^{-1} **[1.0]**

2(d)(ii) $\Delta H^{\ominus} = (360 + 460) - (360 + 460) = 0$ kJ mol^{-1} **[1]**
Bond energy assumes the molecules in the hydrolysis are gaseous but all 4 molecules in the equilibrium are liquid at standard condition. **[1]**

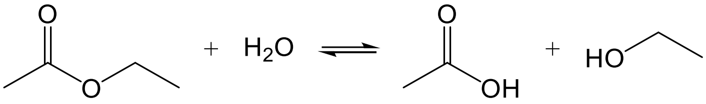
(e) Gibbs free energy under non-standard conditions (ΔG) is related to the standard Gibbs free energy ($\Delta G^\ominus$), gas constant (R), temperature (T) and the reaction quotient (Q).

$$\Delta G = \Delta G^\ominus + RT \ln Q$$

Reaction quotient is the relative amounts of products and reactants present during a reaction at a particular instance and has the same expression as the equilibrium constant, *K*.

(i) Prove that $\Delta G^\ominus = -RT \ln K$, when reaction is at equilibrium. [1]

An aqueous solution at 30 °C is known to have the following composition.



compound	concentration / mol dm^{-3}
ethanol	2.20
ethanoic acid	3.10
ethyl ethanoate	0.82
water	55.3

(ii) Write an expression for the reaction quotient, Q, for the reaction above and use the data to calculate ΔG at this particular instance. [2]

(iii) Hence, suggest what the ΔG value in **(e)(ii)** indicates about the direction of the reaction. [1]

(iv) Sulfuric acid is added as catalyst for the reaction. Suggest how would the addition of sulfuric acid affect the equilibrium constant for the hydrolysis of ethyl ethanoate. [1]

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2(e)(i) At equilibrium, $\Delta G = 0$, $Q = K$.
$0 = \Delta G^\ominus + RT \ln K$
$\Delta G^\ominus = - RT \ln K$ **[1]**

2(e)(ii) Expression for Q **[1]**
$\Delta G = \Delta G^\ominus + RT \ln Q$
$= -4.09 \times 10^3 + (8.31)(303)(\ln (\frac{2.2 \times 3.1}{0.82 \times 55.3})) = -8860 \text{ J mol}^{-1}$ **[1]**

2(e)**(iii)** Since $\Delta G<0$, the forward reaction is spontaneous. **[1]**

2(e)(iv) Equilibrium constant is affected only by temperature and not catalysis. Hence, addition of H_2SO_4 will not affect the value of equilibrium constant. [1]

[Total : 20]

3 **(a)** Electroplating copper spoon with a layer of silver can improve the corrosion resistance of the spoon, ensuring a non-reactive surface when in contact with food and gain anti-microbial properties. Fig 3.1 shows one such set up for the electroplating of copper spoon with a layer of silver.

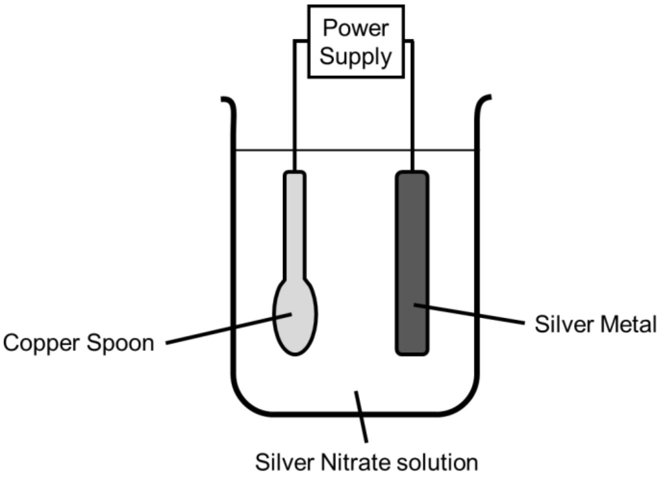

Fig 3.1

(i) Write the half equations for the reaction that happens at each electrode. [1]

(ii) A current of 5A was passed through the system to electroplate the copper spoon with a total surface area of 100 cm^2.

Given the density of silver is 10.5 g cm^{-3}, calculate the amount of time needed to coat the copper spoon with 0.01 mm thickness of silver. [2]

(iii) A way to speed up the electroplating process is by increasing the current supplied. Suggest the disadvantage of increasing the current supplied. [1]

(iv) Under suitable conditions, silver can be oxidised to silver(I) oxide, Ag_2O. With the use of *Data Booklet* and information in Table 3.1, construct an energy cycle to calculate the lattice energy of silver(I) oxide.

Table 3.1

	ΔH /kJ mol^{-1}
Standard enthalpy change of atomisation of Ag(s)	+285
Standard enthalpy change of formation of Ag_2O(s)	–31
First Electron Affinity of O(g)	–141
Second Electron Affinity of O(g)	+744

[4]

3(a)(i)

[Cathode] Copper Spoon: [R] $Ag^+ + e^- \rightarrow Ag$

[Anode] Silver Metal: [O] $Ag \rightarrow Ag^+ + e^-$

3(a)(ii) Mass of silver required = 10.5 x 100 x 0.001 = 1.05 g **[1]**

Amount of silver required = 1.05 / 107.9 = 0.009731 mol **[0.5]**

Amount of electron transfer = 0.009731 mol

$n_e \times F = I \times t$

t = 0.009731 x 96500 / 5 = 188 s **[0.5]**

3(a)(iii) Higher current will speed up the electroplating process but the surface may be rough and non-uniform plating.

3(a)(iv)

$$\begin{tikzcd}
2Ag(s) + \frac{1}{2}O_2(g) \arrow[r, "-31"] \arrow[d, "2 \times (+285)"] & Ag_2O(s) \\
2Ag(g) + \frac{1}{2}O_2(g) \arrow[d, "\frac{1}{2} \times (496)"] & 2Ag^+(g) + O^{2-}(g) \arrow[u, "L.E."'] \\
2Ag(g) + O(g) \arrow[r, "2 \times (731)"'] & 2Ag^+(g) + O(g) + 2e^- \arrow[u, "-141 + 744"']
\end{tikzcd}$$

By Hess's Law,

$-31 = 2 \times 285 + \frac{1}{2} \times 496 + 2 \times 731 + (-141 + 744) + L.E.$

L.E. = $-2914 \approx -2910$ kJ mol^{-1} (3.s.f.)

2m for energy cycle (balance elements and charges and coefficient of ΔH)

- Minus 0.5 for each mistake in the ΔH processes

1m for correct application of Hess's Law

1m for correct final answer (no e.c.f.)

(b) The values of solubility product for some silver compounds are shown in Table 3.2.

Table 3.2

compound	colour of precipitate	solubility product
AgC*l*	white	1.8×10^{-10}
AgBr	cream	5.2×10^{-13}
AgI	yellow	8.3×10^{-17}
Ag_2CrO_4	red	1.1×10^{-12}

(i) Describe what would be observed when aqueous $AgNO_3$ is added drop-wise into a solution containing 1×10^{-4} mol dm^{-3} of C*l*$^-$ and 1×10^{-4} mol dm^{-3} of CrO_4^{2-}. Explain your answer. [2]

(ii) AgC*l* is soluble in excess of NH_3(aq) but AgI is insoluble in excess of NH_3(aq). Explain the observation. [2]

3(b)(i) white ppt is observed first followed by red ppt. [1]
For AgCl,
$1.8 \times 10^{-10} = [Ag^+] \times 1 \times 10^{-4}$
$[Ag^+] = 1.8 \times 10^{-6}$ mol dm^{-3} [0.5]

For Ag_2CrO_4, $1.1 \times 10^{-12} = [Ag^+]^2 \times 1 \times 10^{-4}$
$[Ag^+]^2 = 1.1 \times 10^{-8}$
$[Ag^+] = 1.05 \times 10^{-4}$ mol dm^{-3} [0.5]
Higher concentration of Ag^+ is required to precipitate Ag_2CrO_4.

3(b)(ii) When dilute NH_3(aq) is added to AgC*l* and AgI, $[Ag(NH_3)_2]^+$ complex ion is formed for both scenarios and $[Ag^+]$ decreases. [1]

But only the ionic product of AgC*l* falls below its K_{sp} value [0.5], causing AgC*l* precipitate to dissolve.

K_{sp} value of AgI is very small, thus the ionic product is still greater than its K_{sp} [0.5] the AgI precipitates do not dissolve.

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(c) Write an equation to represent the thermal decomposition of hydrogen halide, HX. Hence, explain the thermal stability of hydrogen halide down Group 17. [2]

3(c) $2HX \rightarrow H_2 + X_2$ [1]

Down the group, the bond energy of H−X decreases

Less energy is required to decompose HX down the group. Thermal stability decreases. [1]

(d) A sample of pure N_2O_5 (g) is placed in an evacuated container and allowed to decompose at a constant temperature of 300K.

$$2N_2O_5\text{ (g)} \rightarrow 4NO_2\text{(g)} + O_2\text{(g)}$$

The concentration of N_2O_5 in the container is measured over a period of time, and the measurement are recorded in Table 3.3. The rate equation for the reaction is found to be Rate = k[N_2O_5].

Table 3.3

Time (min)	[N_2O_5]/ moldm^{-3}
0	0.480
10	0.381
20	0.302
30	0.240
40	0.190
50	0.150

(i) With the use of the data in Table 3.3, show that the order of reaction with respect to N_2O_5 is one. [1]

(ii) Determine the value of the rate constant, k, for the reaction. Include units in your answer. [1]

(iii) The following mechanism is proposed in the decomposition of N_2O_5(g)

Step 1 : $N_2O_5\text{ (g)} \rightarrow NO_2\text{(g)} + NO_3\text{ (g)}$

Step 2 : $NO_2\text{(g)} + NO_3\text{(g)} \rightarrow NO_2\text{(g)} + NO\text{(g)} + O_2\text{(g)}$

Step 3 : $N_2O_5\text{(g)} + NO\text{(g)} \rightarrow 3NO_2\text{(g)}$

Identify and explain which step of the proposed mechanism is the rate determining step. [2]

(iv) If this experiment was repeated at the same condition but with twice the concentration of N_2O_5, explain how would the value of k change. [2]

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(i) Concentration of N_2O_5 decreases with a **constant half-life of 30 mins.**
0.480 to 0.240 takes 30 mins
0.381 to 0.190 takes 30 mins

This shows that the reaction is 1st order with respect to N_2O_5.

(ii) $t_{1/2}$ = 30 min

$t_{1/2} = \frac{In2}{k}$

k = $\frac{In2}{30}$ = 0.0231 **[0.5]** min^{-1} **[0.5]**

(iii) **Step 1 is** the slow step.**[1]**
The reaction is **first order with respect to N_2O_5** as shown from the data above. There can **only be 1 N_2O_5 as the only reactant in the slow step** and it correspond to step 1. **[1]**

(iv) **No change**. **[1]** As the value of **k is only dependent on temperature AND catalyst**. **[1]** Since no change to temperature no addition of catalyst. There will be no change to the value of k.

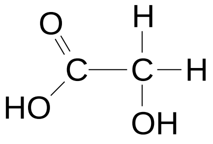
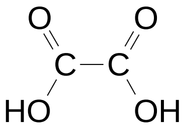
[Total : 20]

Section B

Answer **one** question from this section.

4 **(a)** Table 4.1 shows the pK_a values of glycolic acid and ethanedioic acid.

Table 4.1

Acid	 glycolic acid	 ethanedioic acid
pK_{a1}	3.83	1.27
pK_{a2}	-	4.28

(i) Explain why pK_{a1} of glycolic acid is larger than that of ethanedioic acid. [2]

(ii) Calculate the pH of 0.100 mol dm^{-3} of glycolic acid. [1]

Small portions of 0.100 mol dm^{-3} NaOH(aq) are added to 25.0 cm^3 of 0.100 mol dm^{-3} of glycolic acid.

(iii) Explain, with the aid of an equation, why the pH of the mixture is 7.6 when 25.0 cm^3 of NaOH(aq) is added to glycolic acid. [2]

(iv) When 50.00 cm^3 of 0.100 mol dm^{-3} NaOH(aq) was added, the pH value of the reaction mixture is at 12.5.

Sketch the shape of the pH curve on suitable axis, using all the relevant information given or calculated. Indicate the point at which a buffer of maximum capacity is formed. [2]

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4(a)(i) Lower pK_a value shows stronger acid strength. ½
Conjugate base from both acids are carboxylate ions ½,
There is further dispersion of negatives charge for $HO_2C\text{-}COO^-$ via resonance ½ making the conjugate more stable½ / there are one additional electronegative O atom that disperse the negative charge more than in $HOCH_2COO^-$ ½ thus $HO_2C\text{-}COO^-$ is more stable.
Hence acid dissociation of COOH is more favourable than dissociation of alcohol -OH group. ½

4(a)(ii) $K_a = 1.48 \times 10^{-4}$

$1.48 \times 10^{-4} = \frac{[H^+]^2}{[acid]}$ assume $[H^+] << [acid]$

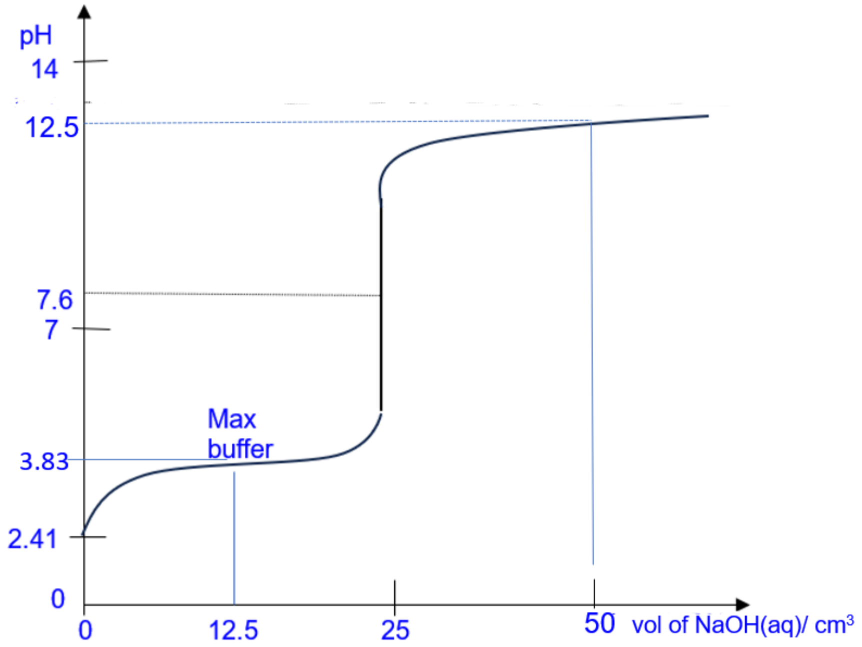
$[H^+] = 3.85 \times 10^{-3}$ moldm^{-3}

pH = 2.41

4(a)(iii) Complete neutralisation takes place. At this point, only the salt, $HOCH_2COONa$, is present. ½
Being a conjugate base of a weak acid½, it is a stronger base than water, thus undergo hydrolysis in water as shown:

$$HOCH_2COO^- + H_2O \rightleftharpoons HOCH_2COOH + OH^-$$ 1

(iv)



Label max buffer at correct volume and pH
Shape
Initial pH = 2.41
pH = 7.6 at 25 cm^3
pH = 12.5 at 50 cm^3

(b) Glycolic acid undergoes reactions as shown in Fig. 4.2.

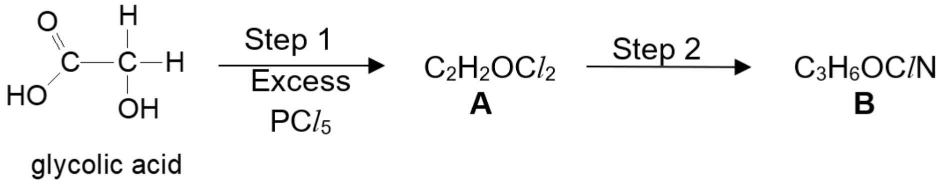
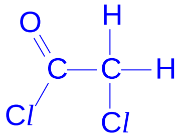
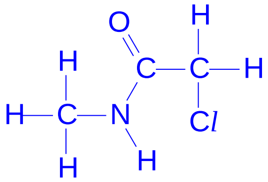


Fig. 4.2

(i) Give the structures of compounds **A** and **B** in Fig 4.2. [2]

(ii) Give the reagent and conditions for step 2 in Fig. 4.2. [1]

4(b)(i)

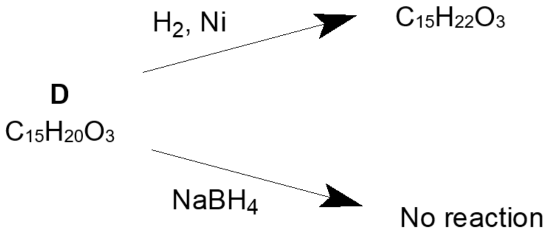
 **compound A**	 **compound B**

4(b)(ii) CH_3NH_2

Question 4 continues on the next page

(c) Compound **D** is an ester with the molecular formula, $C_{15}H_{20}O_3$.

When **D** was treated with different reducing agents, the following observations were made.



On heating with acidified potassium manganate(VII), **D** gives 3 organic products, **E**, $C_8H_6O_5$, **F**, $C_4H_{10}O$ and **G**, C_3H_6O.

- 1 mole of **E** reacts with 2 moles of $SOCl_2$.
- **E** reacts fully with aqueous bromine in the ratio 1:1.
- **G** gives an orange precipitate, **H**, with 2,4-dinitrophenyhydrazine.

Suggest structures for **D** – **H** and explain the observations described above. [10]

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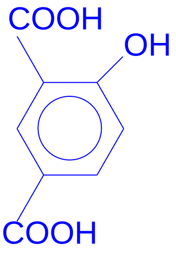
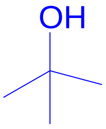
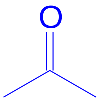
Information	Type of reaction, functional group
D, $C_{15}H_{20}O_3$. DOU = 6	Benzene ring is likely to be present. Side chain has 2 double bonds, 1 is due to ester functional group. ½
D, $C_{15}H_{20}O_3$ + H_2 → **E,** $C_{15}H_{22}O_3$ NOT $NaBH_4$	Reduction ½ **D** must have one C=C, ½ not carbonyl C.
D, $C_{15}H_{20}O_3$ + acidified $KMnO_4$ → **E**, $C_8H_6O_5$, **F**, $C_4H_{10}O$ and **G**, C_3H_6O.	Oxidation, C=C is cleaved. ½ Hydrolysis of ester ½ **F** is 3° alcohol, resistant to oxidation.
E, $C_8H_6O_5$ + 2 $SOCl_2$	2 moles of COOH group½ to undergo nucleophilic acyl substitution to form COCl. ½
E, $C_8H_6O_5$ + 1 Br_2	5th O is the phenolic group. ½ 2 of the 2,4,6 positions to phenolic group has substituents ½
H, C_3H_6O + 2,4 DNPH → orange ppt	Condensation reaction. ½ Ketone is present. ½ Cannot be aldehyde as aldehyde cannot be formed in the presence of strong oxidising agent $KMnO_4$.



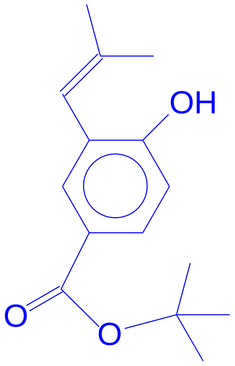
E



F

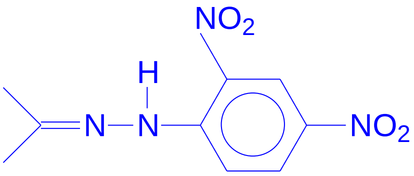


G



D

D allow ecf



H

H allow ecf

[Total : 20]

5 **(a)** PCl_5 dissolves in water to give acidic solution. Write an equation for the reaction of PCl_5 with water. [1]

$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

(b) When compound **W**, $C_{12}H_{12}O_3$, is mixed with 2,4-dinitrophenylhydrazine, an orange precipitate is formed. However, no precipitate is observed when **W** is heated with Tollens' reagent.

When **W** is heated with dilute hydrochloric acid, compounds **X** and **Y** are formed. Compound **X** has the molecular formula $C_3H_4O_2$.

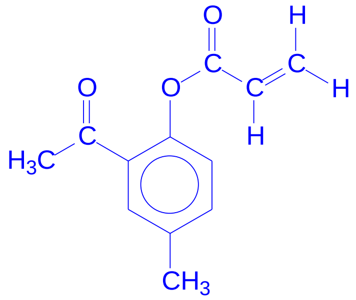
When **Y** is warm with alkaline iodine, yellow precipitate is observed. Compound **Z**, $C_9H_9BrO_2$, is formed when **Y** is mixed with excess Br_2(aq).

Deduce the structures of compounds **W**, **X**, **Y** and **Z**, and explain the observations described above. [6]

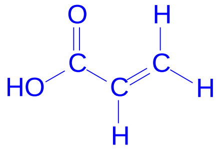
Information	Type of reaction, functional group
W, $C_{12}H_{12}O_3$ + 2,4-DNPH → orange ppt	Condensation reaction W contains a carbonyl functional group.
W + Tollens' → no rxn	W is not an aldehyde, W is a ketone.
W heated with HCl(aq) → X + Y	Hydrolysis reaction W contains an ester
Y + alkaline I_2	Redox reaction Y contains methyl carbonyl ($COCH_3$)
Y + excess Br_2(aq) → Z, $C_9H_9BrO_2$	Electrophilic substitution Y contains phenol functional group. Two of the 2/4/6 position of phenol is occupied by other substituent groups. Y is likely to contain 9C as well.

½ m for correct reaction and ½ m for correct functional group.

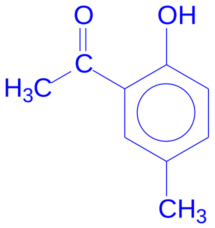
Max 2m for deductions.



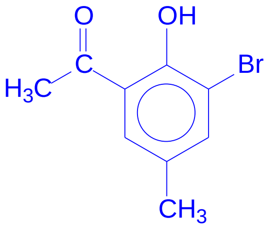
compound W



compound X



compound Y



compound Z

(c) 10 cm^3 of a 0.20 mol dm^{-3} propylamine solution $CH_3CH_2CH_2NH_2$, was titrated against the 0.10 $moldm^{-3}$ HCl solution.

(i) The numerical value of K_b for propylamine is 4.8×10^{-4}. Calculate the value of pK_b for propylamine. [1]

(ii) Calculate the initial pH of the 0.20 mol dm^{-3} propylamine solution. [1]

(iii) Explain with the aid of an equation, why the pH of the solution at equivalence point is less than 7. [2]

(iv) Using your answer from **(a)(i) - (iii),** sketch the titration curve that would result from this titration with the 0.100 mol dm^{-3} HCl. solution. Showing clearly the point of maximum buffering capacity. [2]

(iv) With reference to the structure and bonding, account for the difference in the boiling point between propylamine and trimethylamine.

Compound	boiling point / °C
propylamine, $CH_3CH_2CH_2NH_2$	49
trimethylamine, $(CH_3)_3N$	7

[2]

5(a)(i) $pK_b = -\lg(4.8 \times 10^{-4})$
$= 3.32$ [1]

5(a)(ii) $[OH^-] = \sqrt{4.8 \times 10^{-4} \times 0.20}$
$= 9.80 \times 10^{-3}$
$pOH = -\lg(9.80 \times 10^{-3})$
$= 2.01$
$pH = 14 - pOH$
$= 14 - 2.01$
$= 11.99$ [1]

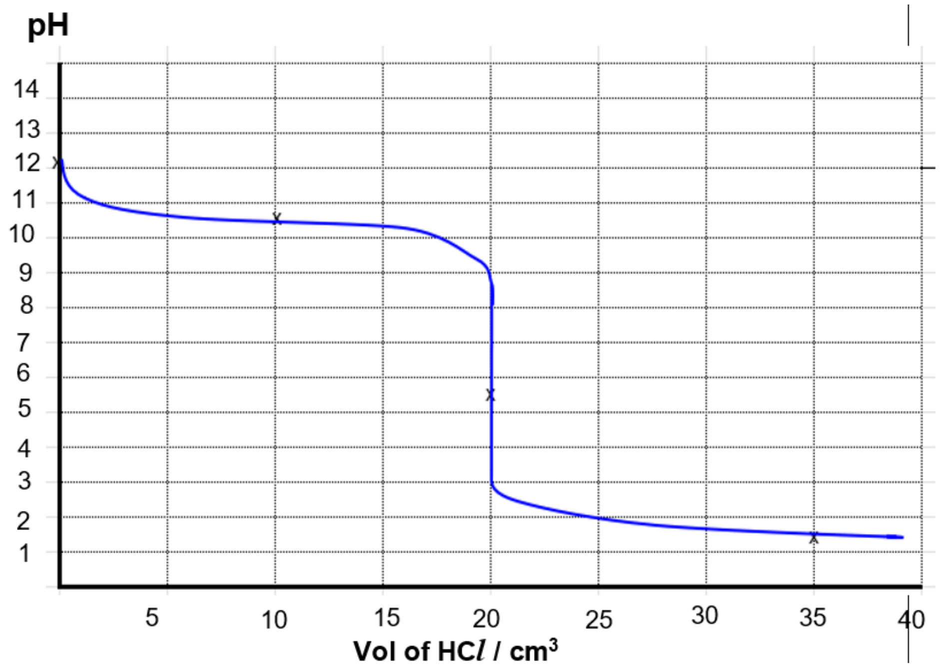
5(a)(iii)

[1/2] sketch shows correct initial pH=12

[1/2] a sketch shows at vol 10cm^3, pH = 14 – 3.32 = 10.68

[1/2] sketch shows the mid point of the vertical section (equivalence pt <7)

[1/2] sketch shows the final pH above 1



5(a)(iv) Both propylamine and trimethylamine have **simple molecular structure.** **[1/2]** **Propylamine have hydrogen bonding** **[1/2]** **and instantaneous dipole-induced dipole (id-id)between the molecules while trimethylamine have permanent dipole-permanent dipole (pd-pd)** **[1/2]** **and id-id between the molecules.** More energy is needed to overcome the **stronger hydrogen bonding in propylamine**, **[1/2]** hence boiling point of propylamine is higher.

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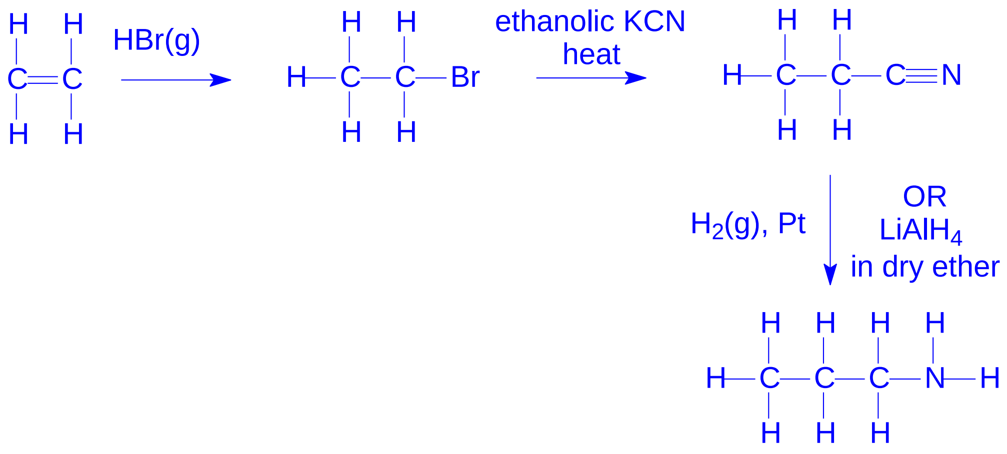
(d) Ethene can be converted into propylamine via a three-step synthesis route.

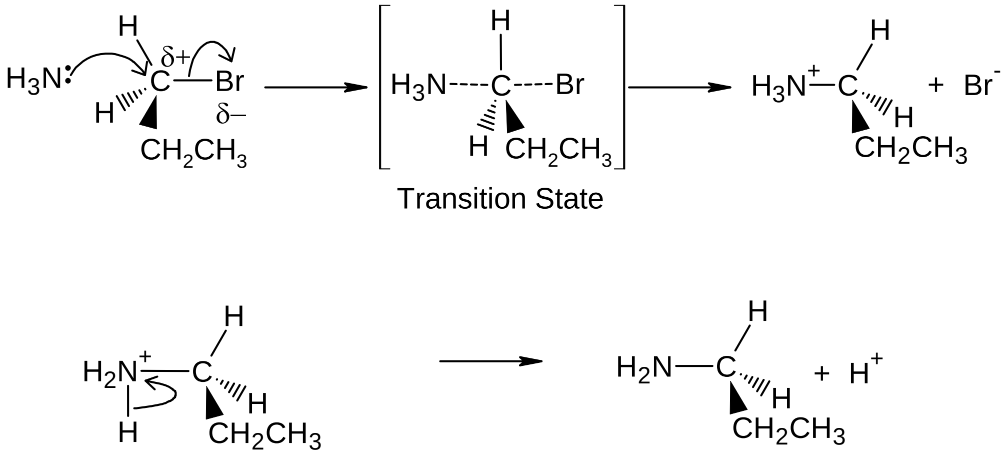
Suggest the reagents and conditions for the synthesis route, showing clearly the structure of the intermediate organic compounds. [3]



(e) Propylamine can also be obtained from the reaction between 1-bromopropane and NH_3 under suitable conditions.

Suggest a mechanism for the reaction between 1-bromopropane and NH_3. Show all relevant dipoles, lone pair electrons and curly arrows. [2]

Nucleophilic substitution, S_N2



Name of mechanism
Dipoles and lone pair electrons
Correct use of curly arrows
Show inversion
Transition state (no net charge)
Losing of H^+ in last step

l : 20]

Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.

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