NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME			
SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY

9729/03
Paper 3 Free Response
13 September 2022
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	**/18**
2	**/19**
3	**/23**
Section B	
4	**/20**
5	**/20**
Paper 3 Total	**/80**

This document consists of **28** printed pages.

Section A

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

1 (a) Amines can be synthesised from methylbenzene, shown by the following steps.

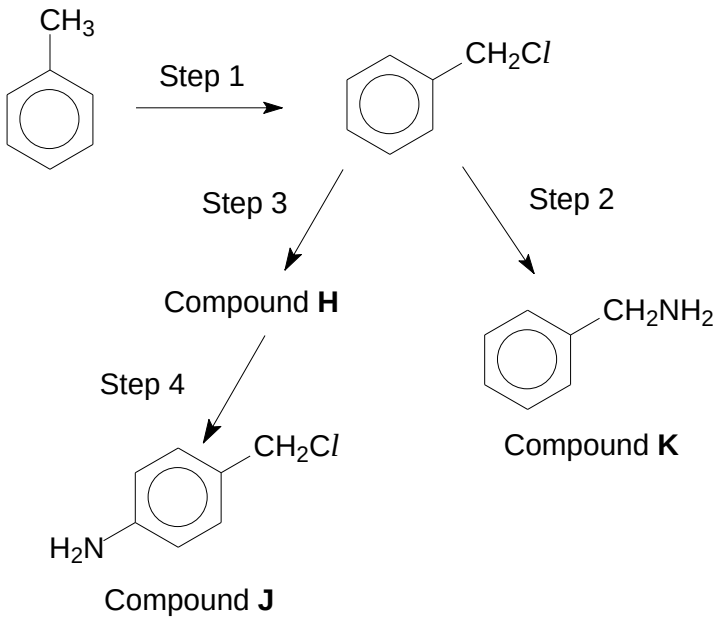


Fig. 1.1

(i) Suggest the structure for compounds **H**. [1]

(ii) Suggest reagents and conditions for steps 1, 2, 3 and 4 in Fig. 1.1. [4]

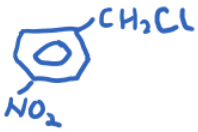
(iii) Suggest why the yield for step 2 is not high. [1]

The K_b values of three bases, at 25°C, are shown in table 1.2.

Table 1.2

base	K_b/moldm^{-3}
ammonia	1.8×10^{-5}
compound **K**	4.5×10^{-4}
compound **J**	7.4×10^{-10}

(iv) Explain the relative magnitudes of the K_b values in table 1.2. [2]



(i) 1 or 0

(ii) Step1: UV light, **limited** Cl_2. 1 or 0

Step 2: ethanolic NH_3, heat in sealed tube.

Step 3: conc H_2SO_4, Conc HNO_3, 60°C ($-CH_2Cl$ has negligible effect on benzene) -accept T lower than 60°C.

Step 4: conc HCl, Sn, heat *followed by* NaOH(aq) or *(step 1 then 2)*

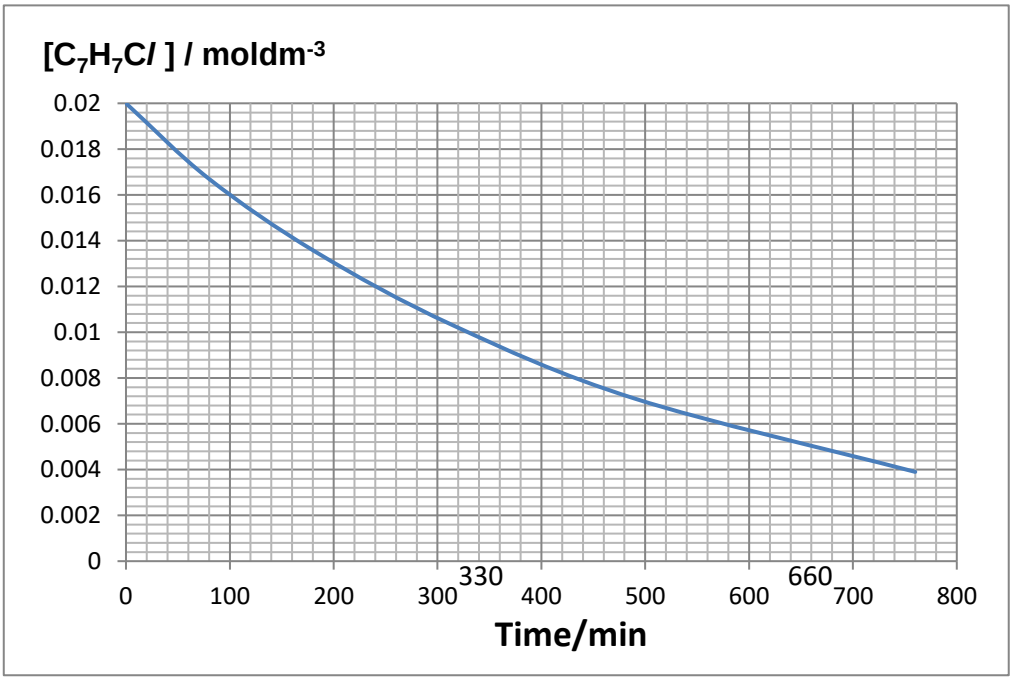
1 or 0 for each step

(iii) The primary amine produced, due to the electron donating alkyl group ½ , is a stronger nucleophile than NH_3, ½ hence can compete/further react with NH_3 for C_7H_7Cl to form a secondary amine instead of the compound K. (½ for stating polysubstitution)

(iv) Smaller K_b value means a weaker base. Lone pair on N in **J** is less available ½ compared to that of **K** to accept H^+ as the electron density at N is reduced½ via resonance with the adjacent benzene½ (lone pair on N is delocalised into the benzene ring) while the electron density at N in **K** is increased by the electron donating effect of the alkyl group½.

(b) The rate of reaction for step 2 in Fig. 1.1 can be followed by measuring the change in concentration of C_7H_7Cl with time. The reaction was carried out with the other reactant in large excess.

Fig. 1.2 shows the concentration of C_7H_7Cl monitored against time for step 2.



Showing all your working and drawing clearly any construction lines, use Fig.1.2 to determine:

(i) The order with respect to C_7H_7Cl. Explain your reasoning. [2]

(ii) The initial rate, in mol dm^{-3} min^{-1} [1]

Given that the half-life magnitude of C_7H_7Cl is not affected by the change in concentration of the other reactant.

(iii) Write the rate equation for step 2 in Fig.1.1, and calculate a value for the rate constant, stating its units. [2]

(iv) Hence, outline a mechanism for step 2 in Fig.1.1 to form all the products.

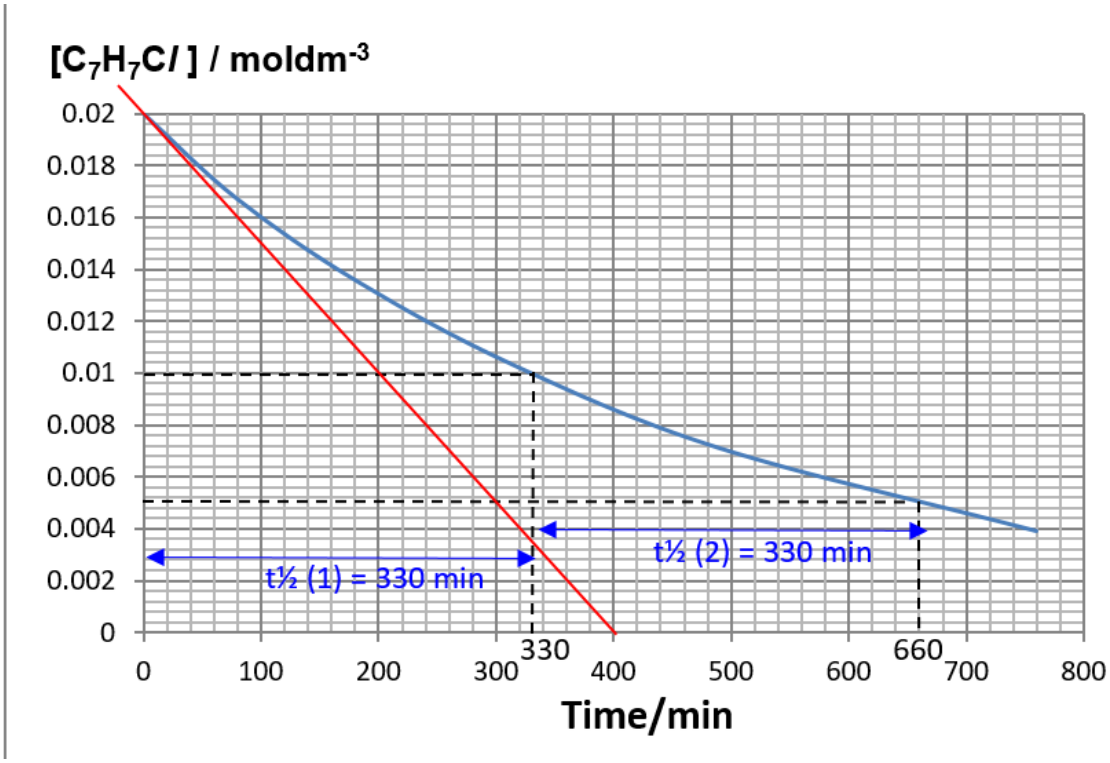
Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [3]

(v) Explain why step 2 proceeds via the mechanism you describe in **b(iv).** [1]

(vi) Suggest and explain the difference in reactivity when 4-bromomethylbenzene undergoes the same reaction. [1]

[Total : 18]

(b)(i)



1m for showing how the half-life is obtained.
Since half-life of to C_7H_7Cl is constant at 330 min, it is 1st order wrt to C_7H_7Cl. 1m

(ii) Initial rate = – (gradient at t = 0) = $-\frac{(-0.0200)}{400} = 5 \times 10^{-5} \text{moldm}^{-3}\text{s}^{-1}$ 1m

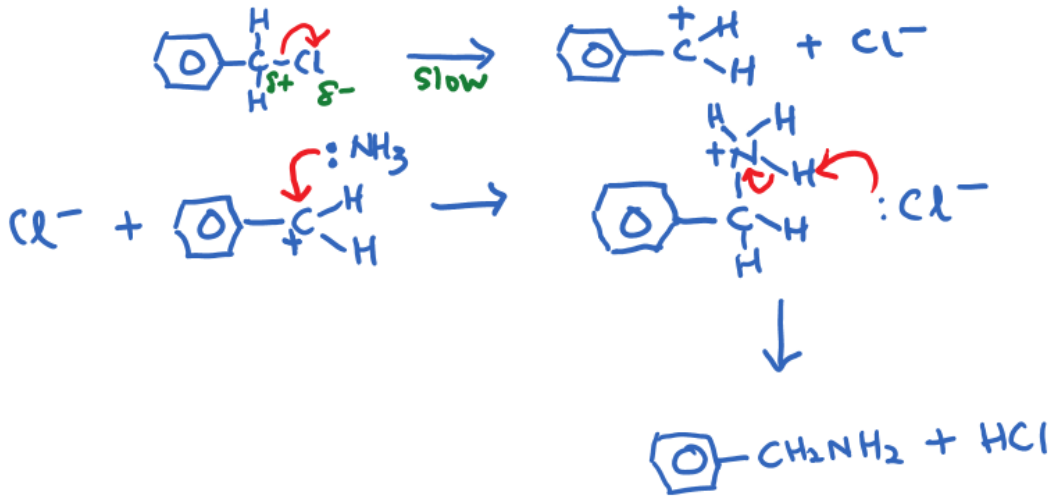
(iii) Rate = k [C_7H_7Cl] 1m

Two methods:
Making use of the initial rate calculated in (ii)
$k = 5 \times 10^{-5} \div 0.02 = 2.5 \times 10^{-3}\ \text{s}^{-1}$

Making use of the half-life magnitude:
$k = \frac{\ln 2}{t_{1/2}} = 2.1 \times 10^{-3}\ \text{s}^{-1}$ ½ m each for answer and units

(iv)

Nucleophilic substitution (S_N1)



Accept show formation of HCl in separate step.
Draw SN2 based on SN1 rate equation on (iii) – 1m for name of mechanism
Draw SN2 based on SN2 rate equation in part (iii) – full credit

……

1m for name of mechanism
½ for slow
1 m for curly arrows and charges
1m for balanced equations

(v) Explain why step 2 proceeds via the mechanism you describe in **b(iv)**. [1]

The carbocation intermediate can be resonance stabilised i.e. the positive charge of the cation can be dispersed via resonance with the adjacent benzene ring. 1m
Or
The bulky benzene ring poses steric hindrance to the incoming nucleophile if it occurs via S_N2 or one step mechanism. 1m

Cannot accept sn2 explanation

(vi) C-Br in 4-bromomethylbenzene is **resistant to substitution [½]**, as it **has double bond character due to the continuous p orbital overlap [½]** involving Br and benzene ring.

2 Hydrogen cyanide, HCN, is extremely toxic and with sufficient concentrations it leads to rapid death. During the Second World War, a form of hydrogen cyanide known as *Zyklon B* was used in the Nazi gas chambers.

(a) **(i)** Draw a dot–and–cross diagram to illustrate the bonding in HCN. [1]

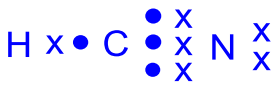
HCN can be oxidised to cyanogen, C_2N_2.

$$C_2N_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons 2HCN(g) \quad E^\ominus = +0.37\ V$$

(ii) Suggest a suitable oxidant to oxidise HCN to C_2N_2 in acidic solution, using the *Data Booklet*.

Write an equation for the reaction and calculate the $E^\ominus_{cell}$. . [2]

2(a)(i)



(ii) $KMnO_4$ in acidic medium

$E^\ominus_{cell} = +1.52 – (+0.37) = +1.15V > 0$ (reaction is spontaneous) 1m

$2MnO_4^- + 6H^+ + 10HCN \rightarrow 5C_2N_2 + 2Mn^{2+} + 8H_2O$ 1m

Note: Can use any oxidizing agent with $E^\ominus > +0.37V$

(b) The synthesis of HCN was developed in the early 1900s. The most commonly used procedure is the *Andrussow* process. A less common method is the *BMA* process.

Andrussow process:

$$CH_4\,(g) + NH_3\,(g) + \frac{3}{2}\,O_2\,(g) \longrightarrow HCN\,(g) + 3\,H_2O\,(l) \qquad \Delta H = -506\ kJ\ mol^{-1}$$

BMA process:

$$CH_4\,(g) + NH_3\,(g) \longrightarrow HCN\,(g) + 3\,H_2\,(g)$$

(i) Using information from the *Data Booklet*, calculate the enthalpy change of reaction for the *BMA* process given above [2]

(ii) By considering the spontaneity of reaction, suggest why the *Andrussow* process is the preferred procedure at low temperature. [2]

(b) **(i)** ΔH = 4 x 410 + 3 x 390 – [410 + 890 + 3 x 436] = + 202 kJ mol^{-1} 1m for final answer, 1 m for working
(correct number and type of bonds identified- 1m)

(ii) *Andrussow* process has a negative ΔS since there is decrease in number of gas particles, which causes an decrease in number of ways to arrange the particles in space. 1m
$\Delta G = \Delta H - T\Delta S$, at low temperature, $\Delta H > |T\Delta S|$, it is more likely to have $\Delta G < 0$ at low temperature.

(c) The *BMA* process is a reversible reaction at 500°C. Starting with equal amount of CH_4 and NH_3, the reaction is allowed to reach equilibrium at 500°C under a constant pressure of 1 atm.

(i) Write an expression for the K_p of *BMA* process stating its units. [1]

(ii) Given that the partial pressure of H_2 is 0.3 atm, calculate the value of K_p at 500°C. [2]

(iii) Discuss the effect of increase in total pressure on
- the proportion of HCN,
- K_p value
- rate of reaction

[3]

C(i)

$$K_p = \frac{P_{HCN}P_{H_2}^3}{P_{CH_4}P_{NH_3}} \quad units: atm^2$$

1/2 each for expression and units (0 if wrong expression)

(ii) $CH_4\,(g) + NH_3\,(g) \rightleftharpoons HCN\,(g) + 3\,H_2\,(g)$

At equilibrium, $P_{H2} = 3 \times P_{HCN}$
$\therefore P_{HCN} = 0.1$ atm

Since the reaction is carried out at a constant pressure of 1 atm,
$P_{CH4} + P_{NH3} + P_{CH4} + P_{NH3} = 1$ atm
since partial pressure of the gaseous products ($P_{HCN} + P_{H2}$) = 0.4 atm
$P_{CH4} + P_{NH3} = 0.6$ atm
1m for partial pressures
Hence $P_{CH4} = 0.3$ atm $= P_{NH3}$

$$K_p = \frac{0.1(0.3)^3}{(0.3)(0.3)} = 0.03$$ 1m (ecf)

(iii)

Increase in pressure will shift the equilibrium to the reactant side as it has smaller number of gas particles ½, this is to partially offset increase in total pressure. Hence proportion of HCN is reduced½.

Changes in pressure has no effect on K_p value½ as K_p values are affected by changes in T only½.

Increase in total pressure increases the concentration of the gaseous particles, increase in collision frequency increases the frequency of effective collision½, hence rate is expected to increase½.

(d) HCN (aq) has pK_a = 4.79 at 25 °C.

(i) Calculate the concentration of CN^- ion at pH 4, when the concentration of HCN(aq) is 0.06 mol dm^{-3}. [1]

Zinc cyanide, $Zn(CN)_2$, is sparingly soluble in water.
The numerical value of K_{sp} is 8.0 x 10^{-12} at 25°C.

(ii) Write an expression for the K_{sp} of $Zn(CN)_2$ stating its units. [1]

(iii) By considering your answer to **(d)(i)**, determine the minimum concentration of Zn^{2+} required to cause precipitation of $Zn(CN)_2$ at pH 4. [2]

(iv) Describe and explain how the solubility of $Zn(CN)_2$ is affected:

- by adding HC*l*(aq)
- by adding concentrated ZnCl_2(aq)

[2]

(i) $10^{-4.79} = \frac{10^{-4}[CN^-]}{0.06}$

$[CN^-] = 9.73 \times 10^{-3} moldm^{-3}$ 1m

(ii) $K_{sp} = [Zn^{2+}][CN^-]^2$ mol^3dm^{-9} ½ each with correct expression.

(iii) For precipitation to occur, ionic product > K_{sp}

$[Zn^{2+}](9.73 \times 10^{-3})^2 > 8.0 \times 10^{-12}$1m

$[Zn^{2+}] = 8.45 \times 10^{-8}$ $moldm^{-3}$ 1m (ecf)

(iv) Addition of strong acid will suppress the dissociation of weak acid HCN, causing the concentration of CN^- to reduce ½ hence *more $Zn(CN)_2$ solid dissolves* ½ to partially offset the reduction in $[CN^-]$/ *solubility of $Zn(CN)_2$ increases*½.

Addition of ZnCl_2(aq) causes the concentration of Zn^{2+} to increase ½ , hence the precipitation ½ process is favoured in order to partially offset the increase in $[Zn^{2+}]$/ hence solubility of $Zn(CN)_2$ decreases ½ .

3 **(a)** GABA, a naturally occurring neurotransmitter, has the condensed formula of $HOOCCH_2CH_2CH_2NH_2$. It can be synthesised from 2-bromoethanal, CH_2BrCHO, shown by the following steps.

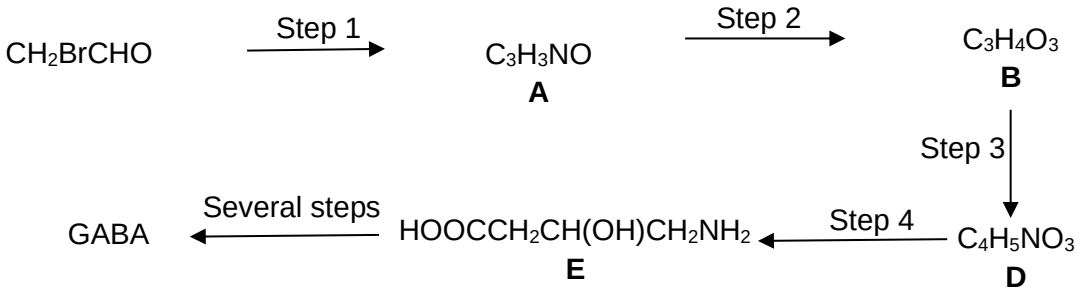


Fig. 3.1

Compound **B** gives effervescence with Na_2CO_3(aq) and it gives a brick red precipitate with warm Fehling's solution.

(i) Suggest what these observations indicate about the functional groups in **B.** [1]

(ii) Give the structures of compounds **A** and **D**. [2]

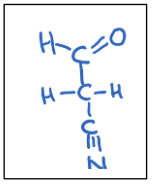
(iii) Suggest reagents and conditions for steps 1, 2, 3 and 4 in Fig. 3.1. [4]

(iv) Suggest why the yield for step 3 is very low. [1]

(v) The conversion of **B** to **D** involves a nucleophilic addition. Suggest why only 50% of compound **D** can be used in drug synthesis. [2]

(i) COOH ½ must be present to react with Na_2CO_3 to give CO_2 gas while Fehling's identified aliphatic aldehyde½. Both functional group must be at the terminal of the 3C compound.

(ii) and (iii)



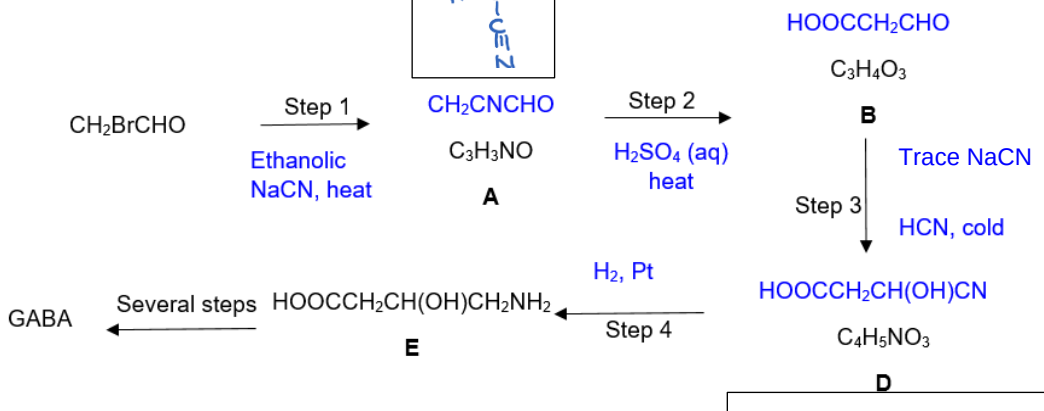
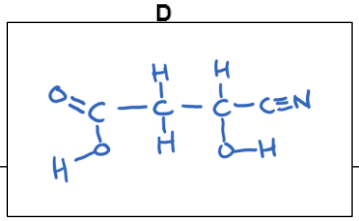


Fig. 1.1



(iv) Presence of the COOH group suppresses the dissociation of HCN, reducing the concentration of $:CN^-$ ion drastically/ the reactive intermediate is protonated by the COOH group instead, so there is no more $:CN^-$ ion present to react with the carbonyl carbon [1].

(v) $:CN^-$ reacts with the trigonal planar carbonyl carbon with equal probability from above and below the plane.1m
This gives rise to a racemic mixture ½ (optical isomers in 1:1 ratio).
Biological system can only work with one of the optical isomer (enantiomer)/ msu be stereospecific. ½

(b) Compound **E** undergoes intramolecular condensation reaction under suitable conditions. Isomer **F** is produced instead of isomer **G**.

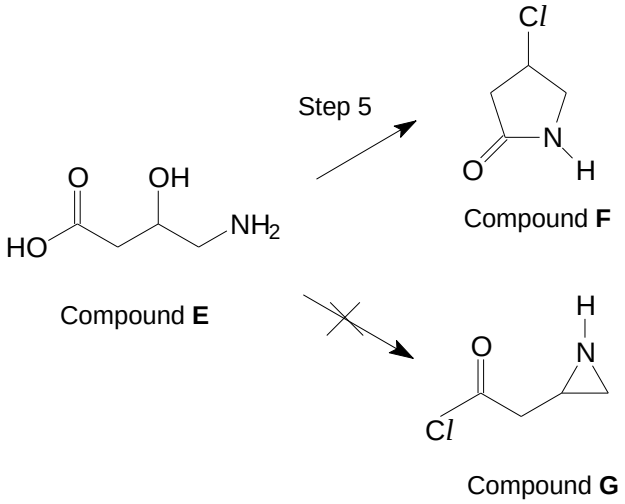


Fig. 3.2

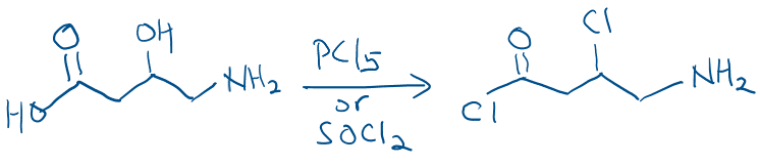
(i) Suggest the reagent and condition for step 5 in Fig. 3.2. [1]

(ii) Give two reasons why isomer **F** is preferentially formed. [2]

(iii) Explain why compound **F** is neutral. [2]

(i) $SOCl_2$, anhydrous / PCl_5, anhydrous 1 or 0

(ii)



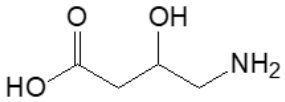
Carboxyl C in acyl chloride is more partial positive/more electron deficient than C in C–Cl hence more likely to be substituted by N. 1

Compound G has a 3 membered ring ½, this is significantly less stable than the 5 membered ring in compound F as the bond angle in 3 membered ring is 60° which is far less than the optimum bond½ angle of 109.5.predicted by VSEPR

(iii)	Lone pair of N is delocalised extensively½ into the carboxyl carbon due to the highly electronegative O½./ electron density at N is significantly reduced due to resonance with carboxyl carbon with highly electronegative O The lone pair½ is no longer available to receive a proton½, hence it is neutral.

(c) Table 3.3 shows the pK_a values of different functional groups present in compound **E** and GABA.

Table 3.3

	pK_{a1} of carboxyl group	pK_{a2} of amino group
$HOOCCH_2CH_2CH_2NH_2$ GABA	2.45	9.10
 Compound **E**	2.05	9.80

(i) Suggest a reason why pK_{a1} value of compound **E** is of lower value than pK_{a1} of GABA. [1]

(ii) Calculate the initial pH of 25.0 cm^3 of 0.050 mol dm^{-3} of compound **E**. [1]

(iii) Calculate the volumes of 0.10 mol dm^{-3} of NaOH required to form a buffer mixture with compound **E** at pH 2.05 and 9.80 respectively. [2]

(iv) Sketch the pH-volume added curve you would expect when compound **E** is titrated against 0.10 mol dm^{-3} of NaOH. Include the volume and pH values given or calculated in **(c)(ii)** and **(c)(iii)** as well as the volumes required for each equivalence point.

You may assume that the graph tends towards pH 13 upon addition of excess NaOH. [2]

(v) The working range for thymolphthalein is 9.3 to 10.5, comment on whether thymolphthalein is a suitable indicator for identifying the first endpoint. [1]

(vi) Write two equations to describe how the buffer mixture at pH 9.80 from **(c)(iii)** can act as buffer when small amount of H^+ or OH^- is added. [1]

[Total: 23]

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(i) The additional OH group exerts electron withdrawing effect ½ which further disperses the negative charge on the carboxylate ion½, making the conjugate base of E more stable than that from GABA, hence E undergoes greater acid dissociation with a smaller pK_{a1} value.

(ii) $$10^{-2.05} = \frac{[H^+]^2}{0.05}$$

$$[H^+] = 0.01257\ moldm^{-3}$$

$$pH = 1.9$$ 1m

(iii) At pH 2.05 and 9.80, the conjugate acid base pair of PK_{a1} and PK_{a2} are equal in concentration.

This occurs when the COOH group is half neutralised.

Amt of OH^- required = amt of –COOH

= ½ × 0.025 × 0.05

= 6.25 x 10^{-4}

Vol of NaOH required = 6.25 x 10^{-4} ÷ 0.1 × 1000

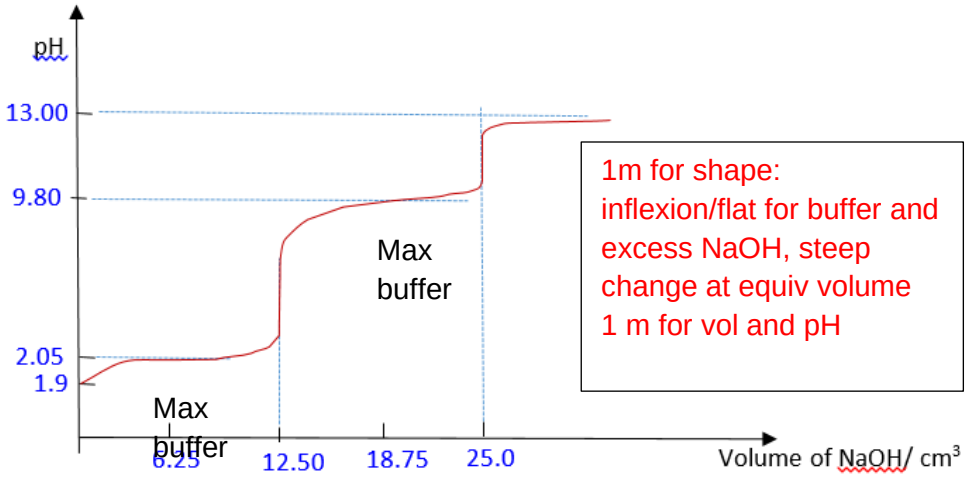
= 6.25 cm^3 1m

Vol of NaOH required for complete neutralisation of –COOH = 12.50 cm^3

Another 6.25 cm^3 more to neutralise half of $–NH_3^+$

So volume of NaOH required to form buffer at pH = 9.80 is 18.75 cm^3. 1m

(iv)



1m for shape: inflexion/flat for buffer and excess NaOH, steep change at equiv volume
1 m for vol and pH

(v) Thymolphathalein is not a suitable indicator½ for the first equivalence point as its working range is beyond the steep change in pH. ½

(vi) $^-OOCCH_2CH(OH)CH_2NH_3^+ + OH^- \rightarrow {}^-OOCCH_2CH(OH)CH_2NH_2 + H_2O$ ½

$^-OOCCH_2CH(OH)CH_2NH_3^+ + H^+ \rightarrow HOOCCH_2CH(OH)\ CH_2NH_3^+$ ½

Section B

Answer **one** question from this section.

4 **(a)** State the electronic configuration of chromium. [1]

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$ [1]

(b) Chromium(VI) ions commonly exist as oxo-anions such as CrO_4^{2-}, which is yellow in color and $Cr_2O_7^{2-}$,which is orange.

(i) Explain why chromium(VI) ions exist as oxo-anions instead of $[Cr(H_2O)_6]^{6+}$. [1]

(ii) Write the equation for the conversion of CrO_4^{2-} to $Cr_2O_7^{2-}$ in acidic medium. Predict the observation when NaOH is added to this solution at equilibrium. [2]

Cr^{6+} has high charge/size [½] and thus undergoes hydrolysis [½] in water to form a $Cr_2O_7^{2-}$ / is able to polarise the electron cloud of oxygen [½] to form an oxo-anion.

$2H^+ + 2CrO_4^{2-} \rightleftharpoons Cr_2O_7^{2-} + H_2O$ [1]

OH^- will react with H^+, hence the $[H^+]$ will decrease, POE will shift LHS [½] to partially offset the decrease, resulting in yellow color of CrO_4^{2-} observed. [½]

(c) **E** is a hydrated salt containing 13.0 % of Cr, 27.0 % of H_2O and 60.0 % of Br by mass. When 0.400 g of **E** is dissolved in water, an octahedral complex cation is formed. When treated with aqueous silver nitrate, this solution **immediately** gives 0.188 g of cream precipitate.

(i) Calculate the mole ratio of Cr: H_2O: Br in the hydrated salt **E**. [1]

(ii) Identify the cream precipitate and hence, determine the formula of the complex cation formed when **E** is dissolved in water [2]

(iii) Draw the structure of the complex cation present in **E**, showing clearly how the ligands are arranged around chromium cation. Indicate the overall charge of this complex ion. [1]

C(i)	**Cr**	**H_2O**	**Br**
% by mass	13.0	27.0	60
No. of moles	0.25	1.5	0.75
Mole ratio	1	6	3 **[1]**
Formula	$Cr(H_2O)_6(Br)_3$		

C(ii) Cream precipitate: AgBr [1]

No. of moles of AgBr = 0.188 / (108 + 79.9) = 0.00100 mol
No. of moles of **E** = 0.400 / (52.0 + 6(18.0) + 3(79.9)) = 0.00100 mol

No. of moles of Br^- anion : No of moles of **E**
1 : 1

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(d) When a current of 1.0 A was passed through aqueous potassium maleate ($KO_2CCH=CHCO_2K$) for 15 minutes, it was found that 110 cm^3 H_2, measured at r.t.p, was collected at the cathode. The following reaction took place.

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

Ethyne, C_2H_2, and CO_2 gas were produced at the anode. In order to determine the stoichiometry of the anode reaction, the volume of the gases collected at the anode was measured. The anode gas was first passed through aqueous NaOH before being collected in a gas syringe. The following data was collected:

- mass of bottle containing NaOH before experiment = 10.501 g
- mass of bottle containing NaOH after experiment = 10.904 g
- initial reading on syringe = 10.0 cm^3
- final reading on syringe = 120.0 cm^3

(i) Using the data *obtained from the cathode* and the *Data Booklet*, calculate a value for Faraday constant.

[2]

(ii) Calculate the volume of CO_2 produced at the anode, assuming r.t.p conditions.

[2]

(iii) Hence, state the volume of ethyne gas and suggest an ionic equation for the reaction that occurred at the anode.

[2]

(i) $Q = It = n_eF$

$Q = 1.0 \times 15 \times 60 = 900$ C [1]

$n(H_2) = 110 / 24000 = 0.00458$ mol

$n(e^-) = 2\ n(H_2) = 0.00917$ mol

$F = 900/(0.00917) = 98100$ (3sf) [1]

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(e) Ethanal used to be manufactured from ethyne. These days, ethene is being used as the reactant instead. Widely known as the Wacker-Tsuji Oxidation, ethene and oxygen are bubbled together through an aqueous solution containing $CuCl_2$ and $PdCl_2$ catalysts:

$$CH_2{=}CH_2 + \tfrac{1}{2}O_2 \xrightarrow[CuCl_2]{PdCl_2} CH_3CHO$$

The Wacker-Tsuji Oxidation is also useful for the synthesis of ketone:

$$RCH{=}CH_2 + \tfrac{1}{2}O_2 \xrightarrow[CuCl_2]{PdCl_2} RCOCH_3$$

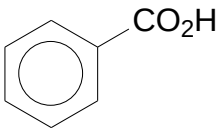
Compound **A**, C_9H_{10}, is used as a reactant in the Wacker-Tsuji oxidation reaction to give compound **B**, $C_9H_{10}O$. **B** gives a yellow precipitate when warmed with aqueous alkaline I_2. When **B** is reacted with $LiAlH_4$ in dry ether, compound **C** is formed. **A**, **B** and **C** all react with hot acidified $KMnO_4$ to give compound **D**, $C_7H_6O_2$.

Suggest the structures of Compound **A** to **D** and explain the reactions described.

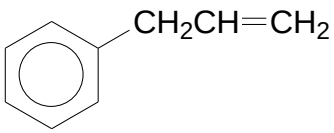
[6]

Clues	**Deductions**
Compound **A has molecular** formula C_9H_{10}	**A** contains benzene **A** has degree of unsaturation =5
Since **A** undergo Wacker-Tsuji oxidation	It must contain a terminal alkene
B gives a yellow precipitate when warmed with aqueous alkaline I_2.	**B** is the product of Wacker-Tsuji oxidation and is a carbonyl compound. B must be a methyl carbonyl.
B is reacted with $LiAlH_4$ in dry ether	**B** undergo reduction
A, **B** and **C** all react with hot acidified $KMnO_4$	**A, B, C** all undergo side chain oxidation to give the same product **A, B, C** all have only 1 alkyl side chain.

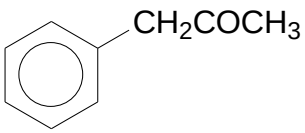
D must be the product of side chain oxidation:



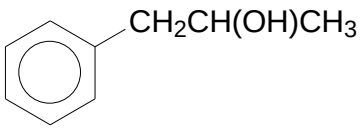
A:



B:

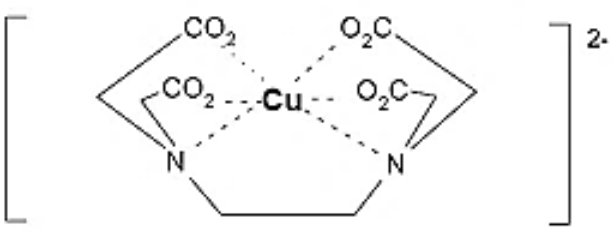


C:



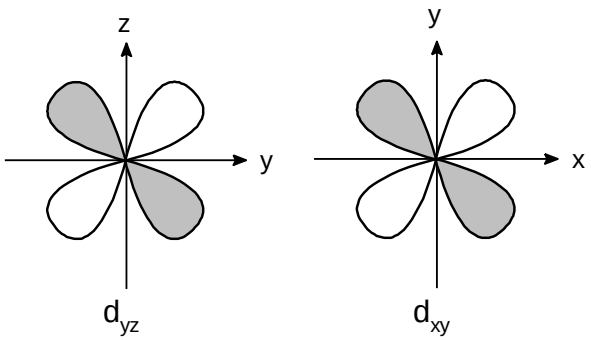
5 **(a)** Copper and its compounds have a wide variety of uses.
Copper-EDTA complexes are commonly used in cosmetics and it gives the blue colour in many shampoos.

The structure of the copper-EDTA complex is given below.



(i) State the electronic configuration of the copper ion in the copper-EDTA complex . [1]

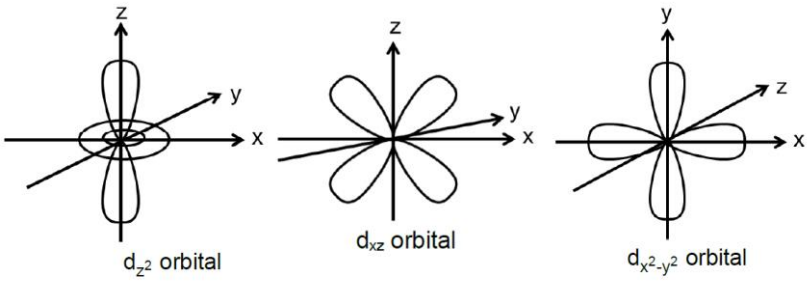
(ii) Two of the d orbitals are given below. Sketch the shapes of the other three d orbitals present in copper, labelling your orbitals clearly.



[2]

(iii) Explain why the copper-EDTA complex is blue. [3]

(i) Let oxidation number of Cu be x.
Since each carboxylate is a −1 charge
X+ (−4) = −2
X = +2
Cu^{2+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$



(ii)

3/3 (including label for orbitals and appropriate axis) –[2]

2/3 -[1] 1/3- [½] without 3d axis-0!!!

(iii) In the presence of EDTA ligands, the degenerate d-orbitals of the Cu^{2+} ion are **split into two different energy levels with a small energy gap, ΔE.** [1]
Electrons in the lower energy d-orbitals can **absorb light of a certain wavelength with energy corresponding to the energy gap, ΔE, and be promoted** to the higher energy d-orbitals. [1] **(d-d transition).**
The light not absorbed would be reflected and the colour of the complex is the **complementary of the wavelength absorbed**[1], giving rise to a colour observed

(iv) Cobalt and copper are both common transition elements.

Comment on the similarity of the atomic radii between cobalt and copper.

[1]

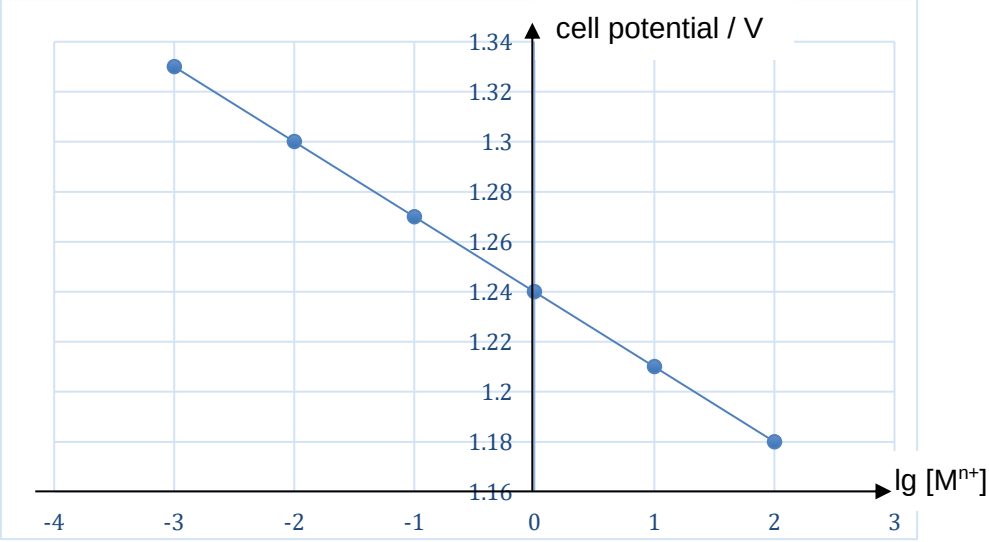
Nuclear charge increases from Co to Cu while **shielding effect also increases [½]** as electrons are added to the inner 3d subshell. As such, **nuclear attraction remains relatively constant [½]** and their atomic radii are similar.

(b) An experiment was set up to investigate how the cell potential of a cell containing a metal, M, in contact with an aqueous solution of its ions, $M^{n+}(aq)$, changed as $M^{n+}(aq)$ was diluted.
As a standard Hydrogen Electrode was not available, a half-cell consisting of Cl^-, ClO^- in alkaline medium under standard conditions was used to connect to the half-cell with M in contact with $M^{n+}(aq)$.

(i) Draw a fully labelled diagram of the electrochemical cell set-up as described above, in order to measure the changes in cell potential.

[3]

(ii) The cell potential was measured for various concentrations of $M^{n+}(aq)$ and the results of cell potential against log $[M^{n+}]$ obtained are plotted in the graph as shown below.



Given that the cell potential of a cell, E_{cell}, is related to the standard electrode potential, $E^{\ominus}_{cell}$, by the equation:

$E_{cell} = E^{\ominus}_{cell} - \frac{0.06 \lg[M^{n+}]}{n}$, use your graph to determine

(I) the charge, n, of the M^{n+} ions

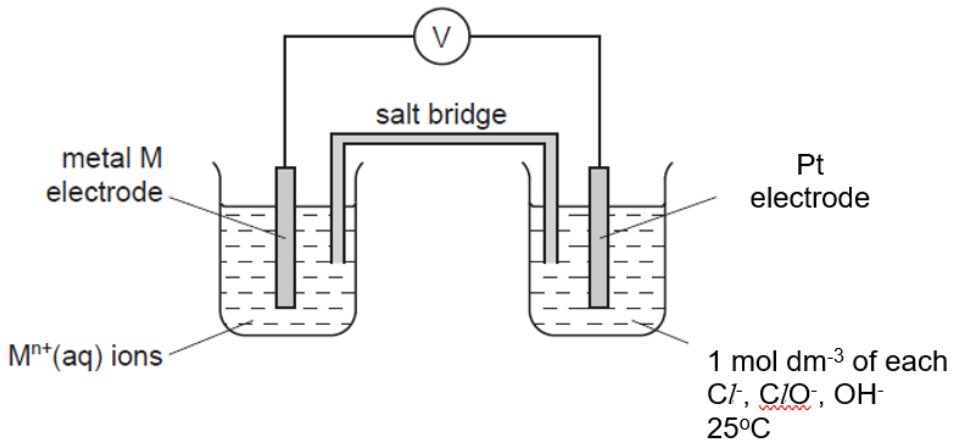
(II) the $E^{\ominus}_{cell}$

[2]

(iii) Given that the standard electrode potential for Cl^-, ClO^- in alkaline conditions is +0.80 V.

Calculate the standard electrode potential of the metal, M, and suggest its identity.

[2]



each electrode within half cell [½]
each correct label of species and concentration [½]
salt bridge [½]
voltmeter [½]
if battery use instead – max 1m

(ii) Gradient = −0.0300
– 0.06 / n = -0.0300
n = 2 [1]
$\log_{10}1 = 0$
y-intercept = 1.24 V [1] or uses equation to calculate

(iii) *1.24* = $E(ClO^-/Cl^-) + E_{ox}(M/M^{2+})$

= +0.80 + $E_{ox}(M/M^{2+})$

($E_{ox}(M/M^{2+})$ = +0.44V [½])

$E(M^{2+}/M)$ = −0.44V [1]

M = Fe [1]

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(c) In the presence of HCl/O_4, alcohols react with nitriles to form *N*–alkylamides. This is known as the *Ritter reaction*, as shown in Fig. 5.1.

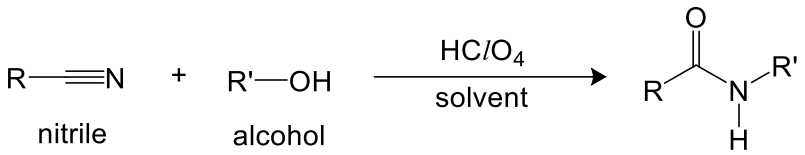


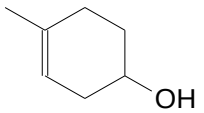
Fig. 5.1

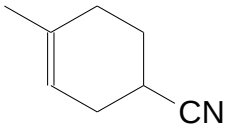
Compounds **A** and **B** react in the presence of HCl/O_4 to give compound **C** via the Ritter reaction.

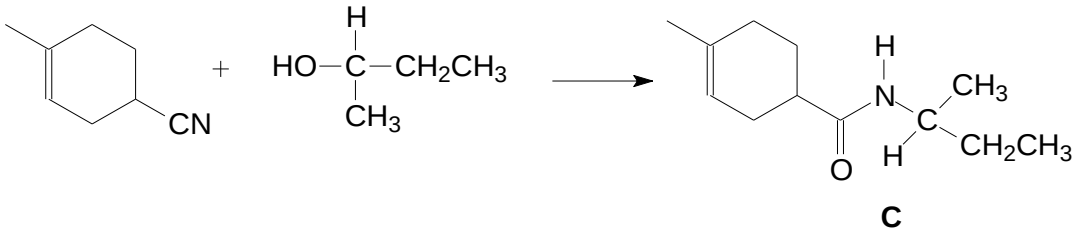
Compound **A** has the molecular formula $C_4H_{10}O$. When heated under reflux with acidified $K_2Cr_2O_7$, it gives a product that gives a yellow precipitate when warmed with aqueous alkaline iodine.

Compound **D** is a 6-membered ring molecule and has the molecular formula $C_7H_{12}O$. When heated with acidified $KMnO_4$, it forms $CH_3COCH_2CH_2COCH_2CO_2H$. **D** reacts with PCl_5 followed by hot ethanolic KCN to give **B**.

Suggest the structures of compounds **A** to **D** and explain the reactions described. [6]

Clue	Deductions
A has the molecular formula $C_4H_{10}O$ and undergo the Ritter reaction.	**A** must be an alcohol.
A react with hot acidified $K_2Cr_2O_7$ to give a product gives a yellow precipitate when warmed with aqueous alkaline iodine	**A** undergo oxidation to give 1° / 2° alcohol **A** must be methyl carbinol. **A**: $CH_3CH(OH)CH_2CH_3$ [1]
D has the molecular formula $C_7H_{12}O$.	**D** has two degree of unsaturation. DOU = $\frac{2n+2-(H+X)-N}{2}$ Where n = number of carbon. H = number of hydrogen X= number of halogen N = Number of nitrogen
D undergo oxidation to give $CH_3COCH_2CH_2COCH_2CO_2H$	Increase of 4 O upon oxidation. **D** must be a ring structure with an alkene. Making use of the formula of the product of D's oxidation: **D** must be  [1]

D reacts with gaseous HCl followed by hot ethanolic KCN to give **B**	**B** is formed from **D** undergoing two nucleophilic sub: 1) to give a RX and then 2) to give RCN.  **B**: [1]



C

From pattern given in question, C is deduced. [1]