1 (a) (i) Transition elements have variable oxidation states and form complex ions.

State **two** other typical chemical properties of a transition element.

1 Catalyst

2 form coloured compounds

[1]

(ii) Explain why transition elements have variable oxidation states.

(4)s and 3(d) sub-shells / orbitals are close in energy

可替换 Smilar / same [1]

(b) An aqueous solution of chromium(III) ions, Cr^{3+}, contains the $[Cr(H_2O)_6]^{3+}$ complex ion.

(i) Complete Figure 1.1 to show the electronic configuration for Cr^{3+}.

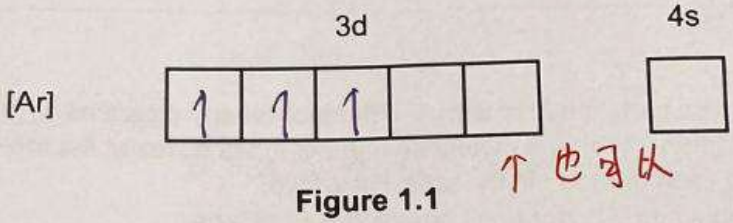


Figure 1.1

[1]

(ii) State the type of bonding that exists between H_2O and Cr^{3+} in $[Cr(H_2O)_6]^{3+}$.

dative / co-ordinate bond [1]

(c) Explain why transition elements form complex ions.

d orbitals that are energetically accessable

[1]

(d) $[Cr(H_2O)_6]^{3+}$ can be converted into the $[Cr(H_2O)_3(OH)_3]$ complex.

(i) Suggest a suitable reagent for this conversion. State the type of reaction.

reagent NaOH (aq) 可换 NH_3

type of reaction precipitation / ligand exchange / Acid-base

可以的

(ii) $[Cr(H_2O)_3(OH)_3]$ reacts with an excess of $NH_3(aq)$ to form $[Cr(NH_3)_6]^{3+}$.

Complete the equation for this reaction. State the type of reaction.

$[Cr(H_2O)_3(OH)_3]$ + ..6.NH3.. → ..[Cr(NH3)6]3+.. + 3H2O + 3OH-

type of reaction ..Ligand exchange..

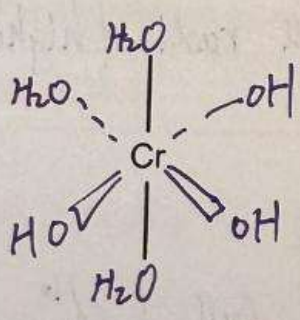
写 $[Cr(NH_3)_6(OH)_3]$ 也对

[2]

(e) $[Cr(H_2O)_3(OH)_3]$ shows stereoisomerism.

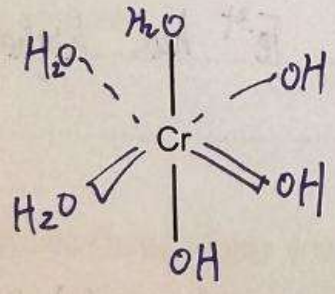
Draw three-dimensional diagrams in Figure 1.2 to suggest the **two** stereoisomers of $[Cr(H_2O)_3(OH)_3]$.

isomer 1



2 H2O . 2 OH at 180°

isomer 2



all H2O / OH- at 90°

Figure 1.2

[2]

(f) **(i)** An aqueous solution of iron(III) ions, Fe^{3+}, contains the $[Fe(H_2O)_6]^{3+}$ complex ion. This solution is acidic in a similar way to an aqueous solution of Al^{3+}.

Suggest why a solution of Fe^{3+} is acidic. Include an equation in your answer.

* Fe^{3+} undergo hydrolysis / weaken O-H / polarise O-H

* $[Fe(H_2O)_6]^{3+} \rightarrow [Fe(H_2O)_5OH]^{2+} + H^+$ [2]

(ii) An aqueous solution of iron(II) ions, Fe^{2+}, contains the $[Fe(H_2O)_6]^{2+}$ complex ion. This solution is also acidic.

Predict how the pH of 1.00 mol dm^{-3} Fe^{2+}(aq) differs from the pH of 1.00 mol dm^{-3} Fe^{3+}(aq). Explain your answer.

Fe^{3+} has lower pH

Fe^{3+} has higher charge / small radii / higher charge density [1]

(g) Suggest why solutions of silver(I) salts are colourless.

① d subshell / [redacted] is full / d^{10}

3 d orbital is full 无3H

② can't absorb light in the visible spectrum

no d-d transition / no electron transition [2]

(h) A mixture contains sodium ethanedioate, $Na_2C_2O_4$, ethanedioic acid dihydrate, $H_2C_2O_4 \cdot 2H_2O$, and an unreactive solid.

5.00 g of this mixture is dissolved in distilled water and made up to 500 cm^3 in a volumetric flask to form solution **A**.

Two different titration experiments are carried out using **A**.

In the first experiment, 25.0 cm^3 of **A** requires 21.80 cm^3 of acidified 0.0250 mol dm^{-3} MnO_4^-(aq) to reach the end-point.

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

In the second experiment, 25.0 cm^3 of **A** requires 13.60 cm^3 of 0.150 mol dm^{-3} OH^-(aq) to reach the end-point.

$$H_2C_2O_4 + 2OH^- \rightarrow C_2O_4^{2-} + 2H_2O$$

Calculate the percentage by mass of $Na_2C_2O_4$ in the mixture.

[M_r: $Na_2C_2O_4$, 134.0]

1' (Moles of MnO_4^- = $0.025 \times 0.02180 = 5.45 \times 10^{-4}$
Moles of $C_2O_4^{2-}$ = $2.5 \times 5.45 \times 10^{-4} = 1.3625 \times 10^{-3}$

1' (Moles of OH^- = $0.150 \times 0.0136 = 2.04 \times 10^{-3}$
Moles of $H_2C_2O_4$ = $\frac{1}{2} \times$ ↓ = 1.02×10^{-3}.

1' Moles of $Na_2C_2O_4$ = $1.3625 \times 10^{-3} - 1.02 \times 10^{-3} = 3.425 \times 10^{-4}$

1' { Moles of $Na_2C_2O_4$ = $3.45 \times 10^{-4} \times 20 = 6.85 \times 10^{-3}$
Mass of --- = ↓ × 134 = 0.9179

percentage by mass of $Na_2C_2O_4$ = 18.4 % [5]

% = 18.4 / 18.358 0

[Total: 20]

DO NOT WRITE IN THIS MARGIN

2 Group 2 carbonates decompose on heating to form the corresponding metal oxide and carbon dioxide.

(a) The mechanism for this decomposition involves the carbonate ion breaking down to form carbon dioxide and oxide ions.

Add **two** curly arrows to the carbonate ion in Figure 2.1 to suggest a mechanism for this decomposition.

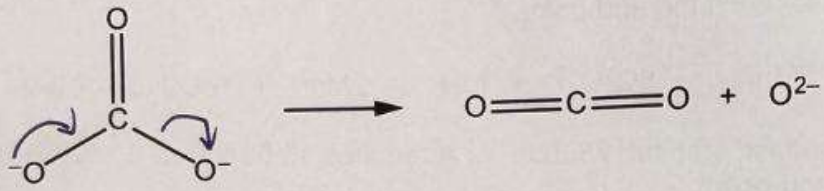


Figure 2.1

[1

(b) The radii of some cations are shown in Table 2.1.

Table 2.1

cation	Ca^{2+}	Cu^{2+}	Pb^{2+}
radius/nm	0.099	0.073	0.120

Use the data in Table 2.1 to predict the trend in thermal stability of the metal carbonates containing these cations.

Explain your answer.

$PbCO_3$ > $CaCO_3$ > $CuCO_3$

most stable — least stable

explanation ✱ Cation / Ionic radii increase

✱ less polarise CO_3^{2-}

(c) Suggest why the solubility of the Group 2 sulfates decreases down the group.

(1) both ΔH_{latt} , ΔH_{hyd} decrease / less exothermic

(2) ΔH_{hyd} changes more

(3) $\Delta H_{sol}^{\ominus}$ less negative

[3]

(d) Magnesium hydroxide, $Mg(OH)_2$, is sparingly soluble in water at 298 K.

(i) Write the expression for the solubility product, K_{sp}, of $Mg(OH)_2$. State the units for K_{sp}.

$K_{sp} = [Mg]^{2+}[OH^-]^2$

units $mol^3 dm^{-9}$

[2]

(ii) A saturated solution of $Mg(OH)_2$ has a pH of 10.35 at 298 K.

Calculate the concentration of hydroxide ions, OH^-, in mol dm^{-3}, in this solution.

$[H^+] = 10^{-10.35} = 4.47 \times 10^{-11}$

$[OH^-] = \frac{K_w}{[H^+]} = 2.24 \times 10^{-4}$

concentration of OH^- = 2.24×10^{-4} mol dm^{-3} [1]

(iii) Use your answers to **2(d)(i)** and **2(d)(ii)** to calculate the value of K_{sp} for $Mg(OH)_2$.

$K_{sp} = (0.5 \times 2.24 \times 10^{-4}) \times (2.24 \times 10^{-4})^2$

$= 5.61 \times 10^{-12}$

K_{sp} for $Mg(OH)_2$ = 5.61×10^{-12} [1]

[Total: 10]

3 (a) Ethanal, CH_3CHO, reacts with methanol, CH_3OH, under acidic conditions to form compound **B**, as shown in reaction 1.

reaction 1 $$CH_3CHO + 2CH_3OH \xrightarrow{H^+} \underset{\textbf{B}}{CH_3CH(OCH_3)_2} + H_2O$$

The initial rate of reaction is investigated using different starting concentrations of CH_3CHO, CH_3OH and H^+. The results obtained are shown in Table 3.1.

Table 3.1

experiment	$[CH_3CHO]$ / mol dm^{-3}	$[CH_3OH]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.500	0.040	0.100	2.500×10^{-3}
2	0.500	0.060	0.100	3.750×10^{-3}
3	0.250	0.120	0.300	1.125×10^{-2}
4	0.250	0.120	0.400	1.500×10^{-2}

(i) Use the information in Table 3.1 to deduce the rate equation for this reaction.

Explain your reasoning. State clearly which experiments you use in your explanation.

Exp 1 & 2: $[CH_3OH] \times 1.5$ rate $\times 1.5$ $[CH_3OH]$ first order

Exp 3 & 4: $[H^+] \times 1.33$ rate $\times 1.33$ $[H^+]$ first order

Exp 2 & 3: $[CH_3CHO] \times 0.5$ $[CH_3OH] \times 2$ $[H^+] \times 3$ rate $\times 3$ $[CH_3CHO]$ first order

rate = $k[CH_3CHO][CH_3OH][H^+]$

(ii) State the units of the rate constant, *k*, for this reaction.

$mol^{-2}\ dm^6\ s^{-1}$

(iii) Another experiment to investigate reaction 1 is carried out as shown in Table 3.2.

Table 3.2

experiment	$[CH_3CHO]$ / mol dm^{-3}	$[CH_3OH]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}
5	0.250	0.250	0.250

Calculate the initial rate of experiment 5.

initial rate = ...0.0195..... mol dm^{-3} s^{-1} [1]

(b) The reaction of propanone, CH_3COCH_3, with bromine, Br_2, in the presence of an acid catalyst is shown in reaction 2.

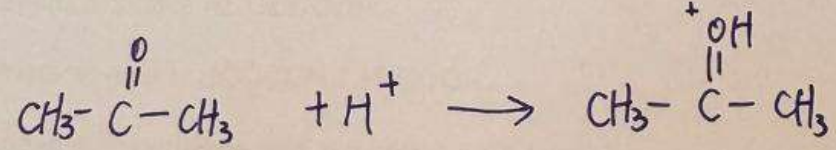
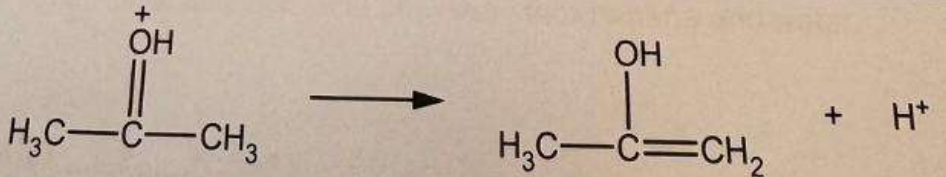
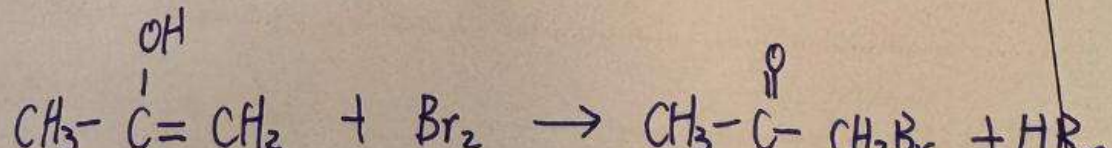
reaction 2 $\quad CH_3COCH_3 + Br_2 \xrightarrow{H^+} CH_3COCH_2Br + HBr$

The rate of reaction is first order with respect to $[CH_3COCH_3]$ and first order with respect to $[H^+]$ under certain conditions.

A three-step mechanism for reaction 2 is suggested.

Complete Table 3.3 to suggest steps 1 and 3 of the mechanism.

Table 3.3

step 1 (fast)	
step 2 (slow)	
step 3 (fast)	

(c) Catalysts can be described as homogeneous or heterogeneous.

Describe the mode of action of a heterogeneous catalyst.

• adsorb

• bond weaken

• products desorbed

[2]

[Total: 10]

4 **(a)** State what is meant by partition coefficient, K_{pc}.

ratio of the concentrations between two immiscible solvents at equilibrium [1]

(b) Ethanedioic acid, $H_2C_2O_4$, is more soluble in water than in the organic solvent ethoxyethane.

2.70 g of ethanedioic acid is shaken with a mixture of 50 cm^3 of ethoxyethane and 50 cm^3 of water at 298 K and left until there is no further change in concentrations.

The ethoxyethane layer requires 16.5 cm^3 of 0.200 mol dm^{-3} NaOH(aq) for complete neutralisation.

$$H_2C_2O_4 + 2NaOH \rightarrow Na_2C_2O_4 + 2H_2O$$

Calculate the partition coefficient, K_{pc}, for ethanedioic acid between ethoxyethane and water.

Initial Moles of $(COOH)_2$ = 2.7/90 = 0.03

Moles of NaOH = 0.0165 × 0.2 = 0.00330

ether: $n[(COOH)_2]$ = 0.00662/2 = 0.00165

H_2O: $n(COOH)_2$ = 0.03 − 0.00165 = 0.02835

K_{pc} = 0.0582 [3]

(c) The formula of ethanedioic acid is HOOCCOOH.

The formula of butanedioic acid is $HOOCCH_2CH_2COOH$.

Both acids are soluble in ethoxyethane and in water.

Suggest how the value of K_{pc} of butanedioic acid between ethoxyethane and water compares to the value of K_{pc} for ethanedioic acid between ethoxyethane and water.

Explain your answer.

Kpc would be higher

butanedioic acid is less polar

less soluble in H_2O

[Tota

5 (a) Define standard electrode potential, $E^{\ominus}$, including a description of standard conditions.

emf between a SHE and another electrode under standard conditions of 1 atm, 298 K all solutions being 1 M [2]

(b) Table 5.1 shows the standard electrode potentials for three redox systems.

Table 5.1

redox system	electrode reaction	$E^{\ominus}$/V
1	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
2	$NO_3^- + 10H^+ + 8e^- \rightleftharpoons NH_4^+ + 3H_2O$	+0.87
3	$Zn^{2+} + 2e^- \rightleftharpoons Zn$	–0.76

(i) Use the information in Table 5.1 to write equations for **two** reactions that are feasible.

Explain why these reactions are feasible.

equation 1 $NO_3^- + 10H^+ + 4Zn \rightarrow NH_4^+ + 3H_2O + 4Zn^{2+}$

equation 2 $Zn + 2Fe^{3+} \rightarrow Zn^{2+} + 2Fe^{2+}$

explanation E_{cell} ? 0

[3]

(ii) Suggest why the feasible reactions in **5(b)(i)** may **not** take place under standard conditions.

high E_a [1]

7

(iii) An electrochemical cell is set up to measure $E^{\ominus}$ for redox system 2 in Table 5.1.

Complete Figure 5.1 to show a labelled diagram of this electrochemical cell.

Include all necessary substances and relevant pieces of apparatus needed to measure $E^{\ominus}$.

It is **not** necessary to state the conditions used.

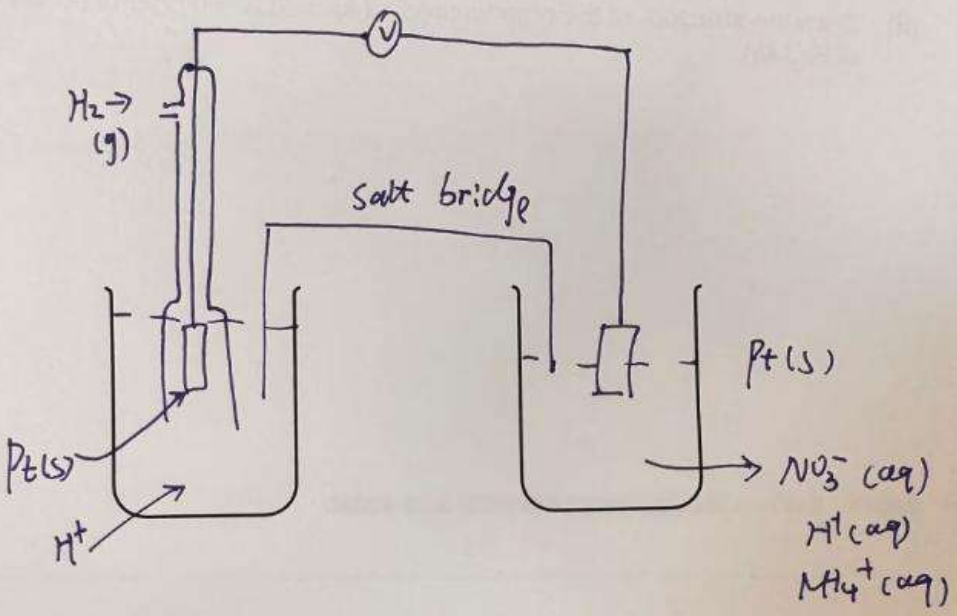


Figure 5.1

[3]

(c) A different electrochemical cell is set up. The cell reaction for this electrochemical cell is shown.

$$Cr + 3Mn^{3+} \rightarrow 3Mn^{2+} + Cr^{3+} \qquad \Delta G^{\ominus} = -645.6\,kJ\,mol^{-1}$$

Calculate the standard cell potential, $E^{\ominus}_{cell}$, for this cell reaction.

$\Delta G^{\ominus} = -nEF$

$E = 2.23$

$E^{\ominus}_{cell}$ = 2.23 V [2]

2sf min

[Total: 11]

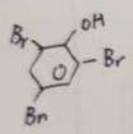
6 (a) Phenol reacts with $Br_2(aq)$.

(i) State **all** the expected observations when $Br_2(aq)$ is added dropwise to a solution of phenol.

white ppt

solution decolourise [1]

(ii) Draw the structure of the organic product formed when phenol reacts with an excess of $Br_2(aq)$.



[1]

(b) Explain the relative acidities of phenol and water.

lp on O delocalised into the ring

weaken O–H, so H^+ easily lost [2]

) Compound **C** can undergo both addition and condensation polymerisation.

C

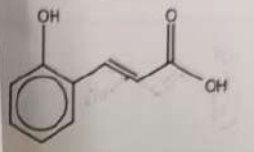
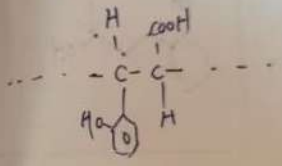


Figure 6.1

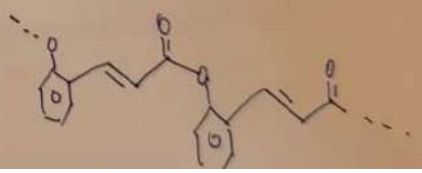
(i) Draw **one** repeat unit of the addition polymer formed from **C**.



[1]

(ii) Draw **two** repeat units of the condensation polymer formed from **C**.

The new functional group formed should be displayed.



(d) **C** can react with $LiAlH_4$. **C** can also react with an excess of $H_2(g)$ with a nickel catalyst.

Draw the structure of the organic product formed in each reaction in Figure 6.2.

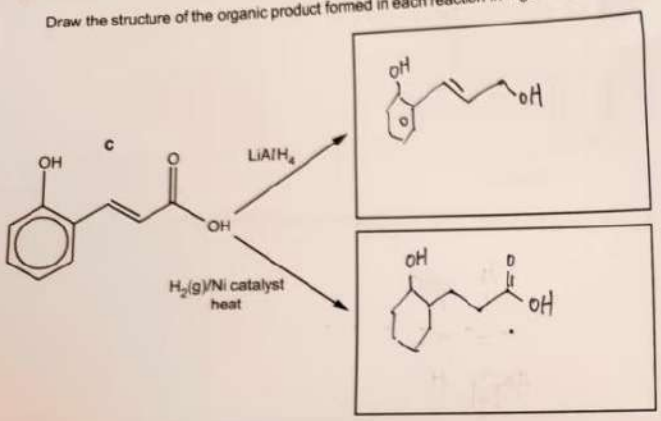


Figure 6.2

[2]

(e) Compound **F** can be synthesised from phenol in three steps, as shown in Figure 6.3.

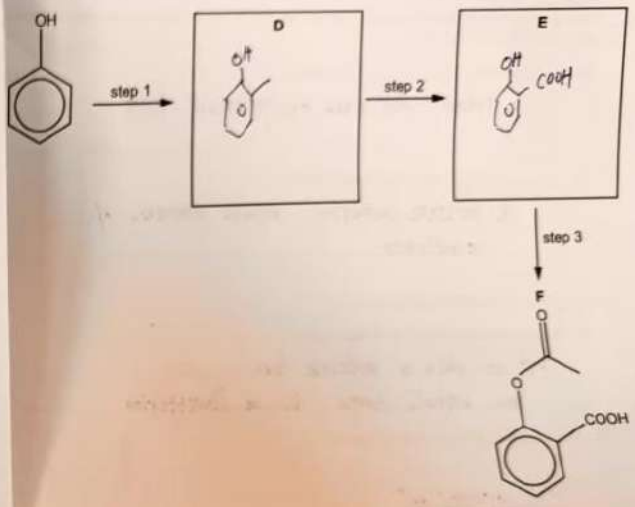


Figure 6.3

(i) Draw the structures of compounds **D** and **E** in the boxes in Figure 6.3. [2]

(ii) Suggest reagents and conditions for steps 1 to 3 in Figure 6.3.

step 1 CH_3Cl $AlCl_3$

step 2 hot $KMnO_4$ (H^+)

step 3 CH_3COCl

7 (a) Alanine, $CH_3CH(NH_2)COOH$, is an amino acid that contains a chiral centre.

Different synthetic routes to produce alanine can lead to the formation of an optically active sample or a racemic mixture.

(i) Describe what is meant by optically active.

rotate the plane of polarised light [1]

(ii) Describe what is meant by racemic mixture.

a mixture containing equal amounts of enantiomer [1]

(b) Alanine has an isoelectric point of 6.11.

(i) Explain what is meant by isoelectric point.

pH at which a molecule has no overall charge / is a zwitterion [1]

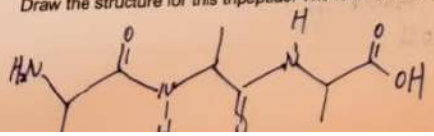
(ii) Draw the structure of alanine at pH 10.

$CH_3CH(NH_2)COO^-$

[1]

(c) Alanine molecules can react together to form the tripeptide Ala–Ala–Ala.

Draw the structure for this tripeptide. The functional groups formed should be displayed.



(d) Compound **J** can be synthesised from alanine in three steps, as shown in Figure 7.1.

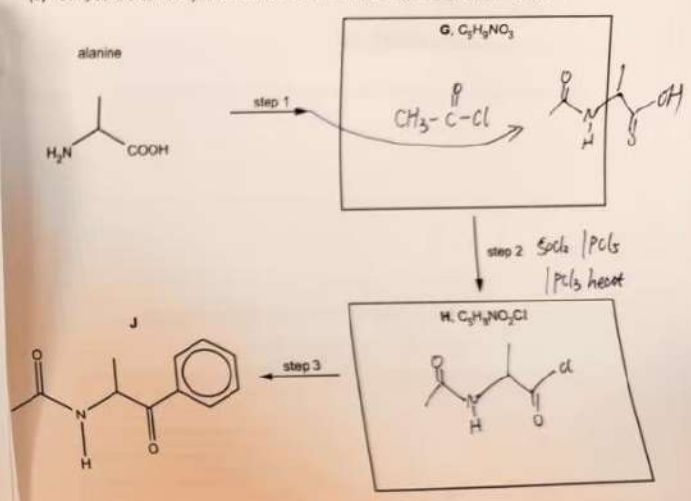


Figure 7.1

(i) Draw the structures of compounds **G** and **H** in the boxes in Figure 7.1. [2]

(ii) Suggest reagents and conditions for steps 1 to 3 in Figure 7.1.

step 1 CH_3COCl

step 2 $SOCl_2$

step 3 Cl_2 cat $AlCl_3$ [3]

[Total: 1

8 (a) Give the full name of the substance used ... shift measurements.

Tetramethylsilane [1]

(b) Compound **K** is analysed by carbon-13 NMR and proton (^{1}H) NMR spectroscopy in D_2O.

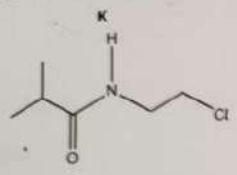


Figure 8.1

(i) Predict the number of peaks in the carbon-13 NMR spectrum of **K**.

5 [1]

(ii) The proton (^{1}H) NMR spectrum of **K** in D_2O shows four peaks, for the proton environments labelled **w**, **x**, **y** and **z** on the structure of **K** in Figure 8.2.

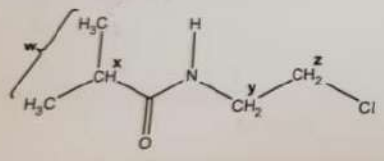


Figure 8.2

Complete Table 8.1 to identify the splitting patterns for proton environments **w**, **x**, **y** and **z**.

Table 8.1

proton environment	name of splitting pattern
w	doublet
x	multiplet
y	triplet
z	triplet

[2]

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN

(iii) A separate sample of **K** is dissolved in $CDCl_3$ and analysed using proton (^{1}H) NMR spectroscopy.

The proton (^{1}H) NMR spectrum of **K** dissolved in $CDCl_3$ contains one more peak than the spectrum of **K** dissolved in D_2O.

Explain why there is one more peak, and suggest the chemical shift range in which it occurs.

δ 3-12
(N-H peak appear)
no H exchange with D_2O

chemical shift range δ = 5-12 ppm [2]

Table 8.2

environment of proton	example	chemical shift range δ / ppm
alkane	$-CH_3$, $-CH_2-$, $>CH-$	0.9–1.7
alkyl next to C=O	$CH_3-C=O$, $-CH_2-C=O$, $>CH-C=O$	2.2–3.0
alkyl next to aromatic ring	CH_3-Ar, $-CH_2-Ar$, $>CH-Ar$	2.3–3.0
alkyl next to electronegative atom	CH_3-O, $-CH_2-O$, $-CH_2-Cl$	3.2–4.0
attached to alkene	$=CHR$	4.5–6.0
attached to aromatic ring	H–Ar	6.0–9.0
aldehyde	HCOR	9.3–10.5
alcohol	ROH	0.5–6.0
phenol	Ar–OH	4.5–7.0
carboxylic acid	RCOOH	9.0–13.0
alkyl amine	R–NH–	1.0–5.0
aryl amine	Ar–NH_2	3.0–6.0
amide	RCONHR	5.0–12.0

(c) Compound **K** reacts with an excess of hot NaOH(aq).

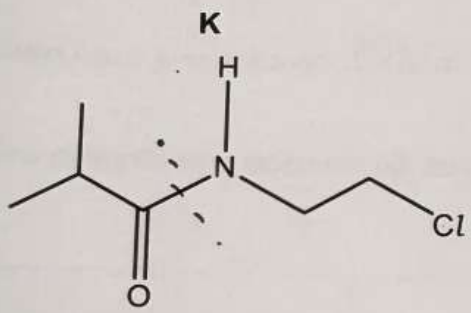
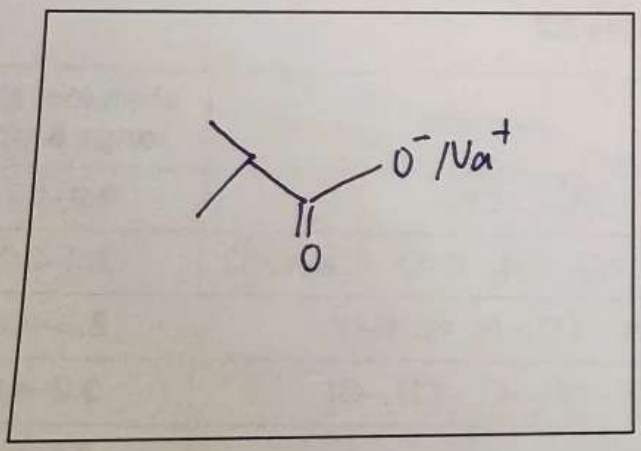
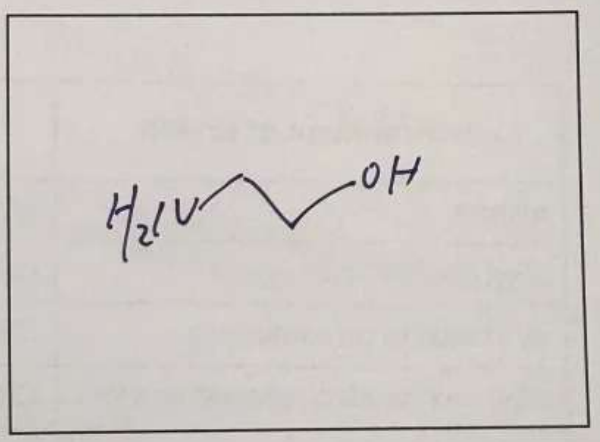


Figure 8.3

The products are isolated from the reaction mixture at pH 10.

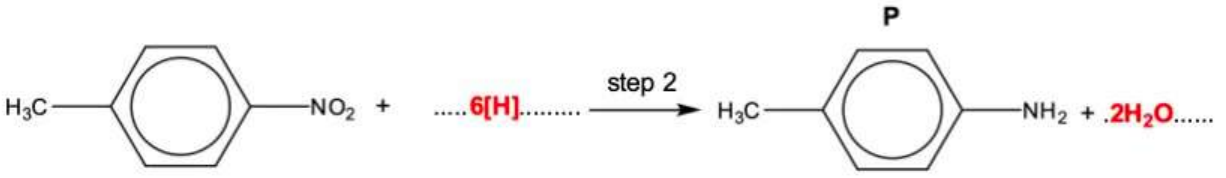
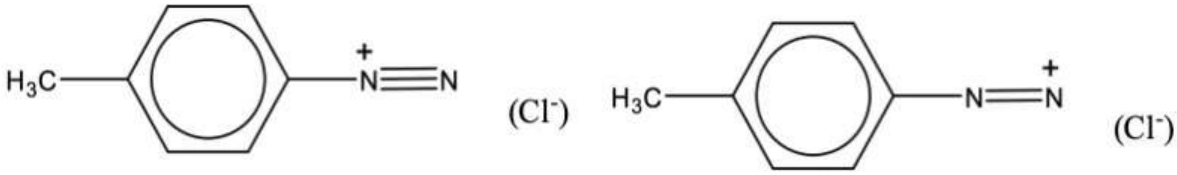
Draw the structures of the **two** organic products of the complete alkaline hydrolysis of **K**.

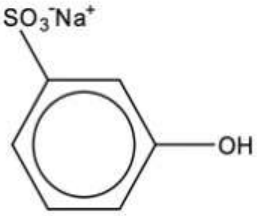




[2]

[Total: 8]

9(b)(i)	**M1** step 1 conc. HNO_3 **AND** conc. H_2SO_4 [1] **M2** step 2 Sn **AND** conc. HCl [1]	2
9(b)(ii)	 [1]	1
9(c)(i)	 [1]	1

Question	Answer	Marks
9(c)(ii)	**M1** step 1 $NaNO_2$ & HCl / HNO_2 **AND** 10 °C [1] **M2** step 2 alkaline / NaOH **AND**  [1]	2
		10