AQA

ASSESSMENT and QUALIFICATIONS ALLIANCE

Mark scheme June 2002

GCE

Chemistry

Unit CHM4

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Kathleen Tattersall: *Director General*

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SECTION A

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

1 Iodine and propanone react in acid solution according to the equation

$$I_2 + CH_3COCH_3 \rightarrow CH_3COCH_2I + HI$$

The rate equation for the reaction is found to be

$$\text{rate} = k\,[CH_3COCH_3][H^+]$$

(a) Deduce the order of reaction with respect to iodine and the overall order of reaction.

Order with respect to iodine ..... 0 (1) .....

Overall order ..... 2 (1) .....

(2 marks)

(b) At the start of the experiment, the rate of reaction was found to be 2.00×10^{-5} mol dm^{-3} s^{-1} when the concentrations of the reactants were as shown below.

Reactant	Concentration/mol dm^{-3}
CH_3COCH_3	1.50
I_2	2.00×10^{-2}
H^+	3.00×10^{-2}

Use these data to calculate a value for the rate constant and deduce its units.

Rate constant ..... $k = \frac{2 \times 10^{-5}}{(1.5)(3 \times 10^{-2})} = 4.4(4) \times 10^{-4}$ (1) .....

..... (1) .....

Units ..... $mol^{-1}\ dm^3\ s^{-1}$ (1) .....

(3 marks)

(c) How can you tell that H^+ acts as a catalyst in this reaction?

appears in rate eqn (or implied by mention of concentration or order) (1)

does not appear in (stoichiometric/overall) equation (1)

.....

(2 marks)

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(d) Calculate the initial rate of reaction if the experiment were to be repeated at the same temperature and with the same concentrations of iodine and propanone as in part (b) but at a pH of 1.25

$pH = -\log_{10}[H^+]$ (1)

$= 1.25$

$[H^+] = 0.056(2)$ (1)

$\therefore$ rate $= (4.44 \times 10^{-4}) \times (1.50) \times (0.0562)$

$= 3.75 \times 10^{-5}$ (1) (mol dm^{-3} s^{-1})

(3.7 – 3.8)

(3 marks)

(can score all 3 conseq on k from part (b))

10

TURN OVER FOR THE NEXT QUESTION

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2 Acid **X** reacts with methanol to form ester **Y** according to the following equation.

$$\begin{array}{l}CH_2COOH\\|\\CH_2COOH\end{array} + 2CH_3OH \rightleftharpoons \begin{array}{l}CH_2COOCH_3\\|\\CH_2COOCH_3\end{array} + 2H_2O \qquad \Delta H^{\ominus} = -15\ kJ\ mol^{-1}$$

acid **X** ester **Y**

A mixture of 0.25 mol of **X** and 0.34 mol of methanol was left to reach equilibrium in the presence of a small amount of concentrated sulphuric acid. The equilibrium mixture thus formed contained 0.13 mol of **Y** in a total volume of V dm^3.

(a) Name **X**.

(1, 4 –) butan(e) dioic acid (1) *(1 mark)*

but penalize wrong numbers

NOT dibutanoic butane dicarboxylic ethane dicarboxylic

(b) Using **X** to represent the acid and **Y** to represent the ester, write an expression for the equilibrium constant, K_c, for this reaction.

$$K_c = \frac{[Y][H_2O]^2}{[X][CH_3OH]^2}$$

must be [ ] (1) *(1 mark)*

if K_c expression wrong lose units mark in (e) also

(c) Calculate the number of moles of **X**, the number of moles of methanol and the number of moles of water in the equilibrium mixture.

Moles of X 0·25 − 0·13 = 0·12 (1)

Moles of methanol 0·34 − 0·26 = 0·08 (1)

Moles of water 0·26 (1)

(3 marks)

(d) State why the volume V need not be known in calculating the value of K_c for the reaction.

Equal no moles on each side of equation (1)

OR V cancels (provided not incorrectly qualified)

(1 mark)

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(e) Calculate the value of K_c for this reaction and deduce its units.

Calculation $K_c = \dfrac{\left(\frac{0.13}{(V)}\right)\left(\frac{0.26}{(V)}\right)^2}{\left(\frac{0.12}{(V)}\right)\left(\frac{0.08}{(V)}\right)^2}$ (1)

$= 11(.4)$ (1)

Units of K_c none (1)

↖ but lose this mark if K_c wrong even if none given.

(3 marks)

Can score all 3 conseq on (b) and (c)

If different values from (c) used, allow units only (conseq on correct K_c)

(f) State the effect, if any, of increasing the temperature on the value of K_c

decrease (1)

(1 mark)

10

TURN OVER FOR THE NEXT QUESTION

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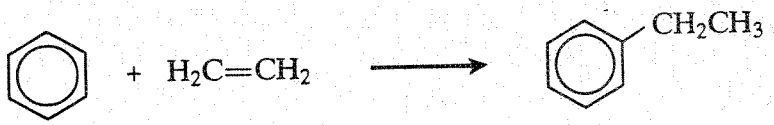
3 Ethylbenzene is made by the reaction shown below.



(a) Identify two other substances required as catalysts in this preparation.

Substance 1 HCl or HBr (1)

Substance 2 $AlCl_3$ / $AlBr_3$ / $FeCl_3$ / $FeBr_3$ (1)

(2 marks)

(b) Write an equation for the reaction of these two substances with ethene to form the reactive intermediate involved in the formation of ethylbenzene.

$H_2C=CH_2 + HCl + AlCl_3 \rightarrow CH_3CH_2^{\oplus} + AlCl_4^{\ominus}$ (1)

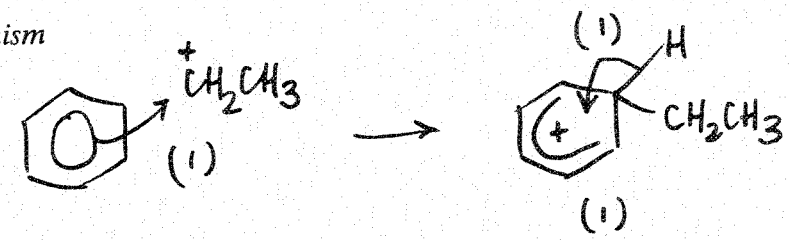
(1 mark)

(allow 2 equations)

(c) Name and outline a mechanism for the reaction between this reactive intermediate and benzene.

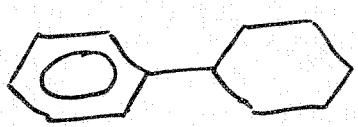
Name of mechanism electrophilic substitution (1)

Mechanism



(4 marks)

(d) Draw the structure of the product formed in a similar reaction between benzene and cyclohexene.



(1)

(1 mark)

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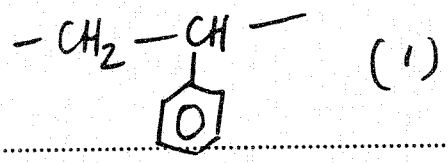
(e) Ethylbenzene is used to make phenylethene which can be polymerised to form poly(phenylethene). Name this type of polymerisation and draw the structure of the repeating unit in the polymer.

Type of polymerisation addition (1)



Repeating unit (1)

(2 marks)

10

TURN OVER FOR THE NEXT QUESTION

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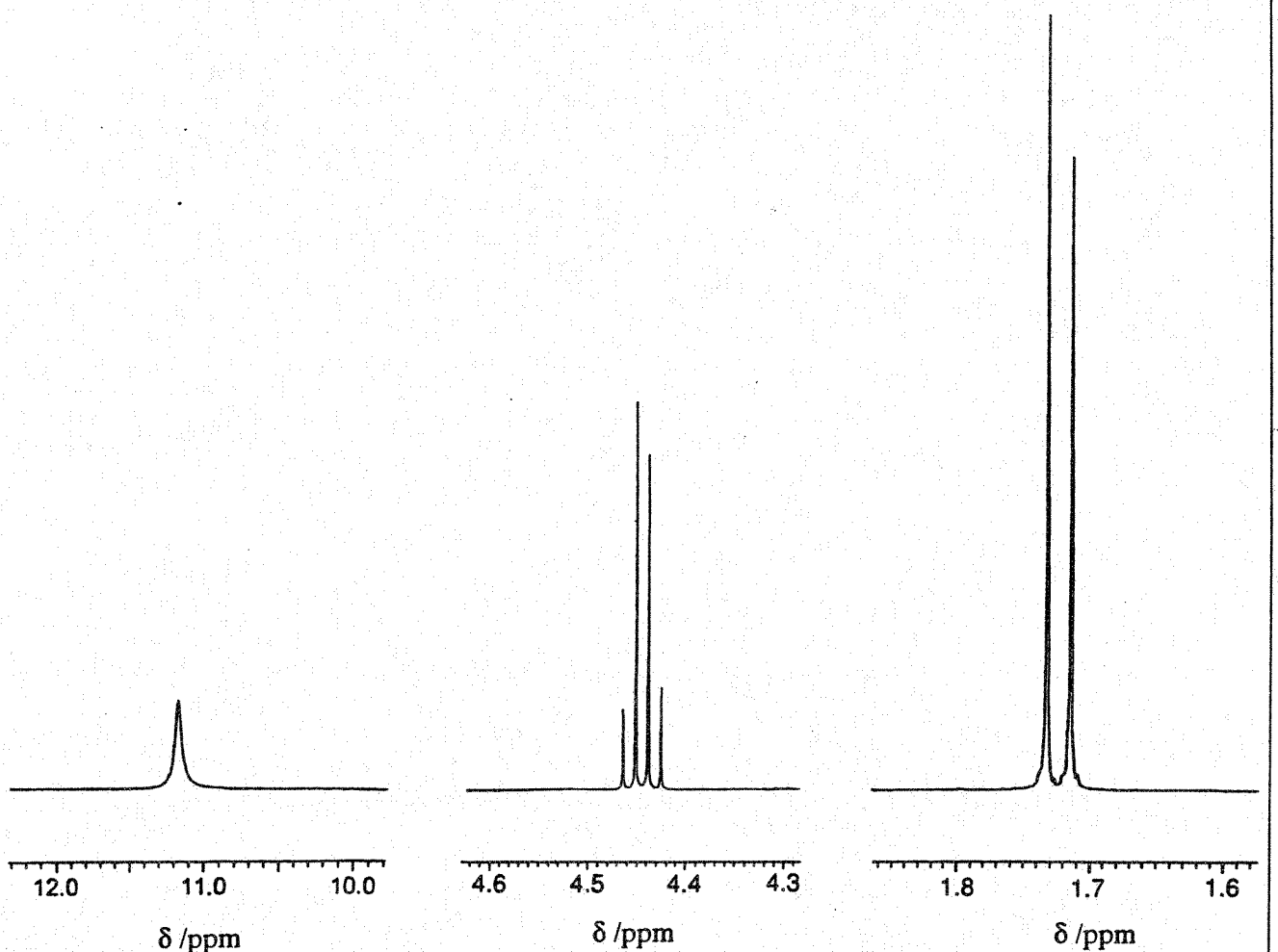
4 Three sections of the proton n.m.r. spectrum of $CH_3CHClCOOH$ are shown below.



(a) Name the compound $CH_3CHClCOOH$

2-chloropropanoic acid (1)

(1 mark)

(b) Explain the splitting patterns in the peaks at δ 1.72 and δ 4.44

δ 1.72 Doublet ∴ next to CH (1)

δ 4.44 Quartet ∴ next to CH_3 (1)

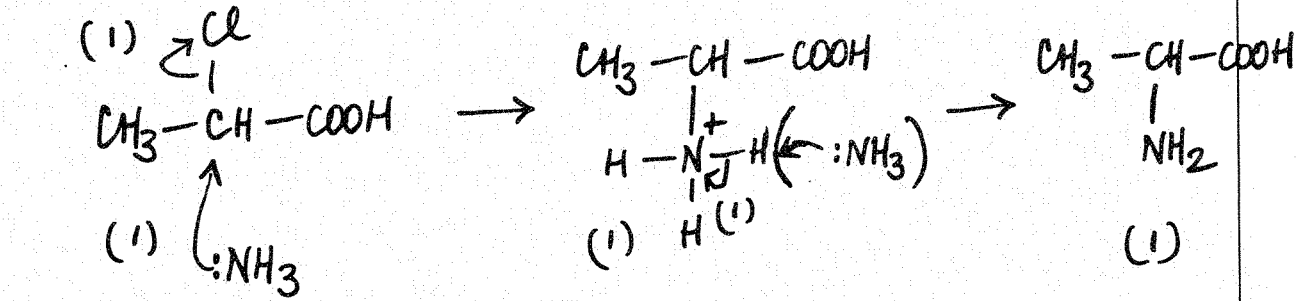
(2 marks)

(c) Predict the splitting pattern that would be seen in the proton n.m.r. spectrum of the isomeric compound $ClCH_2CH_2COOH$

Two triplets (1)

(1 mark)

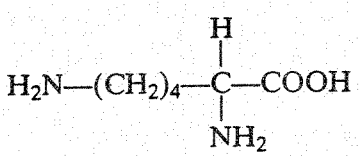
(d) The amino acid *alanine* is formed by the reaction of $CH_3CHClCOOH$ with an excess of ammonia. The mechanism is nucleophilic substitution. Outline this mechanism, showing clearly the structure of *alanine*.



(allow S_N1)

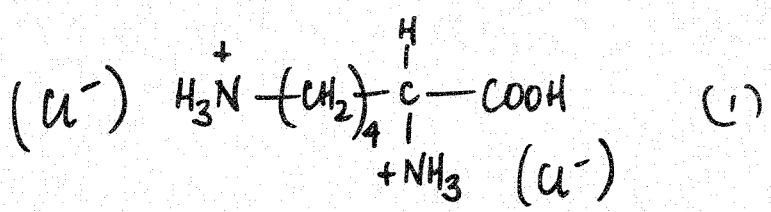
(5 marks)

(e) The amino acid *lysine* has the structure

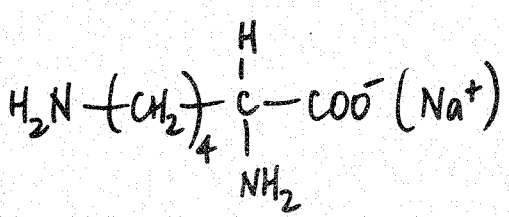


Draw structures to show the product formed in each case when lysine reacts with

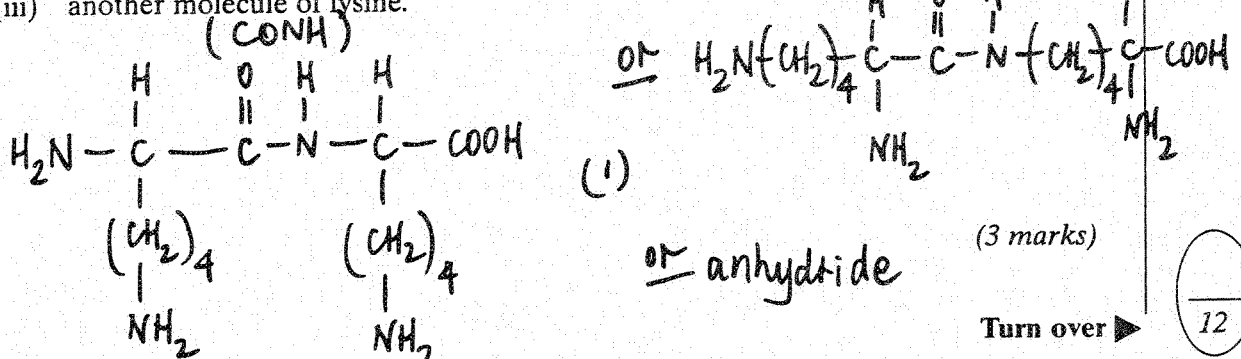
(i) an excess of aqueous HCl,



(ii) an excess of aqueous NaOH,



(iii) another molecule of lysine.



(3 marks)

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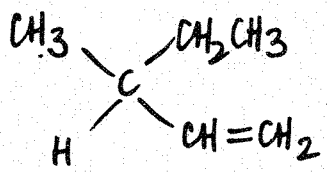
5 (a) **P**, **Q** and **R** have the molecular formula C_6H_{12}
All three are branched-chain molecules and none is cyclic.
P can represent a pair of optical isomers.
Q can represent a pair of geometrical isomers.
R can represent another pair of geometrical isomers different from **Q**.

Draw one possible structure for one of the isomers of each of **P**, **Q** and **R**.

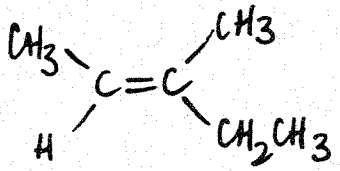
*Structure of **P***



(1)

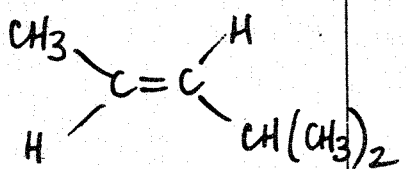
*Structure of **Q***

*Structure of **R***



(1)

and



(1) NOT C_3H_7

(3 marks)

(b) Butanone reacts with reagent **S** to form compound **T** which exists as a racemic mixture.
Dehydration of **T** forms **U**, C_5H_7N, which can represent a pair of geometrical isomers.

(i) State the meaning of the term *racemic mixture* and suggest why such a mixture is formed in this reaction.

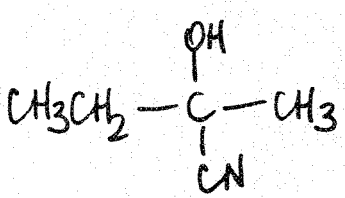
Racemic mixture equal mixture of {optical isomers / enantiomers} (1)
or in explanation

Explanation planar (C=O) (1)
attack from either side (equally) likely (1)

(ii) Identify reagent **S**, and draw a structural formula for each of **T** and **U**.

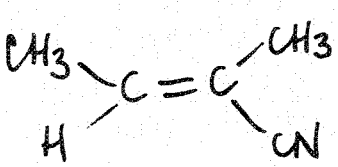
*Reagent **S*** HCN or KCN / HCl or H_2SO_4 (1)

*Compound **T***



(1)

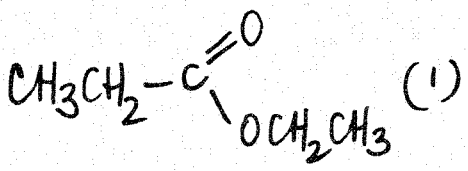
*Compound **U***



(1)

(6 marks)

6 (a) Draw the structure of ethyl propanoate.



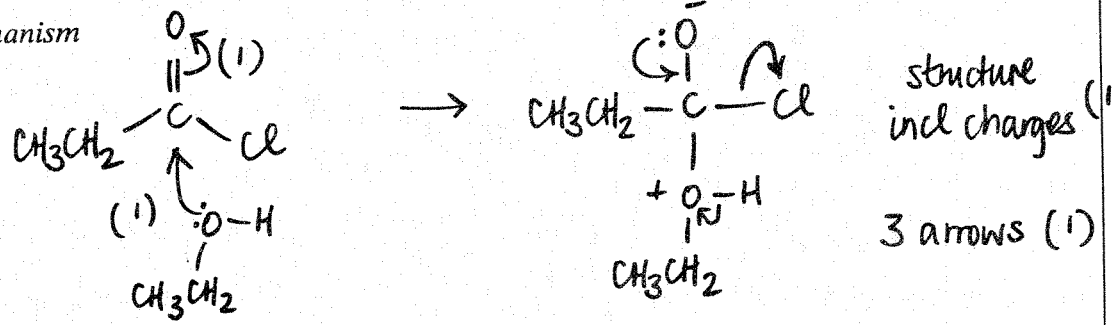
(allow -COO-)

(1 mark)

(b) Name and outline a mechanism for the formation of ethyl propanoate from propanoyl chloride and ethanol.

Name of mechanism (nucleophilic) addition-elimination (1)

Mechanism

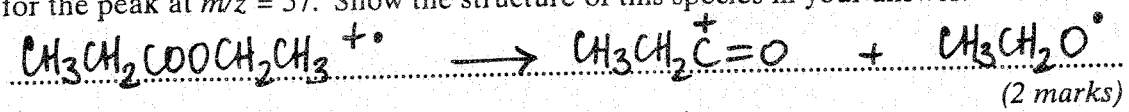


structure incl charges (1)

3 arrows (1)

(5 marks)

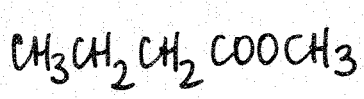
(c) The mass spectrum of ethyl propanoate contains a major peak at $m/z = 57$. Write an equation showing the fragmentation of the molecular ion to form the species responsible for the peak at $m/z = 57$. Show the structure of this species in your answer.

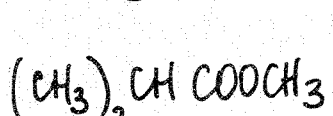


(2 marks)

(1) eqn (1)

(d) Draw the structure of another ester which is an isomer of ethyl propanoate and which gives a major peak at $m/z = 71$ in its mass spectrum.



or 

(1)

allow $C_3H_7COOCH_3$

(1 mark)

9

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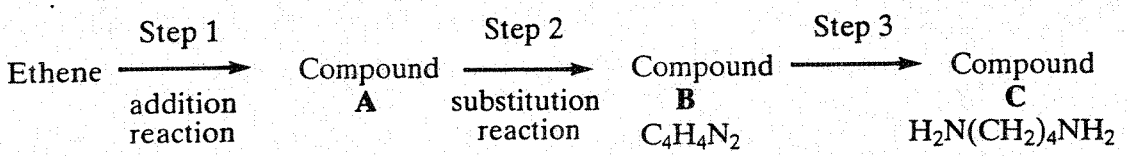
SECTION B

Answer **both** the questions below in the space provided on pages 12 to 16 of this booklet.

7 (a) Compound **C**, $H_2N(CH_2)_4NH_2$, can be synthesised from ethene in three steps as shown below.



Name compound **C** and draw a structure for each of compounds **A** and **B**.
State the reagent(s) required for each step and name the type of reaction involved in the conversion of **B** into **C**. *(7 marks)*

(b) Draw the repeating unit of the polyamide formed when **C** reacts with hexanedioic acid.
Discuss the interactions between the chains of the polyamide. *(4 marks)*

(c) Explain why polyamides are degraded by sodium hydroxide whereas polymers such as poly(ethene) are not. *(3 marks)*

8 A 0.210 mol dm^{-3} solution of potassium hydroxide was added from a burette to 25.0 cm^3 of a 0.160 mol dm^{-3} solution of ethanoic acid in a conical flask.
Given that the value of the acid dissociation constant, K_a, for ethanoic acid is 1.74×10^{-5} mol dm^{-3}, calculate the pH at 25 °C of the solution in the conical flask at the following three points:

before any potassium hydroxide had been added;

after 8.0 cm^3 of potassium hydroxide solution had been added;

after 40.0 cm^3 of potassium hydroxide solution had been added. *(16 marks)*

END OF QUESTIONS

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Question 7

(a) 1,4-diaminobutane or butane-1,4-diamine (1)

A: $BrCH_2CH_2Br$ or $ClCH_2CH_2Cl$ (1)

B: $NCCH_2CH_2CN$ (1)

Step 1: Br_2 or Cl_2 (1) (ignore aq)

Step 2 KCN (1) (NOT HCN)

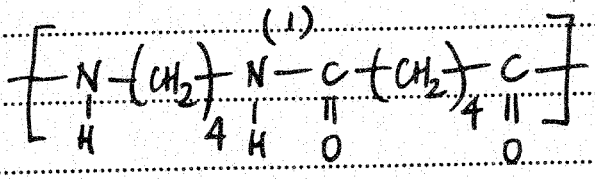
Step 3 H_2/Ni or $LiAlH_4$ or Na/C_2H_5OH (1) Not $NaBH_4$

hydrogenation (only for H_2/Ni) nucleophilic (only for $LiAlH_4$) addition

or reduction or addition (1)

(7 marks)

(b)



(1)

(1)

QL hydrogen bonding (1)

polarity or H-bonding shown or discussed (1)

(4 marks)

(c) polyamides / peptide link can be hydrolysed } (1)
or polyalkenes cannot be hydrolysed }

QL OH^- attacks peptide link or $C^{\delta+}$ (1)

poly(ethene) non-polar (1)

(3 marks)

[TOTAL = 14]

Turn over

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Question 8 Penalize pH to one dp FIRST TIME only

a) before any KOH added:

$K_a = \frac{[H^+][A^-]}{[HA]}$ or $\frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$ (1)

$\therefore K_a = \frac{[H^+]^2}{[CH_3COOH]}$ (1)

$\therefore [H^+] = \sqrt{1.74 \times 10^{-5} \times 0.160} = 1.67 \times 10^{-3}$ (1)

$\therefore$ pH = 2.78 (1) (4 marks)

(b) at $8cm^3$ KOH:

Moles KOH added $= (8 \times 10^{-3}) \times 0.210 = 1.68 \times 10^{-3}$ (1)

$\therefore$ moles CH_3COO^- formed $= 1.68 \times 10^{-3}$ (1)

Original moles $CH_3COOH = (25 \times 10^{-3}) \times 0.160 = 4.0 \times 10^{-3}$ (1)

$\therefore$ moles CH_3COOH left $= (4.0 \times 10^{-3}) - (1.68 \times 10^{-3})$

$= 2.32 \times 10^{-3}$ (1)

$[H^+] = K_a \times \frac{[CH_3COOH]}{[CH_3COO^-]}$ (1)

$= 1.74 \times 10^{-5} \times \frac{(2.32 \times 10^{-3}/V)}{(1.68 \times 10^{-3}/V)} = 2.40 \times 10^{-5}$ (1)

$\therefore$ pH = 4.62 (1) (7 marks)

If forget subtraction: max 5

If K_a expression not used max 5

If moles CH_3COOH wrong but subtraction used max 5

(c) at 40 cm^3 KOH :

Total moles KOH = $(40 \times 10^{-3}) \times 0.21 = 8.4 \times 10^{-3}$ (1)

$\therefore$ excess moles of KOH = $(8.4 \times 10^{-3}) - (4.0 \times 10^{-3})$

$= 4.4 \times 10^{-3}$ (1)

in total volume = $40 + 25 = 65\ cm^3$ (1)

$\therefore [OH^-] = 4.4 \times 10^{-3} \times \frac{1000}{65} = 0.0677$ (1)

$\therefore [H^+] = \frac{10^{-14}}{0.0677}$ OR pOH = 1.17

$= 1.477 \times 10^{-13}$ (1)

$\therefore$ pH = 12.83 (1) (6 marks)

[MAX 16 marks]

If volume missed : max 4

If moles acid wrong but method includes subtraction : max 5

If no subtraction : max 4