Name:	Suggested Solutions	Index Number:		Class:	

DUNMAN HIGH SCHOOL
Preliminary Examination
Year 6

H2 CHEMISTRY 9647/02

Paper 2 Structured **19 September 2013**

2 hours

Additional Materials: Data Booklet

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this cover page.

2 Answer ***all*** questions.

3 Write your answers in the spaces provided on the question paper.

4 A *Data Booklet* is provided.

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

6 You may use a calculator.

FOR EXAMINER'S USE								
Question No.	**1**	**2**	**3**	**4**	**5**	**6**	**Total**	**%**
Marks	/12	/15	/9	/10	/15	/11	/[72]	

[Turn over

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

1 Planning

Solubility is defined as the mass of solid that will dissolve in and just saturate 100 g of solvent at a particular temperature.

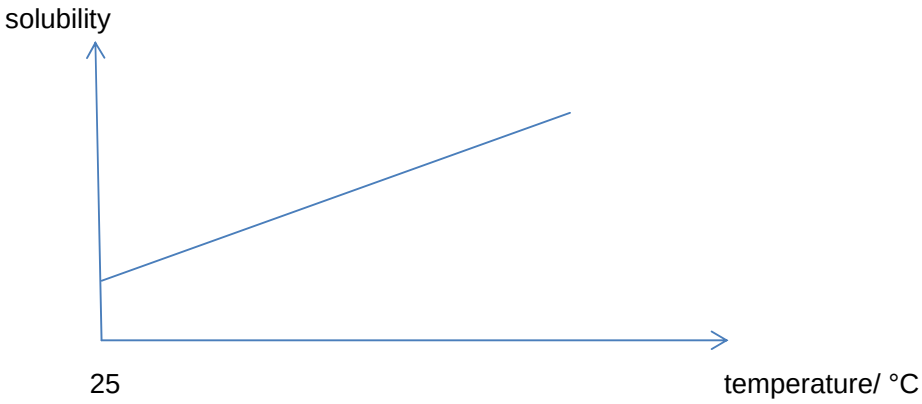
When potassium nitrate dissolves in water, the temperature of the solution decreases as the enthalpy change of solution is endothermic.

You are to plan an experiment to investigate how the solubility of potassium nitrate varies with temperature. The units of solubility are grams per one hundred grams of water (g/100 g of water).

(a) (i) Predict how the solubility of potassium nitrate will change if the solution temperature is increased.

By Le Chatelier's principle, when temperature is increased, the equilibrium will **shift to the right to absorb the excess heat and favour the endothermic reaction**. Hence the solubility will increase with increasing temperature.

(ii) Display your prediction in the form of a sketch, labeling clearly the y-axis.



[3]

(b) You are to design an experiment to test your prediction in **(a)**.

(i) Given that the solubility of potassium nitrate at 70 °C = 11.3 mol dm^{-3}
Calculate the maximum mass of potassium nitrate that can be dissolved in 100 g of water at 70 °C.

Maximum mass = (100/1000) x 11.3 x (39.1 x 14.0 x 3(16.0))
= 114 g

(ii) Describe how you would carry out the experiment. You should

- include the apparatus used;
- ensure a wide range of results suitable for analysis by graph;
- decide on the amount of water and potassium nitrate to be used;
- describe how the temperature of the solution is to be maintained.

You may also assume that standard laboratory apparatus are available.

1. Measure **approximately 120 g** of potassium nitrate using a **weighing balance**. **[1]** Measure **100 ml of water** using a **measuring cylinder/burette** and transfer the water to a 250 cm^3 beaker.

(total mass of solid + water should not exceed 250 g, mass of solid added should be more than 114g in every 100 g of water)

2. Add potassium nitrate to the beaker containing water and stir the mixture.
3. **Heat** the mixture to 70 °C in a **thermostat controlled water bath**.
4. **Stir** the mixture gently throughout the heating.
5. **Allow to stand**/ leave for a long time **to establish equilibrium**

6. **Filter** the solution (not cooled or decanted) .
7. **Heat the residue to dryness** and weigh the residue .
8. Repeat step 1 – 7 for another four experiments (at least) but changing the temperature in step 3 to 30 °C, 40 °C, 50 °C and 60 °C respectively. (accept any temperature range of at least 40 °C)

(iii) Draw a table with appropriate headings to show the data you would record when carrying out your experiments and the values you would calculate in order to construct a graph to support or reject your prediction in **(a)**. The headings must include the appropriate units.

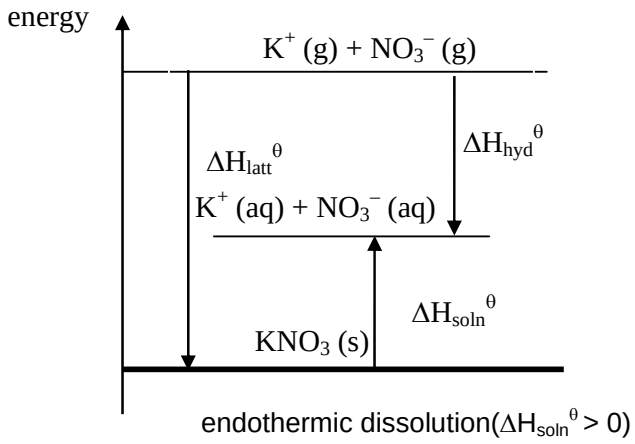
Mass of potassium nitrate /g	
Mass/Volume of water /g or cm^3	
Mass of dry residue /g	

Solubility = Initial mass of potassium nitrate – mass of dry residue

Temperature (°C)	Solubility (g /100g water)
30	
40	
50	
60	
70	

[7]

(c) Potassium nitrate is used as an excellent additive in fertilisers. It dissolves in water with an enthalpy change of solution of +34.9 kJ mol^{-1}.
It is given that the lattice energy of potassium nitrate is –687 kJ mol^{-1} while the enthalpy change of hydration of potassium ion is –322 kJ mol^{-1}. With the aid of an energy level diagram, calculate the enthalpy change of hydration of nitrate ion.



By Hess' Law,
L.E = ∑(ΔH_{hyd} of ions) – ΔH_{sol}
–687 = (–322 + Enthalpy change of hydration of nitrate ion) – (+34.9)
Enthalpy change of hydration of nitrate = –330 kJ mol^{-1}

[2]

2 The *use of Data Booket* is relevant to this question.

The nitrates, carbonates and hydroxides of Group II elements can undergo thermal decomposition.

The nitrates of lead and zinc can undergo thermal decomposition similar to calcium nitrate. The decomposition temperature of the three nitrates are given in the table below.

Compound	**Decomposition temperature / ^{0}C**
Lead(II) nitrate, $Pb(NO_3)_2$	290
Zinc nitrate, $Zn(NO_3)_2$	105
Calcium nitrate, $Ca(NO_3)_2$	132

(a) Explain the data above by quoting relevant values from the Data Booklet and using your knowledge and understanding of the trend in the decomposition temperature of the Group II nitrates.

Cation Ionic radius /nm
Pb^{2+} 0.120
Zn^{2+} 0.074
Ca^{2+} 0.099

The decomposition temperature increases in the order from zinc nitrate to calcium nitrate to lead(II) nitrate. This is because the ionic radius of Zn^{2+} is smaller than Ca^{2+} which in turn is smaller than Pb^{2+}.

Zn^{2+} has highest charge density and hence greatest polarising power.
Zn^{2+} is able to distort the electron cloud of the nitrate anion to the most and weaken the N–O bond to **the greatest extent.** Hence zinc nitrate has a lowest thermal stability and can decompose at the lowest temperature.

(b) The mineral hydromagnesite is a hydrated carbonate of magnesium, with the formula $Mg_x(CO_3)_y(OH)_z.nH_2O$ and a molar mass of 466 g mol^{-1}. Group II carbonates and hydroxides decompose to give the same solid product.

When 1.00 g of a pure sample of hydromagnesite was heated to constant mass, 0.378 g of carbon dioxide was given off. Steam was also produced.

The remaining white solid from the above decomposition was completely dissolved in 50 cm^3 of a 1.0 mol dm^{-3} solution of hydrochloric acid. The resultant solution was transferred into a volumetric flask and diluted to 250 cm^3 with deionised water. A 25.0 cm^3 aliquot of this diluted solution required 28.50 cm^3 of a 0.10 mol dm^{-3} solution of sodium hydroxide for complete neutralisation.

(i) Calculate the value of *y*.

moles of hydromagnesite = 1 / 466 = 2.15 x 10^{-3} mol
moles of CO_2 given off = 0.378 / 44 = 8.59 x 10^{-3} mol

y = 8.59 x 10^{-3} ÷ 2.15 x 10^{-3} = **4**

(ii) Calculate the value of *x*.

moles of HC*l*(aq) used = 50/1000 x 1 = 0.050 mol

moles of NaOH used to neutralize remaining HC*l*(aq) in 25 cm^3
= 28.5/1000 x 0.10 = 0.00285 mol

moles of HCl reacted with MgO
= 0.050 – (0.00285 x 10) = 0.0215 mol

$MgO + 2HCl \rightarrow MgCl_2 + H_2O$

moles of MgO formed
= 0.0215 ÷ 2 = 0.0107 mol

= moles of Mg present
$x = 0.0107 / 2.15 \times 10^{-3} =$ **5**

(iii) Hence or otherwise, deduce the values of *z* and *n*.

For a neutral solid $Mg_5(CO_3)_4(OH)_z.nH_2O$,
+2 x 5 – 2 x 4 + (–1 x *z*) = 0
therefore, *z* = **2** to balance the overall charge.

Mass of water per mole of hydromagnesite
= 466 – (5 x 24.3 + 4 x 60 + 2 x 17) = 70.5 g
n = 70.5 / 18 ≈ **4**

(iv) Using your answers from parts **b(i)-(iii)**, write a balanced equation, with state symbols, for the thermal decomposition of hydromagnesite.

[9]

$Mg_5(CO_3)_4(OH)_2.4H_2O\ (s) \rightarrow 5MgO\ (s) + 4CO_2\ (g) + 5H_2O\ (g)$

2 (c) A mixture of magnesium oxide, alumina (Al_2O_3) and silica (SiO_2) is usually used in the manufacture of refractory material. Suggest with explanation and suitable equations, how magnesium oxide can be separated from a mixture containing these three oxides.

[3]

Magnesium oxide is basic and hence has no reaction with alkali. To the mixture, add excess NaOH (concentrated/aqueous) and both amphoteric (Al_2O_3) and acidic (SiO_2) oxides will dissolve. Hence, the resulting mixture can be filtered and MgO can be obtained as the residue.

$$Al_2O_3 + 2OH^- + 3H_2O \rightarrow 2Al(OH)_4^-$$
$$SiO_2 + 2OH^- \rightarrow SiO_3^{2-} + H_2O$$

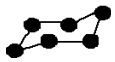
3 The data for some liquids are given below:

	M_r	bp / ^0C	density / g cm^{-3}
ethanol	46	79	0.79
cyclohexane	84	81	0.78
hexane	86	69	0.66

(a) **(i)** Suggest why the boiling point of cyclohexane differs from that of hexane.

There exists Van der Waals' (VDW) forces between molecules of cyclohexane and hexane. However, shape of cyclohexane molecule allows (chair conformation) **more extensive VDW** forces to exist between them. Therefore, boiling point is higher as more energy is needed to overcome the more extensive VDW forces of attractions.

For your knowledge:



chair conformation of cyclohexane

(ii) Suggest why the density of ethanol differs from that of hexane.

There exist stronger hydrogen bonding between molecules of ethanol and weaker Van der Waals' forces of attraction between molecules of hexane. Stronger intermolecular forces of attraction coupled with smaller molecular size of ethanol result in larger number of molecules (or larger mass) of ethanol contained per unit volume **,** hence density is larger than hexane.

(b) Equal volume, V cm^3 of 1.0 mol samples of the following liquids were mixed and the following results were obtained in the following table.

Mixture of liquids	**Heat change**
Hexane mixed with cyclohexane	No heat absorbed or given out
Hexane mixed with ethanol	?

(i) Explain why there was no heat change on mixing hexane and cyclohexane.

VDW forces of attractions are formed between molecules of hexane/cylcohexane mixture and the energy given out is used to overcome intermolecular forces of attractions in hexane and cyclohexane that are of **similar strength**.

(ii) Predict, with reasoning, whether heat is absorbed or evolved on mixing hexane and ethanol.

Heat will be absorbed. Heat is needed to overcome hydrogen bonding between ethanol molecules and this is not compensated by the heat released between ethanol and hexane interactions of very **dissimilar strength**.

3 **(c)** **(i)** Write a balanced equation for the complete combustion of ethanol, C_2H_6O.

$$C_2H_6O(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

(ii) By using appropriate bond energy data from the *Data Booklet*, calculate the enthalpy change of combustion of ethanol.

ΔH_c = [BE(C–C) + 5BE(C–H) + BE(C–O) + BE(O–H) + 3BE(O=O)] – [4BE(C=O) + 6BE(O–H)]
= [350 + 5(410) + 360 + 460 + 3(496)] – [4(740) + 6(460)]
= –1010 kJ mol^{-1} (3 s.f.)

[3]

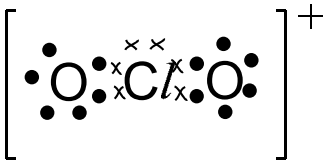
[Total: 9]

4 **(a)** Chlorine forms an oxide ClO_6 which exists as singly charged ions in the solid state. The oxidation states of chlorine are +5 and +7 in the cation and anion respectively.

Suggest the formulae of the ions and draw the dot-and-cross diagram for the **cation**.

[3]

Formulae of ions: **$[ClO_2]^+$ and $[ClO_4]^-$**



(b) When chlorine is bubbled through cold sodium hydroxide solution and acidified silver nitrate solution, only half of the chlorine that has dissolved is precipitated as silver chloride. When the sodium hydroxide is hot, up to five–sixth of the chlorine can be precipitated. Explain the observations, giving balanced equations where appropriate.

cold NaOH: **$2NaOH\ (aq) + Cl_2\ (aq) \rightarrow NaCl\ (aq) + NaClO\ (aq) + H_2O\ (l)$**

hot NaOH: **$6\ OH^-\ (aq) + 3\ Cl_2\ (aq) \rightarrow 5\ Cl^-\ (aq) + ClO_3^-\ (aq) + 3\ H_2O\ (l)$**

The free chloride ions will be precipitated out as silver chloride with silver nitrate.
When chlorine reacts with cold NaOH, $Cl_2 \equiv Cl^- \equiv ClO^-$
When chlorine reacts with hot NaOH, $Cl_2 \equiv 5Cl^- \equiv ClO_3^-$

[3]

(c) Chlorate(VII) ion can be produced from the reaction of Cl_2O_7 with alkali.

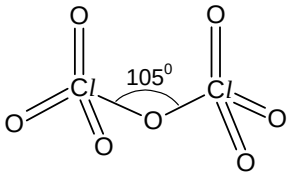
(i) Write an equation for the formation of chlorate(VII) ion.

$Cl_2O_7 + 2OH^- \rightarrow 2ClO_4^- + H_2O$

(ii) State the type of reaction undergone.

Acid-base reaction/neutralisation

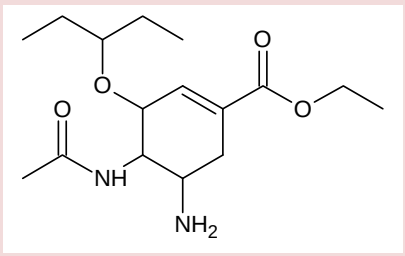
(iii) Given that Cl_2O_7 molecule is symmetrical, draw the shape of the molecule, indicating the possible Cl-O-Cl bond angle.



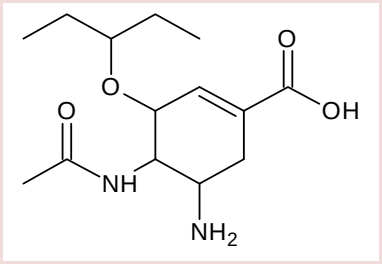
[4]

[Total: 10]

5 **(a)** *Oseltamivir* is the anti-influenza drug being used to treat so called 'Bird-flu'. This anti-viral drug can be converted to its active form *GS 4071*, in the body after being administered. The structure of *Oseltamivir* is shown below:



Oseltamivir



GS 4071

You may assume that the ether (–O–) group in *Oseltamivir* is unreactive in any reactions in this question.

(i) Circle and name four different functional groups present in *Oseltamivir*.

Amide, amine (primary), ester, alkene, (ether)

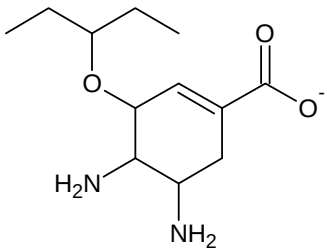
(ii) *Oseltamivir* is actually sold as the phosphate salt rather than in the form as shown above. Suggest why this is so.

To increase its solubility so that it is more easily absorbed by the body.

(iii) What type of reaction is involved in the conversion of *Oseltamivir* into GS 4071?

Hydrolysis (Do not allow acid hydrolysis)

(iv) Draw the structural formula of all organic products formed when *Oseltamivir* is heated with excess sodium hydroxide.

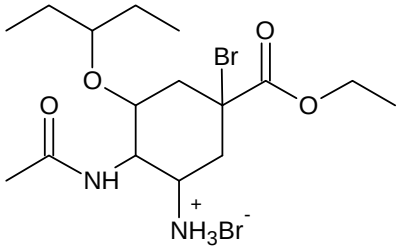


Na^+; $CH_3COO^-\ Na^+$ and CH_3CH_2OH

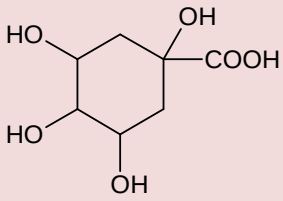
(v) At room conditions, *Oseltamivir* reacts with HBr in 1:2 ratio. Draw the structure of the product formed.

[6]

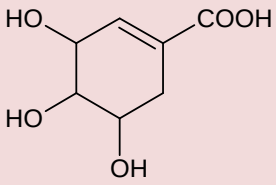
Acid-base with amine group and Addition on alkene group.



(b) *Oseltamivir* can be produced from *Quinic acid*, found in coffee beans or *Shikimic acid*, found in star anise.



Quinic acid

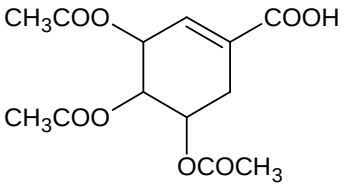


Shikimic acid

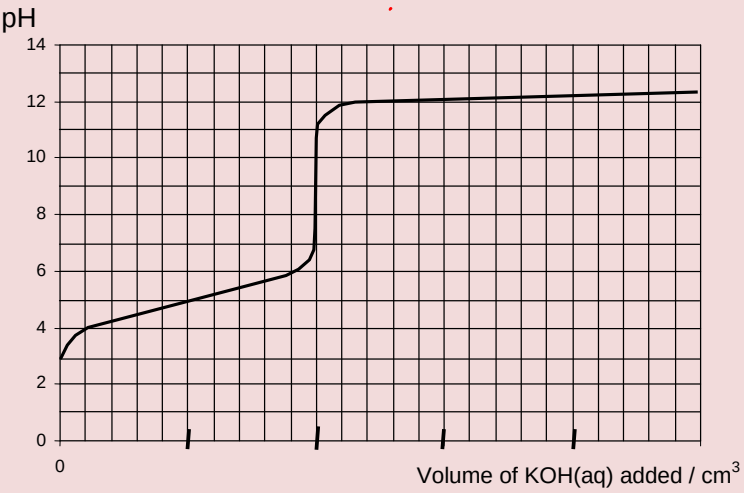
(i) Use the **table of characteristic values for infra-red absorption in the *Data Booklet***, identify an infra-red absorption range shown by *Shikimic* acid but not Quinic acid.

1610-1680 cm^{-1}

(ii) Give the structural formula of the organic product when *Shikimic* acid reacts with excess ethanoyl chloride.



(iii) The titration curve below shows the reaction between a solution of a 10.0 cm^3 of 0.10 mol dm^{-3} solution of *Shikimic* acid and 0.05 mol dm^{-3} KOH solution.



Calculate the value of K_a for *Shikimic* acid.

Volume of KOH needed for complete neutralisation = 20 cm^3.

At maximum buffering capacity, vol of KOH used = 10 cm^3 and pH=pKa.

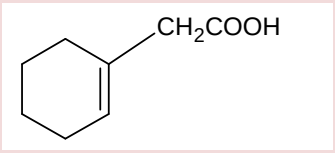
Therefore, Ka of Shikimic acid = 1.00 x 10^{-5} mol dm^{-3}

OR, initial pH of Shikimic acid is 3. $[H^+]$ = 10^{-3} mol dm^{-3}.

Let HA be the general formula of Shikimic acid.

$K_a = [H^+][A^-]/[HA] = (10^{-3})^2 / 0.10 = 1.00 \times 10^{-5}$ mol dm^{-3}

(iv) Suggest the reagents and conditions for a reaction that could be used to distinguish between Shikimic acid and another compound **R**, shown below:



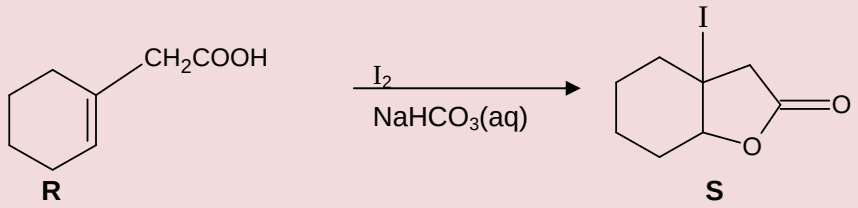
R

State the expected observation of the reaction on each compound.

Reagent/condition: acidified dichromate (VI), warm

Expected observation: orange acidifies dichromate turns from orange to green with *Shikimic* acid while no colour change observed for **R**.

(v) When compound **R** is reacted with iodine in the presence of aqueous sodium hydrogencarbonate, iodine does not add across the carbon-carbon double bond of compound **R** as might be expected. Instead, a compound **S**, which has a molecular formula, $C_8H_{11}O_2I$, is formed as shown:



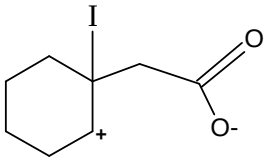
R **S**

Suggest an explanation for the observation.

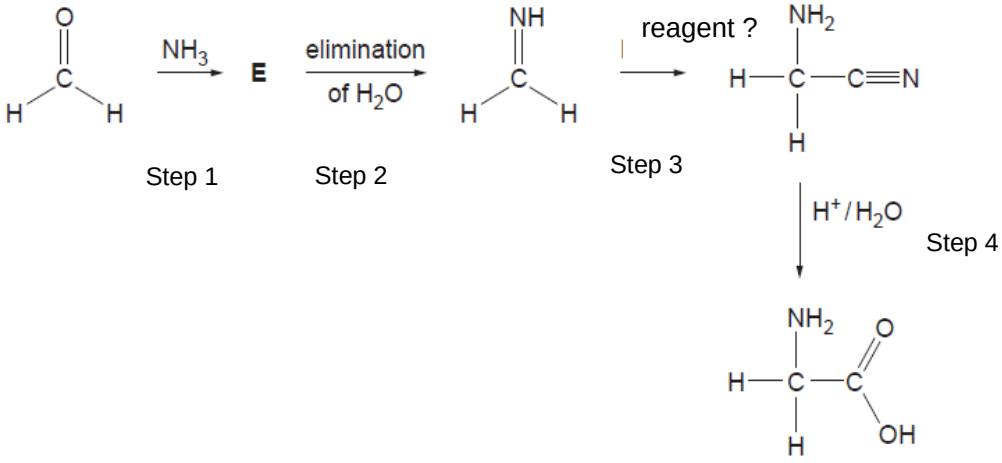
[9]

[Total: 15]

R undergoes electrophilic addition with iodine and acid-base reaction in alkaline medium to form



6 **(a)** The Strecker synthesis is a route to preparing amino acids. Glycine, 2-aminoethanoic acid, can be prepared from methanal, as a starting material. This is shown in the four-steps reaction scheme below:



2-aminoethanoic acid

(i) State the role of ammonia used in Step 1.

Nucleophile

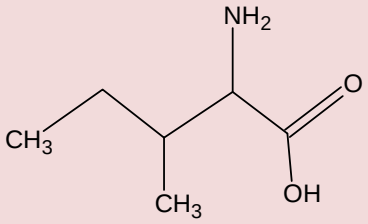
(ii) Suggest a structure for compound **E**

$CH_2(OH)(NH_2)$

(iii) Suggest a suitable reagent used in Step 3.

HCN

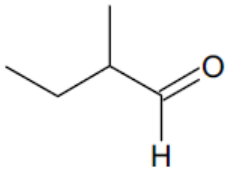
A starting material, compound **Z**, can be used to prepare isoleucine, shown below using a Strecker synthesis.



isoleucine

(iv) Draw the structure of compound **Z**.

[4]



Much research has been carried out in recent years investigating the exact structure of silk. A silk fibre is composed of many identical protein chains, which are mainly made from the amino acids glycine, alanine and serine, with smaller amounts of four other amino acids.

$NH_2–CH_2–CO_2H$	$NH_2–\underset{\displaystyle CH_3}{\underset{\vert}{CH}}–CO_2H$	$NH_2–\underset{\displaystyle CH_2OH}{\underset{\vert}{CH}}–CO_2H$
glycine	alanine	serine

(b) **(i)** A solution of glycine at its isoelectric point can act as a buffer.
By writing appropriate equations, show how a solution of glycine at its isoelectric point can function as a buffer.

$$H_3N^+CH_2COO^- + H^+ \rightarrow H_3N^+CH_2COOH$$

$$H_3N^+CH_2COO^- + OH^- \rightarrow H_2NCH_2COO^- + H_2O$$

(ii) Predict the movement of glycine when a potential difference is applied at pH 13.

[3]

At pH 13, the $–CO_2H$ group is deprotonated to give $\underline{–CO_2^-}$, the glycine species will move towards the <u>positive electrode</u>.

(c) Assuming that a silk protein made from equal amounts of the three amino acids glycine, alanine and serine has M_r of about 600 000. Calculate the average number of amino acids residues in the protein chain. [M_r (glycine = 75; M_r (alanine) = 89; M_r (serine) = 105]

[3]

A H_2O molecule is lost when peptide bond is formed in protein structure,
M_r of the gly-ala-ser fragment = 269 -3(18) = 215

Average number of such gly-ala-ser fragment = 600 000/ 215 = 2791

Average number of amino acids residues = 2791 x 3 = 8732

(d) Unlike silk protein, globular proteins such as enzymes contain relatively small amounts of glycine and alanine when compared to the amounts of some other amino acids. Suggest why this is so.

[1]

[Total: 11]

Globular proteins need polar/H-bonding/ionic side-chains to enhance their solubility.

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