Name:	Answers	Index Number:		Class:	

DUNMAN HIGH SCHOOL
Preliminary Examination 2019
Year 6

H2 CHEMISTRY 9729/03

Paper 3 Free Response

Additional Materials: Data Booklet
Answer Booklet

INSTRUCTIONS TO CANDIDATES

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

2 Write your answers on the separate answer booklet provided.

3 Write in dark blue or black pen.

4 You may use an HB pencil for any diagrams or graphs.

5 Start each question on a fresh sheet of paper.
[Marks will be deducted if you fail to do so.]

6 Do not use staples, paper clips, glue or correction fluid.

Section A

7 Answer **all** questions

Section B

8 Answer **one** question.

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

You are advised to show all workings in calculations.

You are reminded of the need for good English and clear presentation in your answers.

Section A

1 To facilitate better plant growth, there is widespread use of fertilisers and soil additives in the agricultural sector.

(a) Agricultural lime is a soil additive used to increase soil pH so as to facilitate uptake of plant nutrients such as nitrogen and phosphorous. It is usually made up of a combination of calcium carbonate and magnesium carbonate.

A manufacturer claims that a 2.00 g sample of agricultural lime contains 92 % calcium carbonate (M_r = 100.1) and 8 % magnesium carbonate (M_r = 84.3) by mass.

To verify the manufacturer's claim, the following steps were carried out:

Step 1 The solid carbonate mixture was dissolved in 250 cm^3 of 0.25 mol dm^{-3} hydrochloric acid.

Step 2 A 25 cm^3 aliquot of this resultant solution was titrated with 0.14 mol dm^{-3} potassium hydroxide.

It was found that 12.50 cm^3 of potassium hydroxide was required for complete neutralisation.

(i) Based on the manufacturer's claim of 92% calcium carbonate and 8% magnesium carbonate by mass, calculate the amount, in moles, of each carbonate present in the sample of agricultural lime.

[1]

Mass of $CaCO_3$ present = 92 % × 2.00 g = 1.84 g
Mass of $MgCO_3$ present = 8 % × 2.00 g = 0.16 g

Moles of $CaCO_3$ present
= 1.84 g ÷ 100.1 g mol^{-1} = 0.018382 = **0.0184 mol**

Moles of $MgCO_3$ present
= 0.16 g ÷ 84.3 g mol^{-1} = 0.0018980 = **0.00190 mol**

(ii) Use the information above to calculate the amount of HCl that reacted with the carbonate mixture in Step 1.

[2]

Moles of KOH reacted with excess HCl = $\frac{12.50}{1000} \times 0.14$ = 0.00175 mol
Moles of HCl present in 25 cm^3 aliquot = 0.00175 mol

Moles of excess HCl present in 250 cm^3 solution
= 0.00175 × $\frac{250}{25}$ = **0.0175 mol**

Total moles of HCl used = $\frac{250}{1000} \times 0.25$ = 0.0625 mol

Moles of HCl reacted with carbonates = 0.0625 – 0.0175 = **0.045 mol**

(iii) The manufacturer's claim is considered valid if the difference between the actual and theoretical total amount of carbonate present in the sample is less than 0.0010 mol.

Using your answers in **(a)(i)** and **(a)(ii)**, determine if the manufacturer's claim is valid.

[2]

$2H^+ + CO_3^{2-} \rightarrow CO_2 + H_2O$
Total moles of carbonates present = 0.045 ÷ 2 = **0.0225 mol**

Total moles of carbonates based on manufacturer's claim
= 0.0184 + 0.00190 = **0.0203 mol**

Since the **difference** between the calculated moles and theoretical moles of carbonates is **more than 0.0010 mol**, the **manufacturer's claim is false**.

(iii) When solid magnesium chloride is dissolved in water, it produces a slightly acidic solution of pH 6.5.

Using appropriate equation(s), explain the above observation.

[2]

$MgCl_2 + 6H_2O \rightarrow [Mg(H_2O)_6]^{2+} + 2Cl^-$
$[Mg(H_2O)_6]^{2+} + H_2O$ —— $[Mg(H_2O)_5(OH)]^+ + H_3O^+$ [1]

$MgCl_2$ dissolves in water and **Mg^{2+} undergoes** partial **hydrolysis** in water to produce H_3O^+, giving a slightly acidic solution.

(iv) However, the resultant solution is neutral when solid calcium chloride is dissolved in water.

By quoting relevant values from the *Data Booklet*, explain why a solution of calcium chloride is neutral while a solution of magnesium chloride is slightly acidic.

[3]

Cationic radius of Mg^{2+} = 0.065 nm
Cationic radius of Ca^{2+} = 0.099 nm

Since the cationic radius of Ca^{2+} is larger than that of Mg^{2+}, **Ca^{2+} has a lower charge density**.

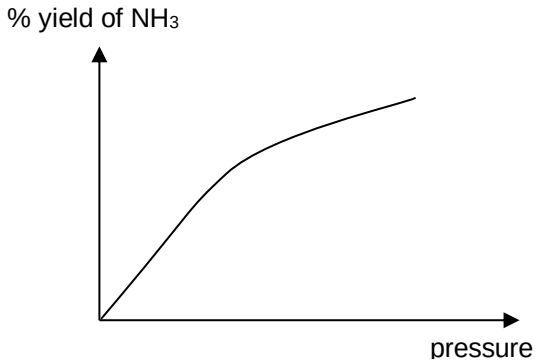
As such, it **polarises the O–H bond of the water molecule to a lesser extent and no H^+ ions are produced**. OR Ca^{2+} **does not hydrolyse in water to produce H^+ ions**. Hence, the solution is neutral.

(b) Nitrogen fertilisers are important in enhancing the growth of plants. Almost all nitrogen fertilisers are produced from ammonia, which in turn, is manufactured in the Haber Process. This process combines nitrogen and hydrogen gas to form ammonia according to the following equilibrium.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(i) State how the percentage yield of ammonia will change with increasing pressure.

[1]



Percentage yield of ammonia will increase with increasing pressure.

(ii) N_2 and H_2 was introduced into an enclosed vessel at 300 °C. The initial partial pressures of N_2 and H_2 were 2 atm and 3 atm respectively. After an equilibrium has been established, the total pressure in the vessel was 4.7 atm.

Calculate the value of K_p at 300 °C, stating its units.

[3]

	$N_2(g)$ +	$3H_2(g)$	⟵⟶	$2NH_3(g)$
Initial partial pressure / atm	2	3		0
Change / atm	– x	– 3x		+2x
Eqm partial pressure / atm	2 – x	3 – 3x		2x

Total pressure = 4.7 atm
Hence, 2 – x + 3 – 3x + 2x = 4.7
x = **0.15 atm**

	$N_2(g)$ +	$3H_2(g)$	⟵⟶	$2NH_3(g)$
Eqm partial pressure / atm	1.85	2.55		0.30

$K_p = \frac{P_{NH_3}{}^2}{P_{N_2}[H_2]^3} = \frac{(0.30)^2}{(1.85)(2.55)^3}$ = 0.0029339 = **0.00293 atm^{-2}**

(iii) 1 atm of N_2 was added to the equilibrium mixture in **(b)(ii)** at 300 °C and time was allowed for a new equilibrium to be established. State and explain how the K_p value at this point will compare to that in **(b)(ii).**

[1]

The K_p value will **remain constant / be the same** as K_p is **only dependent on temperature**.

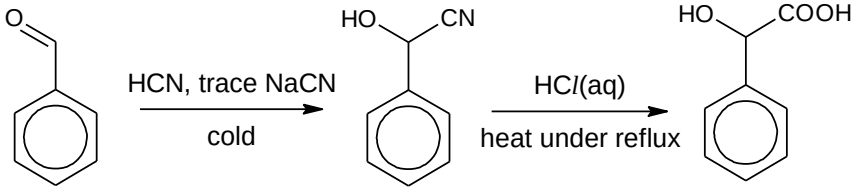
[Total: 15]

2 Mandelic acid, $C_6H_5CH(OH)COOH$, is a white crystalline solid that is soluble in water.

(a) Benzaldehyde is a useful starting material for the preparation of mandelic acid.

Suggest a two–step synthesis of mandelic acid from benzaldehyde, stating clearly the reagents and conditions used and the structure of the intermediate.

[3]



(b) Suggest how you would distinguish between aqueous solutions of mandelic acid and nitric acid of the same concentration by means of a **physical** method.

Explain your reasoning.

[3]

Measure the pH of the aqueous solutions using **pH paper / meter**. The solution of a **lower pH** is that of **nitric acid**.

Nitric acid is a **strong acid** while mandelic acid is a **weak acid**. Nitric acid **dissociates to a greater extent in water** to produce a **higher concentration of H^+** ions which results in a lower pH for its aqueous solution.

(c) **(i)** 20 cm^3 of 1.0 mol dm^{-3} mandelic acid solution was titrated with 2.0 mol dm^{-3} aqueous sodium hydroxide. Calculate the concentration of the salt, sodium mandelate, formed at equivalence point.

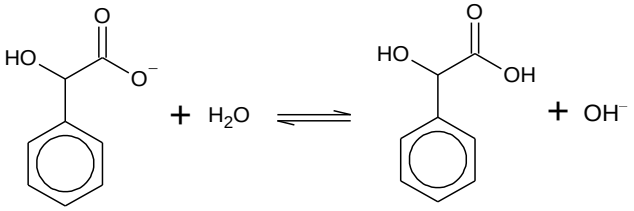
[1]

Let mandelic acid be HA.
$HA \equiv A^-$
moles of $A^- = 0.020 \times 1.0 = 0.0200$ mol
total volume at equivalence point = 20 + 10 = 30 cm^3
$[NaA] = [A^-] = 0.0200 / 0.030 =$ **0.667 mol dm^{-3}**

(ii) Hence calculate the pH of the solution at equivalence point, given pK_a of mandelic acid is 3.41.

[2]

At equivalence point, salt hydrolysis occurs:



$K_b\ (A^-) = 10^{-14} / 10^{-3.41} = 2.5704 \times 10^{-11}$ mol dm^{-3}

$[OH^-] = \sqrt{(2.5704 \times 10^{-11})(0.66667)} = 4.1396 \times 10^{-6}$ mol dm^{-3}
$pH = 14 - pOH = 14 + \lg(4.1396 \times 10^{-6}) =$ **8.62**

(iii) Use your answer in **(c)(ii)** to identify a suitable indicator from Table 2.1 for the titration. Explain your choice.

Table 2.1

Indicator	pH range
Methyl red	4.2 – 6.3
Phenolphthalein	8.2 – 10.0
Titan yellow	12.0 – 13.0

[2]

Phenolphthalein

The **pH range** of phenolphthalein **lies within the region of rapid pH change** (around 8.62).

(d) **(i)** To another 20 cm^3 sample of 1.0 mol dm^{-3} mandelic acid solution, excess sodium carbonate was added and the gas liberated was collected in a gas syringe at 50 °C and atmospheric pressure.

Calculate the volume of gas you would expect to obtain at the end of the reaction.

[2]

$2HA \equiv CO_2$
moles of $CO_2 = ½ \times 0.0200 = 0.0100$ mol

$V = nRT / p$
$= [(0.0100)(8.31)(323)] / 101325$
$= 2.65 \times 10^{-4}\ m^3$
$=$ **$265\ cm^3$**

(ii) The volume of gas collected was found to be smaller than the calculated value in **(d)(i)**. Assuming that no gas escaped in the experiment, suggest **two** reasons for the discrepancy.

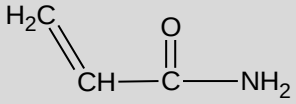
[2]

The volume of gas was measured after the **gas has cooled** (at constant pressure) from 50 °C.

The gas particles have **significant intermolecular forces of attraction** that result in them being **closer together** and hence occupy a smaller than expected volume.

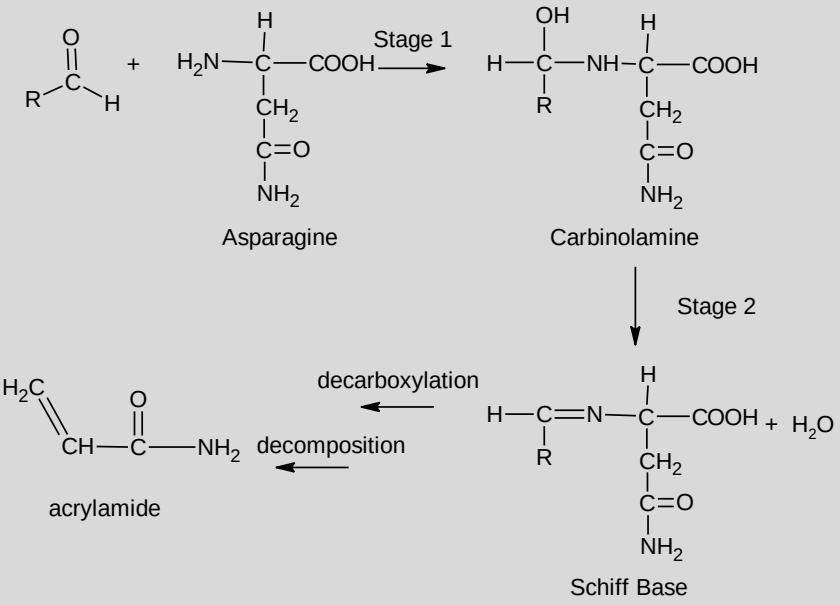
[Total: 15]

3 **(a)** High levels of acrylamide, which is harmful to human health, are produced when starchy foods are heated at high temperature.



acrylamide

The formation of acrylamide begins with the reaction between an aldehyde and asparagine, $H_2NCH(CH_2CONH_2)COOH$. This process involves the formation of carbinolamine and a Schiff Base.



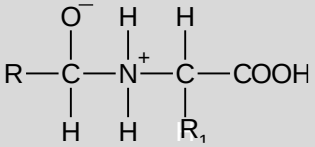
(i) State the type of reaction for stages 1 and 2 respectively.

[2]

Stage 1: Nucleophilic Addition
Stage 2: Elimination

The mechanism for stage 1 is thought to involve the following three steps.

step 1 Nucleophilic attack of α–NH_2 of asparagine on carbonyl carbon atom to form the following intermediate where R_1 is $-CH_2CONH_2$.



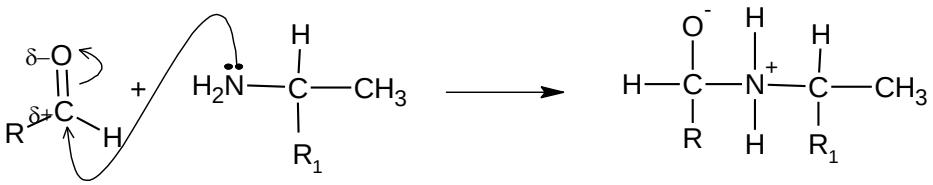
step 2 The intermediate is deprotonated by a water molecule, breaking the N–H bond.

step 3 The protonated water molecule from step 2 then transfers the proton to the negatively charged oxygen to form carbinolamine.

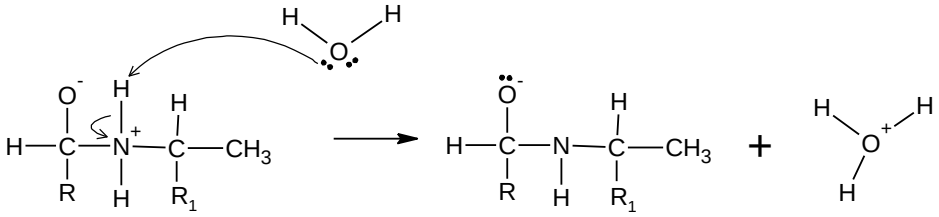
(ii) Use the information above, draw the mechanism for stage 1 by showing relevant lone pairs of electrons, dipoles and curly arrows to represent the movement of electron pairs.

[3]

Step 1: Nucleophilic addition

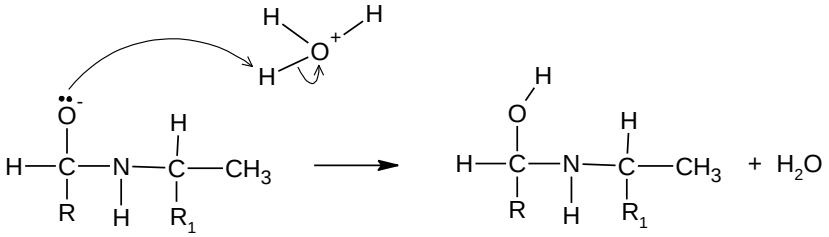


Step 2: N—H bond breaks in the presence of water solvent.



where R_1 is $—CH_2CONH_2$

Step 3: The protonated water transfers the proton to the negatively charged oxygen to form carbinolamine.



where R_1 is $—CH_2CONH_2$

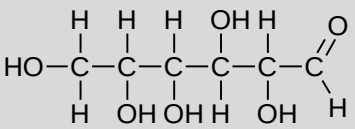
(iii) The experiment was repeated with the use of an aparaginase enzyme which hydrolyses asparagine, $H_2NCH(CH_2CONH_2)COOH$ to aspartic acid, $H_2NCH(CH_2COOH)COOH$. The level of acrylamide, $CH_2=CHCONH_2$ in food products is reduced by 99 %. Suggest a reason why this is so.

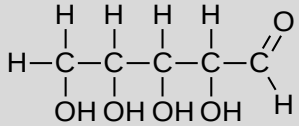
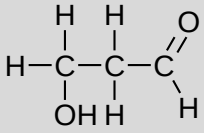
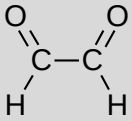
[1]

Amide group of acrylamide comes from the side chain amide group of asparagine. (During the reaction, the side chain amide group of asparagine is incorporated into acrylamide as the amide bond.) Asparaginase hydrolyses the side chain amide group of asparagine, forming aspartic acid and ammonia, and hence acrylamide is no longer produced.

(b) Several aldehydes can be found in starchy foods. Fixed amount of each aldehyde was heated with asparagine. The mass of acrylamide formed from each aldehyde is shown in Table 3.1 below.

Table 3.1

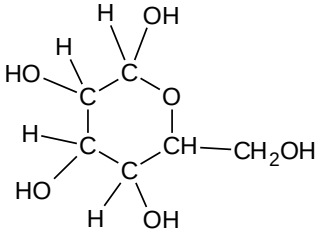
Aldehyde	Structure	Mass of acrylamide (μg)
glucose		1454

ribose		2425
glyceraldehye		2669
glyoxal		3936

(i) In solution, glucose molecules can exist in an isomeric cyclic form. The oxygen of the hydroxyl group on carbon number 5 joins to the carbonyl carbon atom and the total number of hydroxyl groups remain unchanged. The mechanism for the formation of the isomeric cyclic form is similar to that for stage 1 in **(a)**.

Draw the structural formula of glucose in the isomeric cyclic form.

[1]



(ii) Using the data in Table 3.1, state the relationship between the mass of acrylamide formed and the length of carbon chain of the aldehydes. Suggest a reason for it.

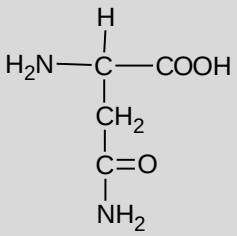
[2]

Higher mass of acrylamide obtained when shorter carbon chain is reacted.

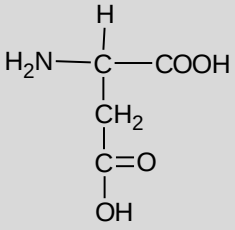
Aldehydes with shorter carbon chain are more reactive.
Possible reasons:

- Carbonyl carbon of shorter carbon chain sugar is more electrophilic, more susceptible to nucleophilic attack from α–NH_2 of asparagine;
- Carbonyl carbon of shorter carbon chain is less sterically hindered for nucleophilic attack from α–NH_2 of asparagine;
- Long carbon chain such as ribose or glucose able to form cyclic (hemiacetal) structure, therefore lower the proportion of carbonyl group for nucleophilic attack.

(c) The structures of two amino acids, asparagine and aspartic acid are given below.



asparagine



aspartic acid

(i) Suggest a simple chemical test to distinguish between asparagine and aspartic acid.

[2]

Heat both with dilute NaOH in water bath.

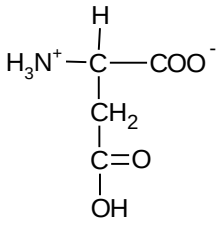
Asparagine give off ammonia which turns moist red litmus paper blue but aspartic acid does not give off ammonia gas.

(ii) The three pKa values associated with aspartic acid are 1.88, 3.65 and 9.60.

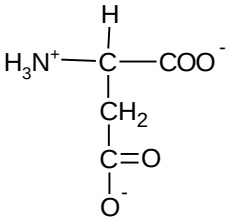
Suggest the major species present in solutions of aspartic acid with the following pH values.

- pH 3
- pH 7

[2]

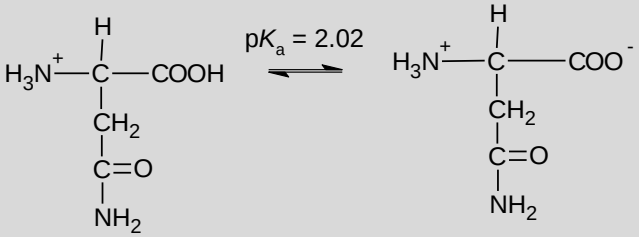


pH 3



pH 7

(iii) The following equilibrium exists in an aqueous solution of asparagine at pH 2.02.



protonated cation

zwitterion

Calculate the ratio of the concentration of asparagine zwitterion to the concentration of the protonated cation when the pH of the solution is 3.10.

You may represent the cation as HA and the zwitterion as A^- in your working. [2]

At pH 2.02 = pK_a, the equilibrium exists. The concentration of protonated cation and zwitterion would be the same. At pH 3.10, the equilibrium position is shifted to the right, concentration of zwitterion is expected to be larger than concentration of the protonated cation.

Use pH of solution = $pK_a + \log_{10} \frac{[A^-]}{[HA]}$

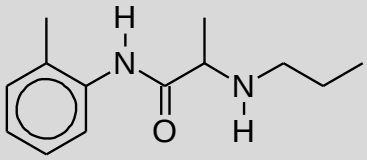
$3.10 = 2.02 + \log_{10} \frac{[A^-]}{[HA]}$

$\log_{10} \frac{[A^-]}{[HA]} = 1.08$

$\frac{[A^-]}{[HA]} = 10^{1.08} = 12.02 =$ **12.0**

[Total: 15]

4 **(a)** Prilocaine is a local anaesthesia used in dentistry.

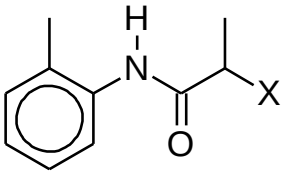


prilocaine

It can be synthesised by reacting propylamine, $CH_3CH_2CH_2NH_2$, with a suitable alkyl halide.

(i) Draw the structure of the alkyl halide.

[1]



X = C*l*, Br or I

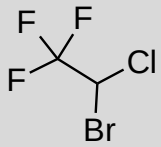
Propylamine can be formed from bromoethane in 2 steps.

(ii) Suggest the reagents and conditions needed for each step.

[2]

Step 1: ethanolic KCN, heat under reflux
Step 2: H_2 with Ni catalyst, heat OR Li*A*lH_4 in dry ether

(b) Halothane is a general anaesthetic given by inhalation.



halothane

0.1 mol of (+)–halothane is warmed with 0.1 mol of aqueous sodium hydroxide.

(i) State which halogen atom reacts. Give a reason for your answer.

[1]

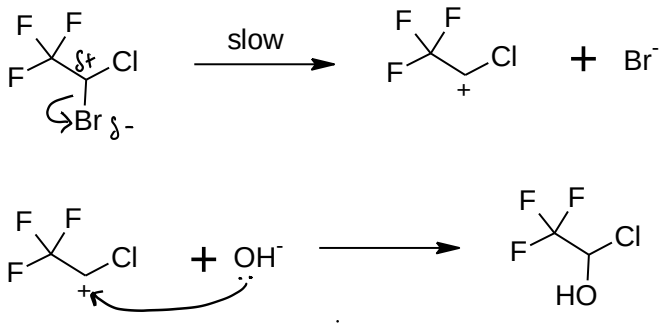
Bromine as the C–Br bond is the weakest C–X bond present.

The progress of the reaction can be followed using a polarimeter as the reactant rotates plane–polarised light while the resulting mixture is optically inactive.

(ii) Draw the mechanism for the reaction between halothane and sodium hydroxide.

[2]

Unimolecular nucleophilic substitution (S_N1)



(iii) Considering your answer to **(b)(ii)**, suggest a reason why it is unexpected for halothane to undergo substitution via the mechanism drawn.

[1]

The presence of multiple **electronegative atoms** / **electron–withdrawing groups** **intensify the positive charge** on the carbocation intermediate, destabilising it.

(c) The presence of alkyl halides can be verified by warming the sample with aqueous sodium hydroxide, followed by addition of nitric acid and lastly silver nitrate.

A student used sulfuric acid instead of nitric acid, leading to the formation of silver(I) sulfate precipitate, Ag_2SO_4.

(i) Explain how the formation of silver(I) sulfate affects the test.

[1]

A ppt will be observed whether an alkylhalide was present / It gives a false positive result / cannot distinguish between white silver(I) sulfate and white silver chloride ppt

(ii) Calculate the solubility of silver(I) sulfate given that its K_{sp} value is 1.2×10^{-5}.

[2]

Ag_2SO_4 (s) ⟷ 2 Ag^+ (aq) + SO_4^{2-} (aq)

$K_{sp} = [Ag^+]^2[SO_4^{2-}]$
$1.2 \times 10^{-5} = (2s)^2(s) = 4s^3$
s = **0.0144** mol dm^{-3}

(iii) State and explain how the solubility of silver(I) sulfate is affected by the addition of aqueous ammonia.

[1]

Solubility increases / silver(I) sulfate **ppt dissolves** due to **formation of soluble** $[Ag(NH_3)_2]^+$ **complex**.

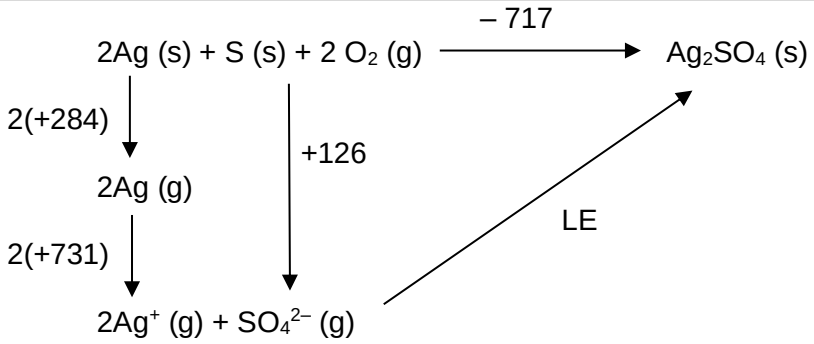
(d) Table 4.1 contains thermochemical information related to silver(I) sulfate.

Table 4.1

Enthalpy change of formation of silver(I) sulfate	–717 kJ mol^{-1}
Enthalpy change of formation of gaseous sulfate anions	+126 kJ mol^{-1}
Enthalpy change of atomisation of silver	+284 kJ mol^{-1}
Enthalpy change of hydration of silver cations	–473 kJ mol^{-1}
Enthalpy change of hydration of sulfate anions	–1035 kJ mol^{-1}

(i) Using relevant information from the *Data Booklet* and Table 4.1, draw an energy cycle to determine the lattice energy of silver(I) sulfate.

[3]



By Hess' Law,
LE = –126 – 2(731) – 2(284) – 717 = **– 2873** kJ mol^{-1}

(ii) Using your answer to **(d)(i)** and appropriate data in Table 4.1, calculate the standard enthalpy change of solution for silver(I) sulfate.

[1]

$\Delta H^{\ominus}_{sol} = \sum \Delta H^{\ominus}_{hyd} - LE = 2(-473) - 1035 + 2873 =$ **+ 892** kJ mol^{-1}

[Total: 15]

Section B

*Answer **one** question from this section*

5 **(a)** Fig 5.1 shows a sequence of reactions involving acrylic acid, the simplest unsaturated carboxylic acid.

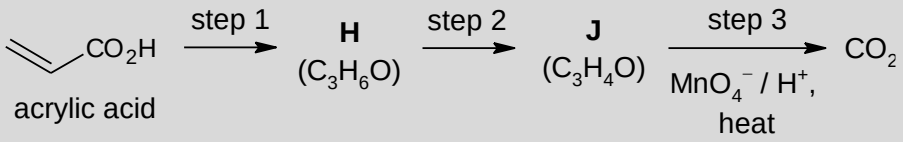
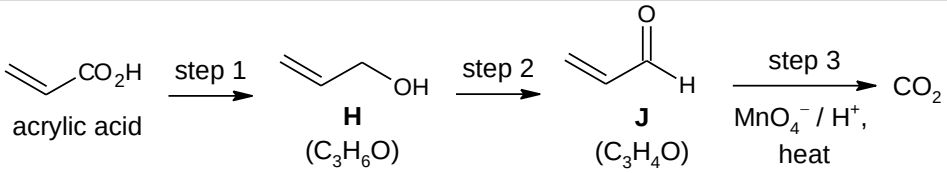


Fig. 5.1

(i) Compound **H** effervesces with sodium and compound **J** reacts with 2,4-dinitrophenylhydrazine.

Suggest structures for compounds **H** and **J**.

[2]



(ii) Suggest reagents and conditions for steps 1 and 2 in Fig. 5.1.

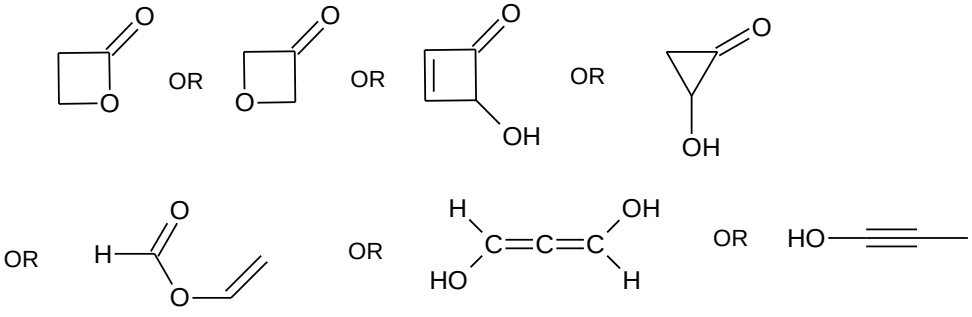
[2]

Step 1: LiA*l*H_4 in dry ether

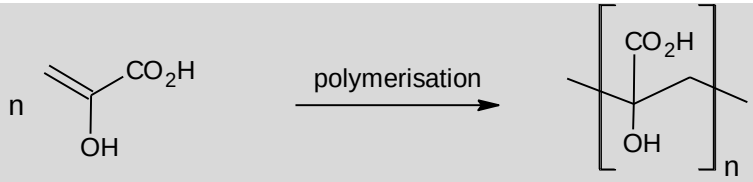
Step 2: $K_2Cr_2O_7$ in dilute/aqueous H_2SO_4, heat with immediate distillation

(iii) Compound **G**, an isomer of acrylic acid, is neutral and does not react with Tollens' reagent. Deduce the structure of **G**.

[1]



(b) α-hydroxyacrylic acid undergoes addition polymerisation to give a polymer, PHA.



α-hydroxyacrylic acid PHA

(i) Suggest and explain the relative acidities of α-hydroxyacrylic acid and acrylic acid, $CH_2=CHCO_2H$.

[2]

α-hydroxyacrylic acid is **more acidic** than acrylic acid.

The presence of the **electron-withdrawing –OH group** in the conjugate base of α-hydroxyacrylic acid **disperses the negative charge** on the COO^- group, making the conjugate base **more stable** √ than that of acrylic acid.

(ii) Studies suggests that PHA interacts with divalent metal cations such as calcium and magnesium under alkaline conditions.

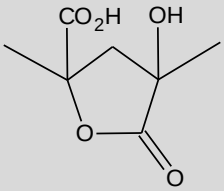
Suggest and explain the type of interaction that is likely to exist between PHA and the metal cations in alkaline medium.

[2]

Ionic interactions.

Under alkaline conditions, the carboxylic acid groups in PHA are deprotonated/neutralised. The **negatively charged carboxylate** (COO^-) groups can form **electrostatic forces of attraction** with the positively charged **metal cations**.

(c) PHA can form intramolecular lactone rings between –COOH and –OH groups on adjacent repeat units. Part of the structure of PHA with an intramolecular ring is shown below.



(i) State the type of reaction occurring in the formation of the lactone ring.

[1]

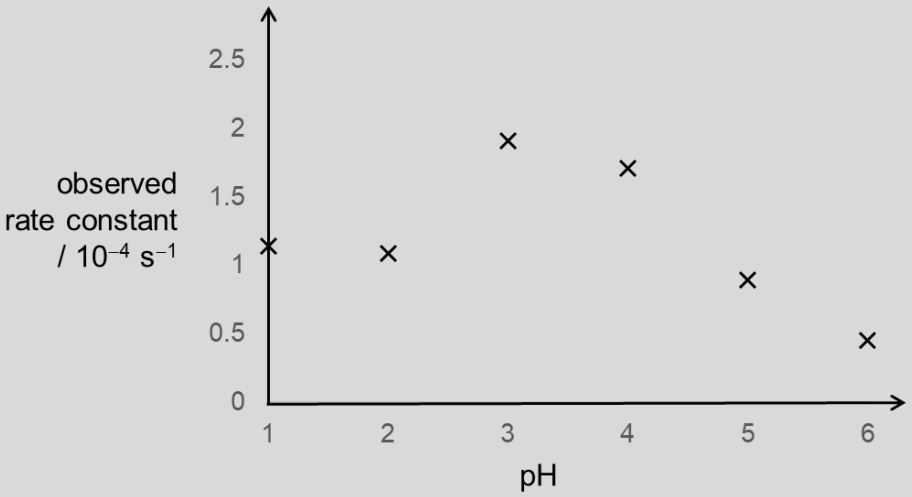
Condensation

A series of experiments were carried out to investigate the rate of the lactone ring build-up of PHA as a function of pH at constant temperature.

The rate equation for the reaction is given as follows.

$$\text{rate} = k[\text{PHA}]^m[\text{H}^+]^n$$

The reaction was observed to follow pseudo first order kinetics with respect to PHA and the following graph of the observed rate constant against pH was obtained.



(ii) Suggest how the pseudo first order kinetics with respect to PHA was achieved experimentally.

[1]

The **acid** (to provide H^+ ions) was used in **large excess** as compared to PHA.

(iii) From the graph, identify the pH range for which the value of ***n***, order of reaction with respect to H^+, is zero.

Explain your reasoning.

[2]

pH 1 to pH 2

Since reaction follows pseudo first order kinetics with respect to PHA,
rate = k'[PHA] where k' = $k[H^+]^n$

From pH 1 to pH 2, the **observed rate constant**, k', was **relatively constant**, suggesting that the **rate was independent of $[H^+]$**.

(iv) At a certain pH that lies within the range identified in **(c)(iii)**, the observed rate constant was found to be 1.14×10^{-4} s^{-1}. Calculate the time taken for 75% of lactone rings to be formed at this pH.

[2]

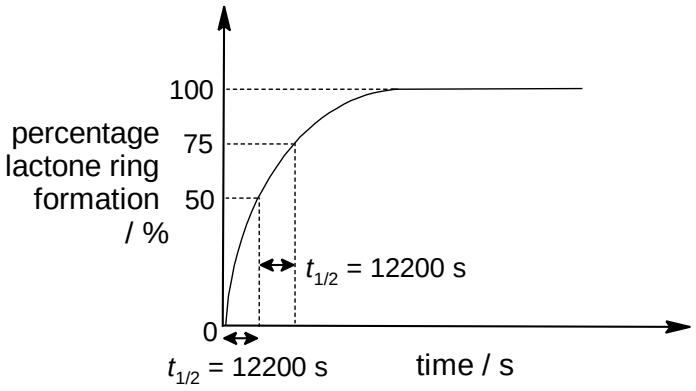
$t_{\frac{1}{2}} = \frac{\ln 2}{k'} = \frac{\ln 2}{0.000114}$ = 6080.2 s

Since $\frac{25}{100} = \left(\frac{1}{2}\right)^n$, number of half-lives passed, n = 2

Time taken = 6080.2×2 = **12200 s**

(v) Hence sketch a graph of percentage lactone ring formation against time, assuming that the reaction goes to completion. Label clearly how the percentage of lactone changes with time.

[2]



(d) The PHA samples used in the kinetic study was prepared by dilution of the reagent solution with heavy water, D_2O.

[Deuterium, D = ^2H]

(i) Suggest, with reasoning, how the first ionisation energy of deuterium would compare with that of hydrogen.

[1]

The first ionisation energy of deuterium would be **similar to / the same** as that of hydrogen.

Deuterium and hydrogen have the **same number of protons** and the additional neutron present in the nucleus of deuterium is uncharged. Hence the **effective nuclear charge/ electrostatic attraction between the valence electron and nucleus** is **similar / the same** for deuterium and hydrogen.

(ii) Beams of D^+ and H^+ particles, at the same speed, were passed through an electric field.
Explain, qualitatively, how the angle and direction of deflection of the two beams would compare.

[1]

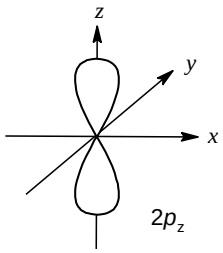
Since angle of deflection $\propto \frac{\text{charge}}{\text{mass}}$, the D^+ particles (which are of the same charge but twice as heavy than H^+ particles) will be **deflected in the same direction but by half the angle** of that of H^+ particles.

(iii) Water enriched in heavier oxygen-18 isotope, $H_2{}^{18}O$, is also commercially available.

Draw the orbital from which the electron is removed in the **third** ionisation energy of an oxygen-18 isotope.

[1]

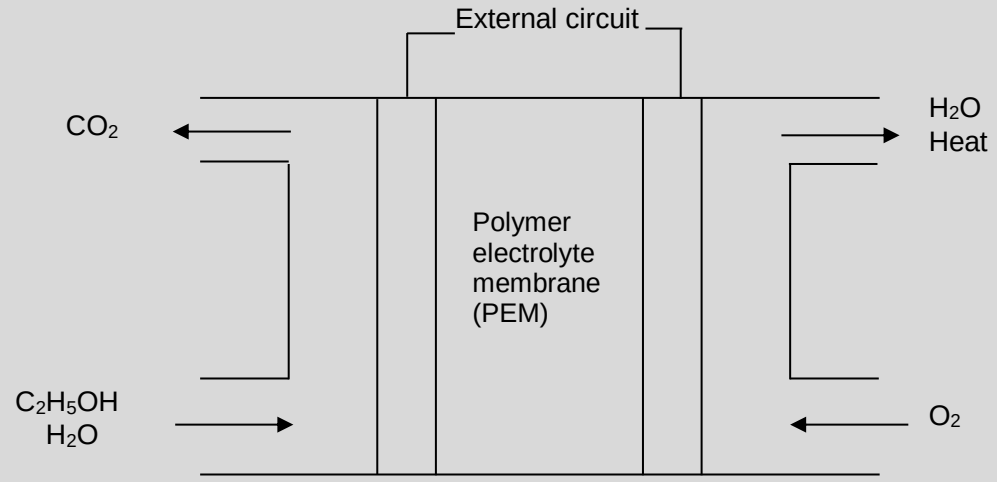
^{18}O: $1s^2 2s^2 2p^4$ and a 2*p* electron is removed in the 3rd ionisation energy.



[Total: 20]

6 (a) The direct oxidation of alcohols in a fuel cell represents potentially the most efficient method of obtaining useful energy from a renewable fuel.

Direct–ethanol fuel cell or DEFC is one common example of fuel cells where ethanol is fed directly into the cell to produce carbon dioxide. Hydrogen ions travel through the polymer electrolyte membrane (PEM) to the electrode to react with oxygen to produce water, while the electrons travel through the external electrical circuit to generate electrical power.



(i) Write the ion–electron half–equations for the reactions which take place at the electrodes of the DEFC, and hence an overall equation for the cell reaction.

[2]

Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
Anode: $C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$

Overall equation: $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

(ii) The cell is capable of producing an e.m.f of +1.62 V. By using suitable data from the *Data Booklet*, suggest a value for the $E^\ominus$ of the CO_2/C_2H_5OH electrode reaction.

[1]

$E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode}$
$+1.62 = +1.23 - E^\ominus_{anode}$
$E^\ominus_{anode} = +1.23 - 1.62$
$= -0.39V$

(iii) Pyrogallol solution is an organic compound that absorbs oxygen efficiently. Explain qualitatively the change in the overall E_{cell} value measured when the electrodes are contaminated with pyrogallol solution.

[2]

$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$
When a small amount of pyrogallol solution is added, it decreases the partial pressure of O_2 / $[O_2]$. Hence **equilibrium** above will **shift to the left to increase partial pressure of** O_2 / $[O_2]$**.**

$\boldsymbol{E^\ominus_{cathode}}$ will be **more negative/less positive** and hence **overall** $\boldsymbol{E_{cell}}$ **value** will be **more negative/less positive**.

(iv) Suggest a possible advantage of using the DEFC compared to a hydrogen fuel cell.

[1]

The cost of transportation will be lower as ethanol is in the liquid state. /
It is safer to transport ethanol as it is less explosive than hydrogen / ethanol takes up less space than hydrogen.

(b) One method for the construction of the fuel cell involves electroplating a layer of platinum onto the surface of the PEM. The electrolyte used for this process is a solution of $[Pt(NH_3)_4]^{2+}$ and the PEM is the cathode in the electrolytic cell.

(i) Write the half–equation for the reaction occurring at the cathode.

[1]

$[Pt(NH_3)_4]^{2+} + 2e^- \rightarrow Pt + 4NH_3$

(ii) Calculate the mass of platinum deposited onto a PEM with surface area of 25 cm^2 if a current of 3.5 x 10^{-3} A cm^{-2} was passed through the circuit for 75 minutes.

[2]

Q = It
= $(3.5 \times 10^{-3})(25)(75 \times 60)$
= 393.75 C

Number of moles of electrons = 393.75 / 96500
= 0.00408 mol

Number of moles of platinum deposited = 0.00204 mol

Mass of platinum = 2.04 x 10^{-3} x 195.1 = **<u>0.398 g</u>**

(c) Selective oxidation of alcohols to aldehydes and ketones is a key reaction in organic synthesis, both for fundamental research and industrial manufacturing.

When alkaline potassium manganate(VII) is added to a primary alcohol, the purple solution first becomes dark green and then produces a brown precipitate.

(i) State the identities of the dark green solution and the brown precipitate. You may find the use of *Data Booklet* to be relevant.

[1]

Dark green solution : MnO_4^{2-}
Brown ppt : MnO_2

When acidified potassium manganate(VII) is added to a secondary alcohol, the purple solution decolourises. Propan–2–ol reacts with acidified potassium manganate(VII) to yield propanone, according to the **unbalanced** equation as shown below.

$$CH_3{}^{a}CH(OH)CH_3 + MnO_4^- \rightarrow CH_3{}^{b}COCH_3 + Mn^{2+}$$

(ii) State the oxidation number of ^{a}C and ^{b}C respectively.

[1]

^{a}C – 0
^{b}C – +2

(iii) Hence, or otherwise, determine the reacting mole ratio of propan–2–ol to potassium manganate(VII).

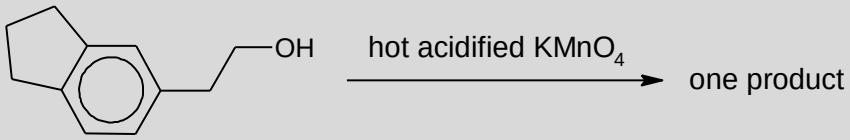
[1]

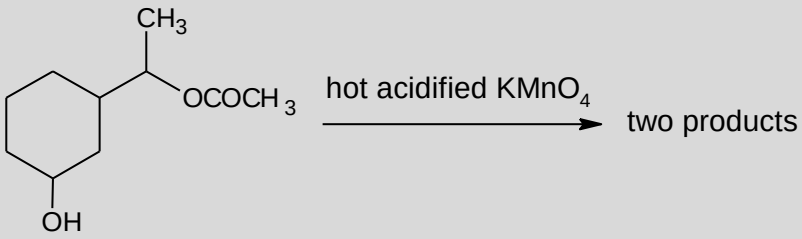
Since oxidation number of reacting carbon increases from 0 in propan-2-ol to +2 in propanone, there is a loss of 2 electrons per mole of propan-2-ol.

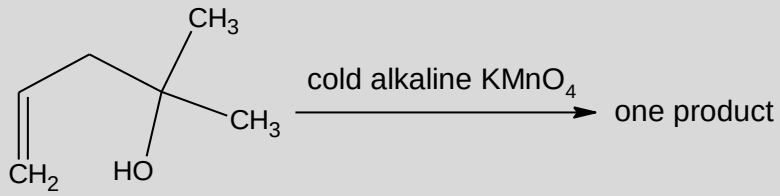
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
There is a gain of 5 electrons per mole of MnO_4^-

Since electrons lost = electrons gained in the reaction,
Reacting mole ratio of $CH_3CH(OH)CH_3$: MnO_4^- = 5 : 2

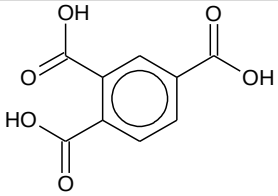
(iv) Predict the organic products of the following reactions with $KMnO_4$(aq).

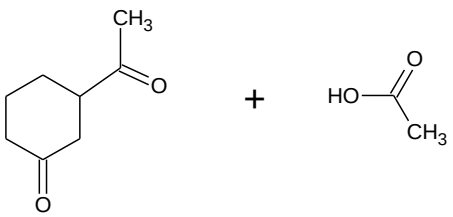


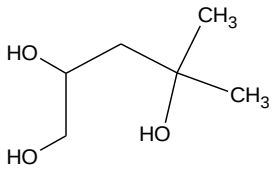




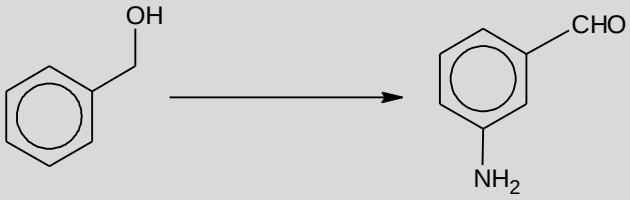
[4]





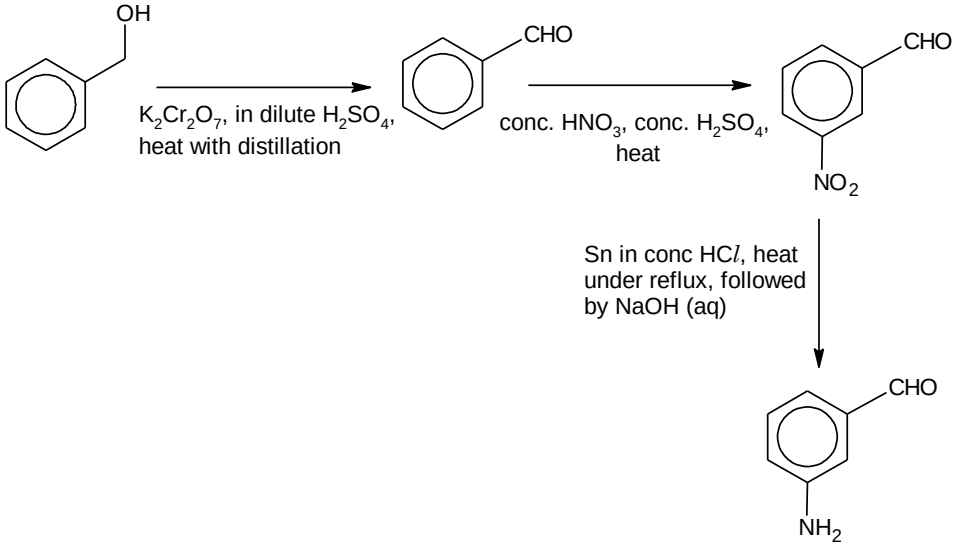


(d) Devise a synthetic pathway (in no more than 3 steps) for the following conversion.



In your answer, state the reagents and conditions required for each step as well as the structure of any intermediates formed.

[4]



[Total:20]