Name:		Index Number:		Class:	

DUNMAN HIGH SCHOOL
Preliminary Examination 2019
Year 6

H2 CHEMISTRY

9729/03

Paper 3 Free Response

25 September 2019
2 hours

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 page.

[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

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

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 theoretical amount, in moles, of each carbonate present in the sample of agricultural lime.

[1]

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

[2]

(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]

(iv) 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]

(v) 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]

(b) Nitrogen fertilisers are also 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]

(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]

(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]

[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]

(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]

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

[2]

(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]

(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.

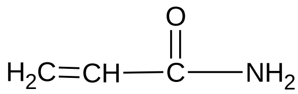
[2]

(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]

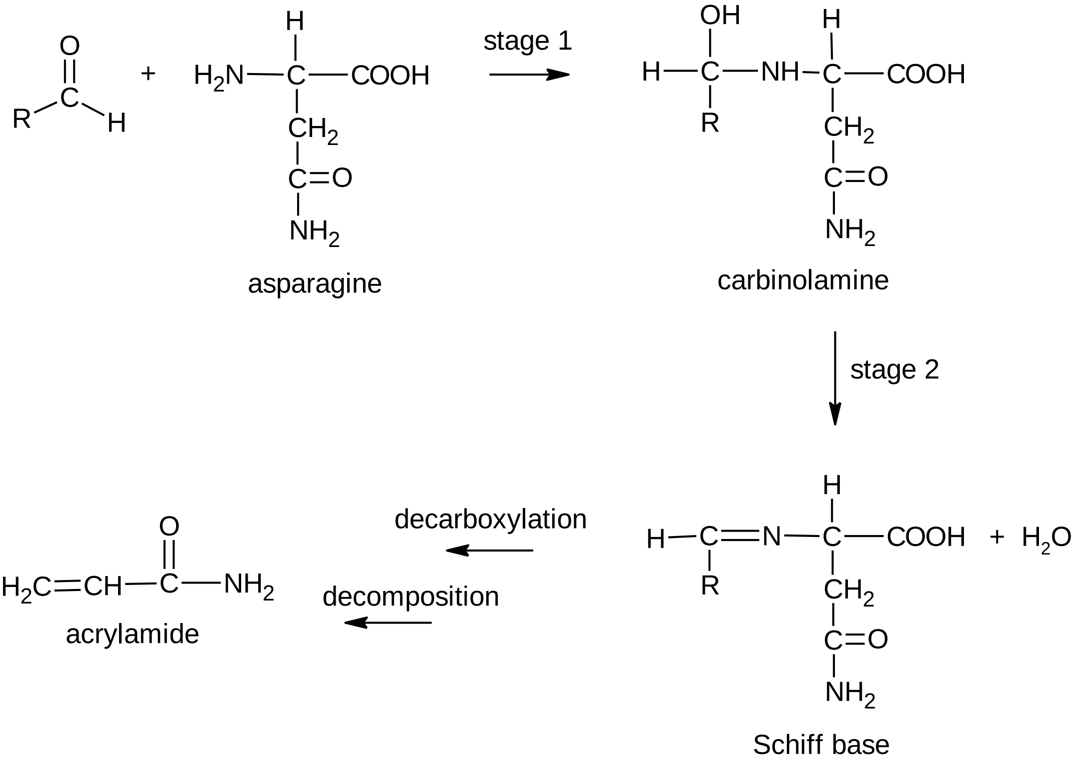
[Total: 15]

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.

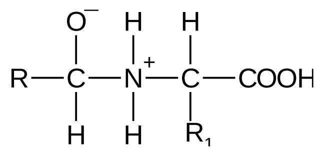


(i) State the type of reaction occurring in stages 1 and 2 respectively.

[2]

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) Using 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.

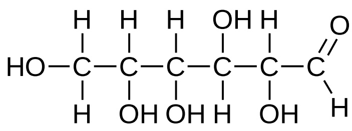
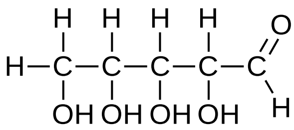
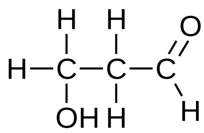
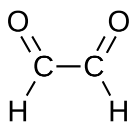
[3]

(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]

(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)**.

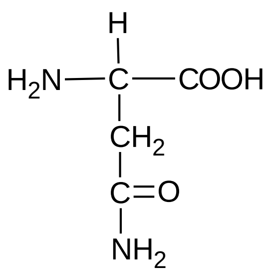
Draw the structural formula of glucose in the isomeric cyclic form.

[1]

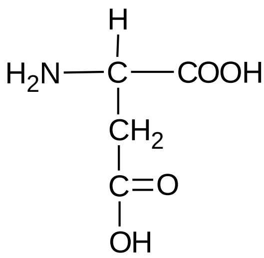
(ii) Using the data in Table 3.1, state the relationship between the mass of acrylamide formed and the length of carbon chain of the aldehydes. Suggest a reason for it.

[2]

(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]

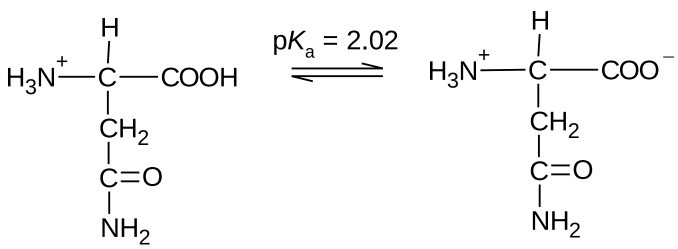
(ii) The three pK_a values associated with aspartic acid are 1.88, 3.65 and 9.60.

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

- pH 3
- pH 7

[2]

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



protonated cation

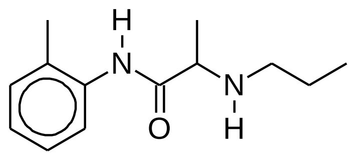
zwitterion

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]

[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.

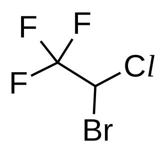
[1]

Propylamine can be formed from bromoethane in 2 steps.

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

[2]

(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]

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]

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

[1]

(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]

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

[2]

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

[1]

(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]

(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]

[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.

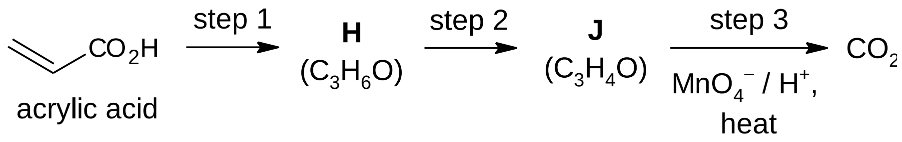


Fig. 5.1

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

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

[2]

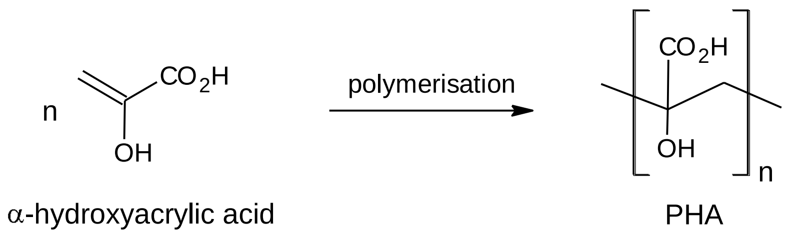
(ii) Suggest reagents and conditions for steps 1 and 2 in Fig. 5.1.

[2]

(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.



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

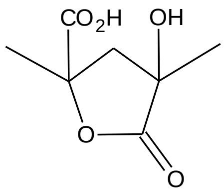
[2]

(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]

(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.

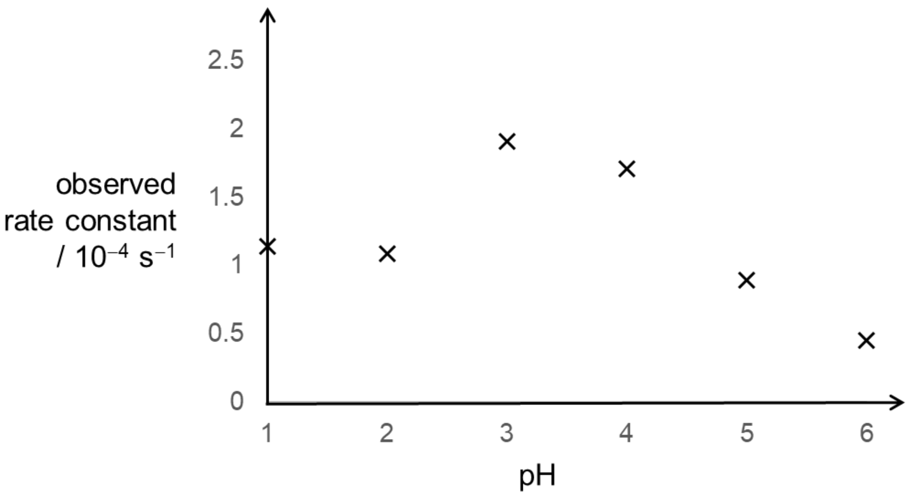
[1]

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]

(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]

(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]

(v) Hence sketch a graph of percentage of 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 = ^{2}H]

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

[1]

(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]

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

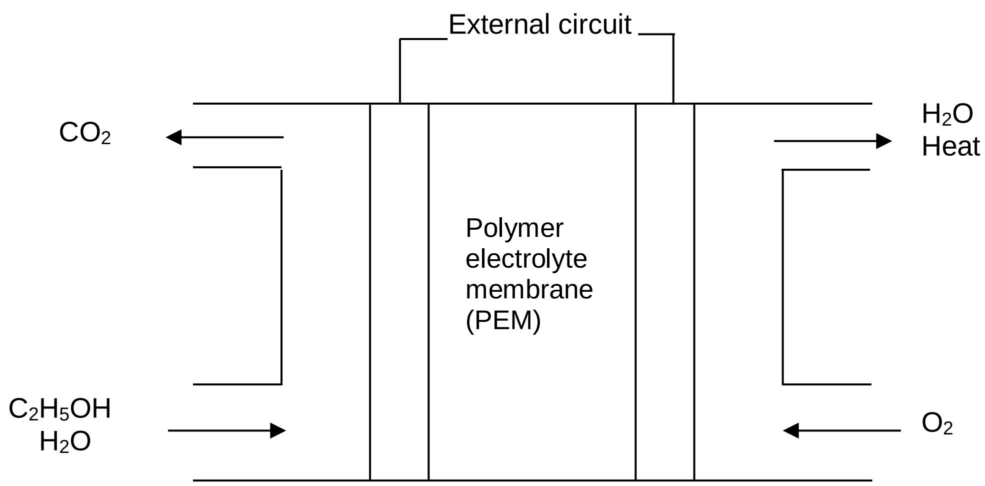
Draw the orbital from which the electron is removed in the **third** ionisation energy of an oxygen–18 isotope.

[1]

[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]

(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]

(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]

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

[1]

(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 an aqueous 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]

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

[2]

(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]

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.

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

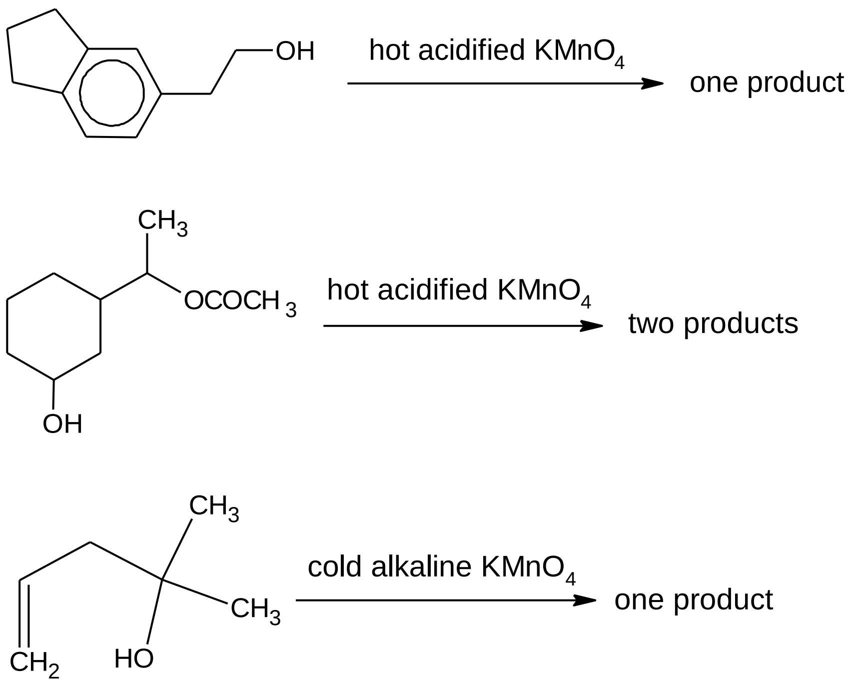
(ii) State the oxidation number of ${}^{a}C$ and ${}^{b}C$ respectively.

[1]

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

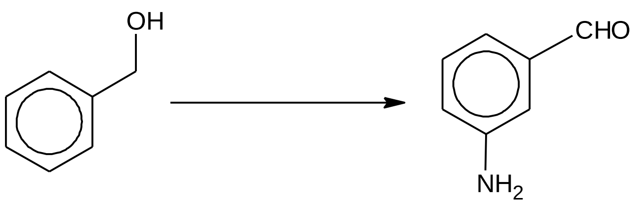
[1]

(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]