Catholic Junior College
JC2 Preliminary Examinations
Higher 2

CHEMISTRY 9729/03

Paper 3 Free Response **25 August 2017**

2 hours

Candidates answer on separate paper.
Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Section A

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

1 *Use of the Data Booklet is relevant to this question.*

(a) Under acidic conditions, ethanol reacts with dichromate(VI) ions quantitatively to give ethanoic acid and chromium(III) ions.

$$3CH_3CH_2OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 3CH_3CO_2H + 4Cr^{3+} + 11H_2O$$

A student carried out the following experiment to determine the concentration of ethanol in a brand of wine.

A 10.0 cm^3 sample of the wine was diluted to 250 cm^3. He then added 25.0 cm^3 of 0.156 mol dm^{-3} $K_2Cr_2O_7(aq)$ and excess dilute H_2SO_4 to a 25.0 cm^3 portion of the diluted solution. After allowing the mixture to stand for about an hour at room temperature, the excess $K_2Cr_2O_7$ in the mixture was then titrated with 0.118 mol dm^{-3} $(NH_4)_2Fe(SO_4)_2(aq)$ using an appropriate indicator. At the end-point of the titration, he used 12.25 cm^3 of the $Fe^{2+}(aq)$ solution.

(i) Write an ionic equation for the reaction that occurs during titration. [1]

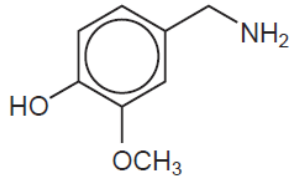
(ii) Calculate the concentration, in mol dm^{-3}, of ethanol in this brand of wine. [4]

(b) The relatively high alcohol content in wine makes it difficult to pair wine with spicy food because the combination can create a painful burning sensation on the lips and tongue that cannot be wiped or rinsed away.

Capsaicin, $C_{18}H_{27}NO_3$, is the active ingredient in spicy food that gives the hot taste of chilli peppers. The structure of capsaicin can be deduced from the following reactions.

When capsaicin is boiled with dilute sulfuric acid, compound **A**, $C_{10}H_{18}O_2$, and the salt of compound **B**, are produced. Compound **B**, $C_8H_{11}NO_2$, has the structure shown, where the $CH_3O–$ group can be regarded as inert.

compound **B**



When **A** is heated with concentrated acidified $KMnO_4$, compound **C**, $C_6H_{10}O_4$, and compound **D**, $C_4H_8O_2$, are produced. **C** can be prepared from $Br(CH_2)_4Br$ in two steps whereas **D** can be prepared directly from $(CH_3)_2CHCH_2OH$.

Compounds **A**, **C** and **D** all react with aqueous sodium carbonate.

(i) What observations and deductions could be made from the reaction of **A**, **C** and **D** with aqueous sodium carbonate? [2]

(ii) Draw the structural formula of **D** and state the reagents and conditions required for its preparation from $(CH_3)_2CHCH_2OH$. [2]

(iii) Show how compound **C** can be prepared from $Br(CH_2)_4Br$, stating clearly the reagents and conditions required for each step, and give the structural formulae of **C** and the intermediate formed. [4]

(iv) Hence suggest the structure for **A** and two possible structures for capsaicin. [3]

(c) Methanol, CH_3OH, is the simplest alcohol that could be used to power a fuel cell in an electric car.

Figure 1.1 shows a preliminary design of a methanol fuel cell. The fuel and oxygen are fed continuously to the two electrodes which are made of platinum. Methanol is oxidised when the fuel cell is operated.

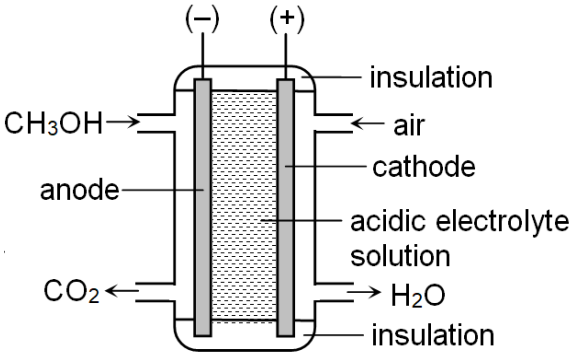


Fig. 1.1

(i) Write balanced equations for the half reactions at each electrode and for the overall cell reaction. [2]

(ii) Write a cell representation, indicating clearly on the cell representation the direction of electron flow in the external circuit. [1]

(iii) Use appropriate data from the *Data Booklet* to explain why an acidic electrolyte is often preferred to an alkaline electrolyte. [1]

(iv) The design of the above fuel cell could be improved by replacing the acidic electrolyte solution with a film of solid H^+ ion-conducting polymer.

Suggest a reason for doing so. [1]

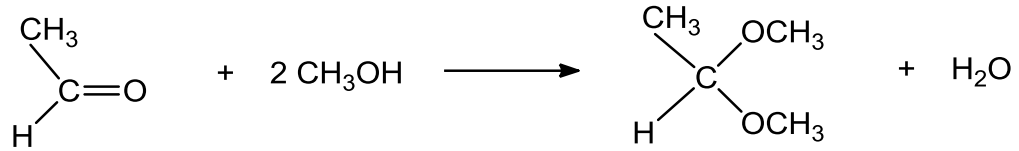
(v) Methanol could also be used as fuel in an internal combustion engine.

Suggest one advantage of the methanol fuel cell over such an internal combustion engine that uses methanol. [1]

[Total: 22]

[Turn over

2 Acetals are molecules that contain 2 –OR groups bonded to the same carbon and are formed when aldehydes are reacted with an alcohol in the presence of an acid. The reaction between ethanal and methanol in the presence of acid, to produce acetal **A** was studied.



acetal **A**

(a) When the initial rate of this reaction was measured at various starting concentrations of ethanal, methanol and H^+, the following results were obtained:

Experiment number	$[CH_3CHO]$ / mol dm^{-3}	$[CH_3OH]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	relative rate
1	0.20	0.10	0.05	1.00
2	0.25	0.10	0.05	1.25
3	0.25	0.32	0.05	4.00
4	0.10	0.16	0.10	1.60

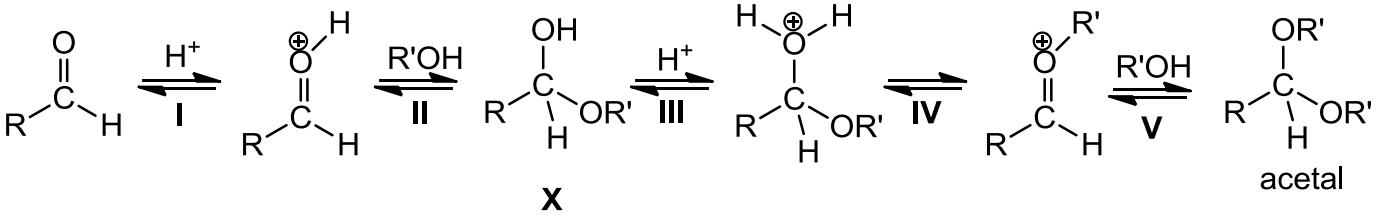
(i) Use the data in the table to determine the order with respect to
I ethanal
II methanol and
III H^+.

[3]

(ii) Use your results from **(a)(i)** to write the rate equation for the reaction. [1]

(iii) Calculate the relative rate of reaction for a mixture in which the starting concentrations of all three reactants are 0.20 mol dm^{-3}. [1]

(b) The mechanism of acetal formation is proposed to proceed through the following steps.

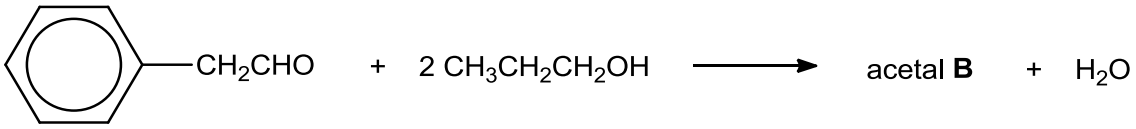


(i) The protonation of the carbonyl group in step **I** is necessary for step **II** to take place. Suggest a reason for this. [1]

(ii) Using your answer to **(a)(ii)**, state with reasons, which one is the rate-determining step of the reaction mechanism. [2]

(iii) The species in the mechanism have various roles. They can be reactants, products, catalysts or intermediates. Suggest, with a reason in each case, the roles of H^+ and **X**. [2]

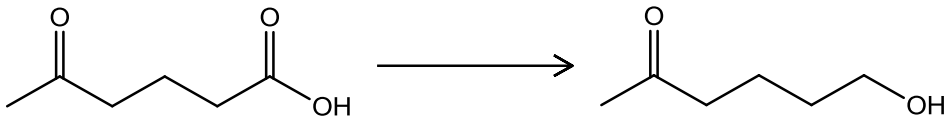
(c) Draw the structure of the acetal **B** formed from the reaction between phenylethanal and propan-1-ol.



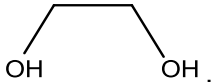
[1]

(d) Acetal formation is useful in organic synthesis. When an aldehyde or ketone is converted to an acetal, the carbonyl group is protected from attack by reagents such as bases and reducing agents. The acetal can later be hydrolysed by a strong acid to form the original aldehyde or ketone since the formation of acetals is a reversible reaction.

Suggest a suitable synthesis route for the following conversion



which involves the initial formation of an acetal group using ethane-1,2-diol,



. [2]

(e) Methanol is currently studied as a potential green fuel that greatly reduces the pollution to the environment.

$$CH_3OH(l) + \frac{3}{2} O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

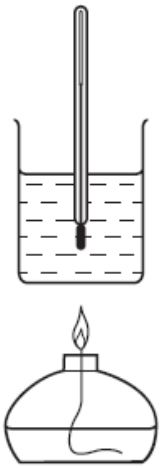
(i) The standard molar entropy, $S^{\ominus}$ is the entropy content of one mole of substance under standard conditions. Given the following standard molar entropy values, calculate the standard entropy change of combustion of methanol. [1]

	$S^{\ominus}$ /J K^{-1} mol^{-1}
$CH_3OH(l)$	126.8
$O_2(g)$	205.0
$CO_2(g)$	213.6
$H_2O(l)$	69.9

(ii) Hence, explain the significance of the sign of the standard entropy change of combustion of methanol. [1]

[Turn over

(iii) A student carried out an experiment to determine the enthalpy change for the combustion of methanol. A sample of methanol was burnt under laboratory conditions and the following results were obtained by the student.



initial temperature of the water	25.0 °C
final temperature of the water	48.2°C
mass of alcohol burner before burning	259.65 g
mass of alcohol burner after burning	259.15 g
mass of glass beaker and water	150.00 g
mass of glass beaker	50.00 g

Given that the theoretical enthalpy change of combustion of methanol is –726 kJ mol^{-1}, calculate the percentage of heat evolved used to heat up the water.

[2]

(iv) Using the theoretical enthalpy change of combustion and other relevant information given above, calculate the change in standard Gibbs free energy for the combustion reaction. [1]

(v) Predict and explain the effect on the spontaneity of this reaction of increasing the temperature. [2]

[Total: 20]

3 **(a)** Water pollution is any chemical, physical or biological change in the quality of water that has a harmful effect on any living thing that consumes it. In 2008, a cholera outbreak in Zimbabwe occurred due to a lack of proper water treatment. It is possible to stop the spread of cholera by treating water with chlorine or solid calcium chlorate(I). Calcium chlorate(I), $Ca(ClO)_2$, reacts with water to form chloric(I) acid, $HClO$, which acts as a general biocide.

(i) Write an ionic equation for the reaction of calcium chlorate(I) with water. [1]

(ii) Chloric(I) acid, $HClO$, can also be formed by adding chlorine dioxide gas, ClO_2, to water as shown in the equation below:

$$4ClO_2 + 2H_2O \rightarrow HClO + HClO_3$$

Identify the specific type of reaction that chlorine has undergone by stating the oxidation states of chlorine in the relevant species. [2]

(iii) An environmental scientist decides to analyse a sample of treated water to find out the amount of chlorine it contains. A 250 cm^3 sample of the chlorine–containing water was treated with an excess of potassium iodide solution.

$$Cl_2(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2Cl^-(aq)$$

The sample was subsequently titrated with 12.30 cm^3 of 0.001 mol dm^{-3} sodium thiosulfate solution to find out how much iodine had been formed.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

Calculate the concentration of Cl_2, in mol dm^{-3}, in the original sample of treated water. [2]

(iv) Suggest a reason why it may be preferable to use calcium chlorate(I) rather than chlorine for treating drinking water. [1]

(b) The extraction of aluminium from its ore is highly energy intensive and often results in pollution of the environment. Phosphorus, however, poses a threat to biodiversity in aquatic ecosystems through the depletion of oxygen via the excessive growth and decomposition of aquatic plants and algae.

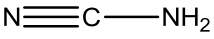
When heated in chlorine, both aluminium and phosphorus form chlorides.

(i) Describe the observations when a **limited** amount of water is added to the chlorides of aluminium and phosphorus respectively and write equations for any reactions that occur. [2]

(ii) Write equations for any reactions that might occur when an **excess** amount of water is added to the chlorides of aluminium and phosphorus respectively and suggest the pH of each solution formed. [2]

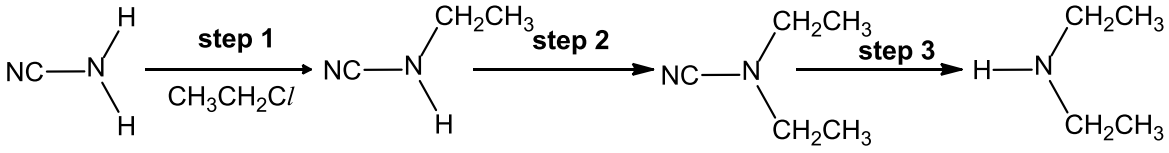
[Turn over

(c) Cyanamide, CH_2N_2, is a compound commonly used in fertilisers that could also cause eutrophication, which deplete the water's oxygen supply through excessive growth and decomposition of algae and water plants.



cyanamide

Cyanamide is a useful precursor for the synthesis of secondary amines with a relatively high yield. Below is the sequence of steps for the synthesis of N-ethylethylamine.



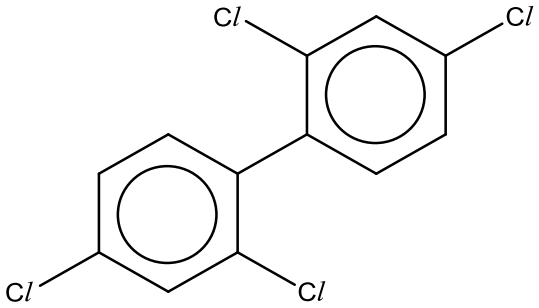
cyanamide N-ethylethylamine

(i) Describe the mechanism for the reaction in **step 1**. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons. [4]

(ii) Identify the two roles of cyanamide in your mechanism. [1]

(iii) Besides using a specific catalyst and heating under reflux for **steps 1** and **2**, suggest another condition which would give a high yield of the intermediate formed in **step 2**. [1]

(d) 2,2',4,4'-tetrachlorobiphenyl is a common organic pollutant that is immiscible in water.



2,2',4,4'-tetrachlorobiphenyl

Suggest two reasons why 2,2',4,4'-tetrachlorobiphenyl is typically inert and chemically unreactive to nucleophilic reagents. [2]

[Total: 18]

Section B

Answer **one** question from this section.

4 Transition elements show unique properties that distinguish them from s-block elements, such as calcium. These include variable oxidation states in their compounds, and the formation of coloured complex ions.

(a) Chromium, a transition element, forms two common series of compounds. One containing chromium in the +3 oxidation state while the other containing chromium in +6 oxidation state.

The complex ion $[Cr(OH)_6]^{3-}$ is green whereas the complex ion $[Cr(NH_3)_6]^{3+}$ is purple. Both of these complexes are octahedral.

In an octahedral complex, the d subshell of a transition metal ion is split into two energy levels.

(i) Using the Cartesian axes, like those shown in Fig 4.1, draw fully-labelled diagrams of the following.

- One of the d orbitals at the lower energy level in an octahedral complex. Label this diagram 'lower'.
- One of the d orbitals at the upper energy level in an octahedral complex. Label this diagram upper.

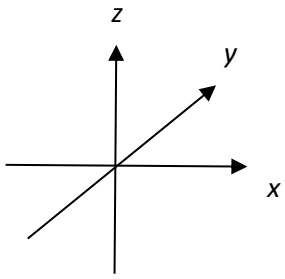


Fig. 4.1

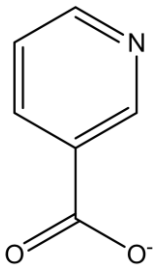
[2]

(ii) Explain why splitting of the d-subshell occurs in an octahedral complex, using your d orbital diagrams in **(a)(i)**. [2]

(iii) By considering your answer to **(a)(ii)**, suggest why $[Cr(OH)_6]^{3-}$ and $[Cr(NH_3)_6]^{3+}$ have different colours. [1]

[Turn over

(b) Chromium(III) nicotinate is commonly used as chromium supplementation for medical conditions associated with diabetes mellitus type 2. This octahedral complex contains three nicotinate ions per chromium ion. The nicotinate ion has the structure shown below.



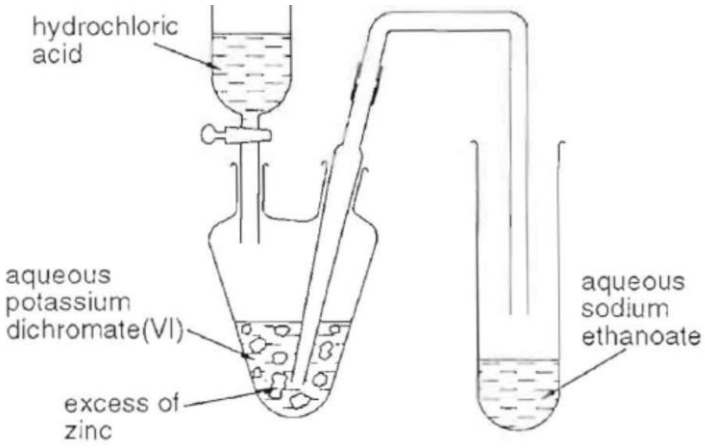
nicotinate ion

(i) Copy the structure of nicotinate ion and circle the atoms that are bonded to chromium(III) ion. Explain your choice of atoms. [2]

(ii) What is the overall charge of this complex? [1]

(c) Chromium-containing compounds are useful reagents in the laboratory.

The apparatus and reagents shown in the diagram are used to prepare chromium(II) ethanoate, which is a reducing agent.



All the acid is added to the dichromate solution and the zinc in the flask. The tap funnel is left open. The flask is shaken and chromium soon reaches the Cr^{3+} state.

(i) Write balanced equations for the **two** reactions involving zinc which take place initially in the flask. [2]

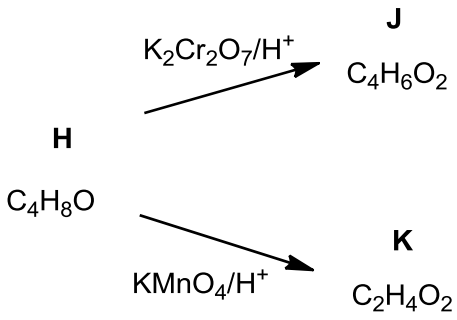
The colour of the solution in the flask subsequently changes as $Cr^{2+}(aq)$ is produced.

(ii) Using relevant redox potential values in the *Data Booklet*, show why the reduction of Cr^{3+} to Cr^{2+} is likely to proceed. [2]

The tap funnel is subsequently closed and the liquid in the flask forced over into the tube containing the aqueous sodium ethanoate to form chromium(II) ethanoate.

(iii) By considering your answers to **(c)(i)**, suggest what causes the liquid to be forced over into the tube. [1]

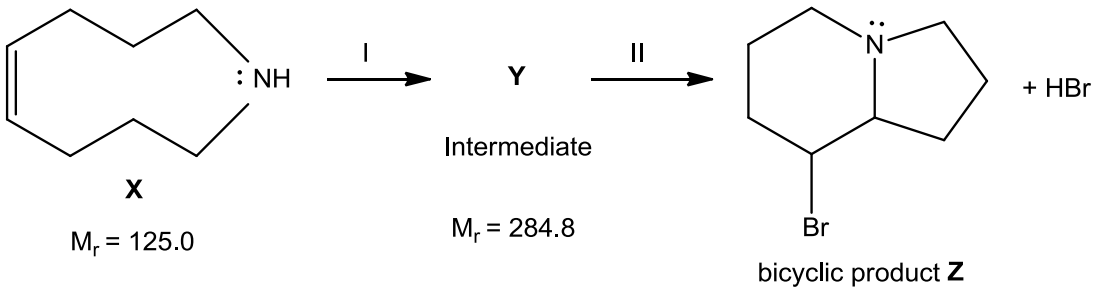
(d) Another chromium-containing compound, $K_2Cr_2O_7$, together with $KMnO_4$ are common oxidising agents used in organic synthesis. $KMnO_4$ is the more powerful of the two, as shown by the following scheme.



All three compounds, **H**, **J** and **K** react with sodium metal. **J** and **K** react with Na_2CO_3, but **H** does not. **H** and **J** decolourise aqueous bromine.

Suggest structures for **H**, **J** and **K**. [3]

(e) The bicyclic product **Z** shown below can be formed from **X** in the following scheme:



(i) Suggest reagents and conditions for Step I and the structure of **Y**. [2]

(ii) Given that Step II is an intramolecular reaction, explain the conversion of **Y** into **Z**, drawing curly arrows to show the movement of electron pair where necessary. State the type of reaction in Step II. [2]

[Total: 20]

[Turn over

5 Hydroformylation is used commercially for producing aldehydes from alkenes. The aldehyde produced is then converted into other organic compounds.

Butanal is synthesised from propene from the following hydroformylation reaction at 500 K.

$$CH_3CH{=}CH_2(g) + CO(g) + H_2(g) \rightleftharpoons CH_3CH_2CH_2CHO(g) \qquad \Delta H < 0$$

(a) An equimolar mixture of $CH_3CH{=}CH_2$, CO and H_2 at an initial total pressure of 150 atm is allowed to reach dynamic equilibrium. Figure 5.1 below shows the graphs of partial pressure of $CH_3CH{=}CH_2$ and $CH_3CH_2CH_2CHO$ against time.

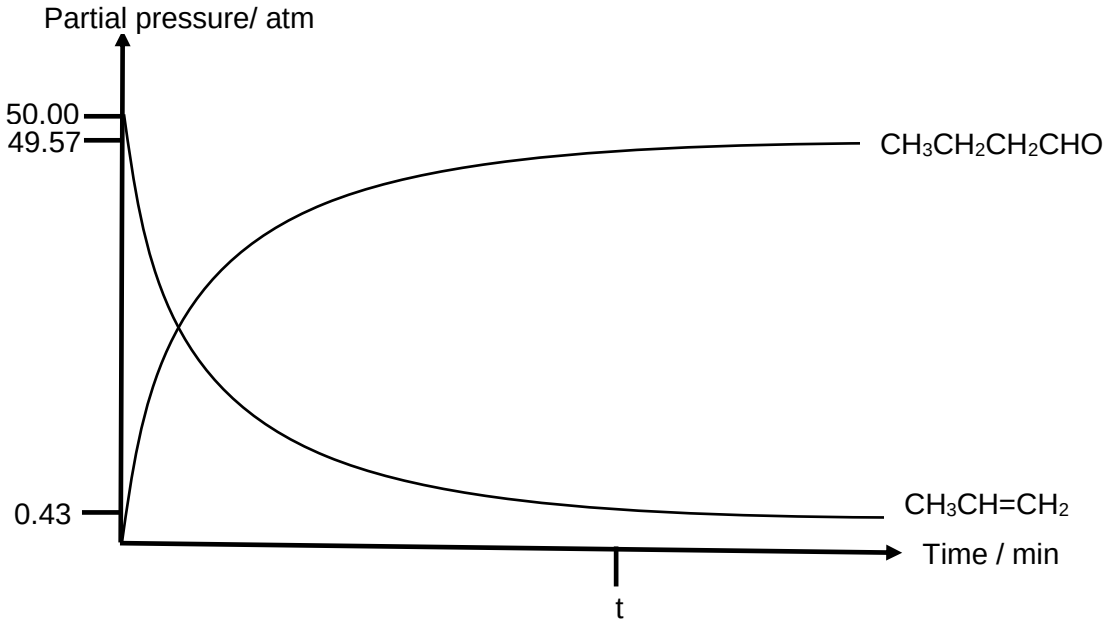


Figure 5.1

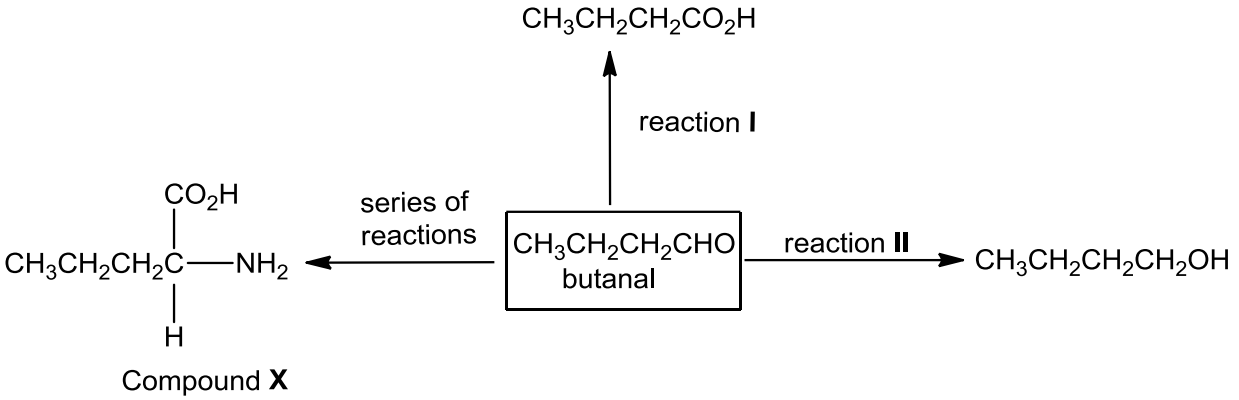
(i) Define the term *dynamic equilibrium*. [1]

(ii) Write an expression for K_p for the above reaction. [1]

(iii) Using Figure 5.1 above, calculate K_p for the hydroformylation reaction at 500 K, stating its units. [3]

(iv) Suggest how the graphs of partial pressure against time for $CH_3CH{=}CH_2$ and $CH_3CH_2CH_2CHO$ would differ from that shown in Figure 5.1 when the experiment is repeated at a higher temperature. [2]

Butanal, synthesised from hydroformylation reaction, can undergo further reactions as shown in the reaction scheme below.



(b) From reaction **I** above, butanoic acid is produced. Comment on the difference in the solubility of butanal and butanoic acid in water. [2]

(c) In reaction **II**, butanal is reduced to give butan-1-ol. One of the commonly used reducing agents is lithium aluminium hydride, $LiAlH_4$, which is usually dissolved in dry ether.

(i) Given that $LiAlH_4$ exist as $Li^+[AlH_4]^-$, draw the dot-and-cross diagram for $LiAlH_4$. [1]

(ii) The reaction between $LiAlH_4$ and butanal to form butan-1-ol happens in two-steps.

The first step involves a nucleophilic addition reaction between the hydride ion, H^-, from $LiAlH_4$ and butanal to form an anion.
The second step involves the protonation of the anion to form butan-1-ol.

Using the information above, show how the anion in the first step is formed with the use of curly arrows, showing the movement of electrons and charges. [2]

(iii) Other than $LiAlH_4$, $NaBH_4$ can also be used to convert butanal to butan-1-ol. By considering the chemical bonds in $LiAlH_4$ and $NaBH_4$, suggest why $LiAlH_4$ is a more powerful reducing agent $NaBH_4$. [1]

(iv) State a reason why $LiAlH_4$ cannot be used to reduce alkenes even though it is a powerful reducing agent. [1]

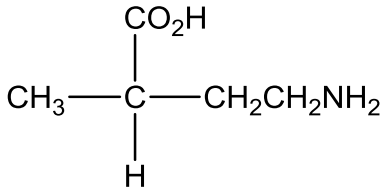
(v) Expain how the rate of the reaction in **(c)(ii)** would differ if butanone is used in place of butanal. [2]

(d) Draw the structure of the predominant form produced when compound **X** is in an aqueous solution of pH 7. [1]

(e) Write two equations to show how the solution in **(d)** is able to resist the change in pH upon addition of small amounts of acid and base. [2]

[Turn over

(f) Compound **Y** is an isomer of compound **X**. Draw the structural formula of the **final** product when compound **Y** reacts with PCl_5. [1]



Compound **Y**

[Total: 20]