Catholic Junior College
JC 2 Preliminary Examinations
Higher 2

CHEMISTRY
9729/01

Paper 1 Multiple Choice
29 August 2017

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, HT group and NRIC/FIN number on the Answer Sheet in the spaces provided.
Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

This document consists of **14** printed pages and **0** blank page.

For each question there are ***four*** possible answers, ***A***, ***B***, ***C*** and ***D***. Choose the **one** you consider to be correct.

1 When an unknown organic compound is burned completely in excess oxygen, 90 cm^3 of gaseous products is collected. When cooled to room temperature, the gaseous volume decreased to 50 cm^3. A further decrease of 40 cm^3 in the gaseous volume was observed when the gaseous mixture is passed through aqueous potassium hydroxide.

What is the possible identity of the organic compound?

1 CH_2CH_2
2 CH_3CO_2H
3 $CH_3CH_2CH_3$
4 CH_2CHCH_2OH

A 1 and 3 only
B 1 and 4 only
C 1, 2 and 4 only
D 2 and 4 only

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

A vanadium salt of unknown oxidation state was dissolved in water to form a solution of 0.500 mol dm^{-3}. It was found that 20.4 cm^3 of this solution will react with 1.00 g of zinc powder to form vanadium(II) solution.

What is the possible identity of the vanadium salt used?

A V^{2+} **B** V^{3+} **C** VO^{2+} **D** VO_2^+

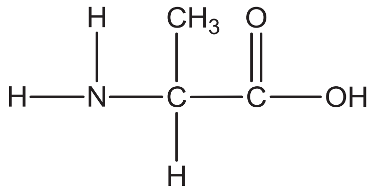
3 The table below gives some data about four ions.

ions	number of neutrons	number of nucleons
Q$^-$	16	33
R$^+$	19	39
S^{2-}	17	33
T^{2+}	18	35

Which of the following pairs consists of ions that are isoelectronic?

A **Q**$^-$ and **S**$^{2-}$
B **R**$^+$ and **S**$^{2-}$
C **S**$^{2-}$ and **T**$^{2+}$
D **Q**$^-$ and **T**$^{2+}$

4 Which bond angle is present in a molecule of alanine, $H_2NCH(CH_3)CO_2H$, but is **not** present in its zwitterion?



alanine

A 90° **B** 107° **C** 109° **D** 120°

5 What are the types of chemical bonds present in solid phenylammonium chloride, $C_6H_5NH_3Cl$?

1 dative covalent bonds
2 ionic bonds
3 hydrogen bonds

A 2 only
B 1 and 2 only
C 2 and 3 only
D 1, 2 and 3

6 Which one of the following shows the standard enthalpy change of formation of carbon monoxide?

A $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$
B $C(s) + CO_2(g) \rightarrow 2CO(g)$
C $C(g) + \frac{1}{2}O_2(g) \rightarrow CO(g)$
D $C(g) + CO_2(g) \rightarrow 2CO(g)$

7 Nitrogen dioxide, NO_2, has an unpaired electron and dimerises to form N_2O_4.

$$2NO_2(g) \rightarrow N_2O_4(g)$$

Which of the following statements about the spontaneity of the reaction is true?

A The reaction is only spontaneous at low temperatures.

B The reaction is only spontaneous at high temperatures.

C The reaction is spontaneous at all temperatures.

D The reaction is non-spontaneous at all temperatures.

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

Gas canisters used in camping stoves contain partially liquefied hydrocarbon. A canister was connected to a gas syringe and the valve opened slightly to allow some gas into the syringe. 0.200 g of the gas occupied a volume of 96.0 cm^3 at a temperature of 30.0 °C and a pressure of 101 kPa.

What is the average M_r of the gas mixture?

A 31 **B** 52 **C** 479 **D** 519

9 At a certain temperature, three gases N_2, O_2 and HCl were mixed and the following reaction occurred:

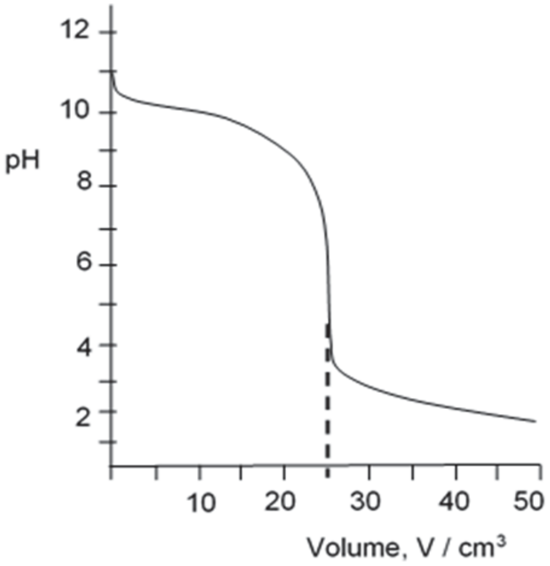
$$2N_2(g) + 3O_2(g) + 4HCl(g) \rightleftharpoons 4NOCl(g) + 2H_2O(g)$$

The initial partial pressures of N_2, O_2 and HCl are 0.800 atm, 0.800 atm and 0.400 atm respectively. After equilibrium has been established, it is found that the partial pressure of steam is 0.15 atm.
What is the numerical value of K_p for this reaction at this temperature?

A 1.20 **B** 22.7 **C** 0.0217 **D** 0.0251

10 In an acid-base titration, a 0.10 mol dm^{-3} solution of an acid is added to a 25 cm^3 of a 0.10 mol dm^{-3} solution of a base.

The pH value of the solution is plotted against the volume, V, of acid added as shown in the diagram.



Which of the following statements is **incorrect**?

A The titration involved a strong acid and a weak base.

B The pair of solutions could have been HC*l*(aq) and CH_3NH_2(aq).

C Methyl orange is a suitable indicator for the above titration.

D When concentration of acid is doubled, the end point volume of the titration would be halved while the pH at equivalence point would remain unchanged.

11 The following two reactions are examples of acid-base reactions.

Reaction 1: $HNO_3 + H_2SO_4 \rightleftharpoons H_2NO_3^+ + HSO_4^-$

Reaction 2: $NH_3 + BF_3 \rightarrow NH_3BF_3$

Which of the following correctly describes the behaviour of each species?

	Brønsted acid	Brønsted base	Lewis acid	Lewis base
A	HNO_3	NH_3	H_2SO_4	HSO_4^-
B	H_2SO_4	HNO_3	BF_3	NH_3
C	HSO_4^-	NH_3	BF_3	$H_2NO_3^+$
D	$H_2NO_3^+$	HSO_4^-	NH_3BF_3	NH_3

12 The decomposition of hydrogen peroxide is known to be a first order reaction.

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

The rate constant is found to be 4.95 x 10^{-2} min^{-1}. If the initial concentration of H_2O_2 is 4.00 mol dm^{-3}, what will be the concentration of H_2O_2 after 64 min?

A	0.50 mol dm^{-3}	**C**	0.17 mol dm^{-3}
B	0.20 mol dm^{-3}	**D**	0.13 mol dm^{-3}

13 The rate equation for the reaction 2**W** + **X** → **Y** + **Z** is given as rate = k[**W**][**X**]. In an experiment to study the kinetics of the reaction, the initial concentration of **W** used is 0.20 mol dm^{-3} and the initial concentration of **X** used is 0.001 mol dm^{-3}.

Which of the following statements regarding the experiment is correct?

A The half-life for the [**X**] against time curve is approximately constant.

B The mechanism for the above reaction involves one step.

C The units of the rate constant is $mol^{-2}dm^{6}s^{-1}$.

D Doubling the initial concentration of **W** to 0.40 mol dm^{-3} will not affect the half-life of **X**.

14 The oxide and chloride of an element **E** are mixed separately with water. The two resulting solutions have the same effect on litmus.
What is element **E**?

A Mg **B** A*l* **C** Si **D** P

15 Which of the following statements about iodine or its compounds are correct?

1 A crystal of iodine contains covalent bonds and instantaneous dipole-induced dipole forces of attraction.

2 When aqueous chlorine is added to potassium iodide and the aqueous mixture shaken with tetrachloromethane, a purple organic layer is obtained.

3 The first ionisation energy of iodine is less than that of bromine.

4 The thermal stability of hydrogen iodide is higher than that of hydrogen bromide.

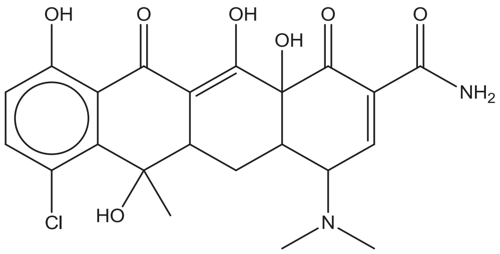
A 1 and 3 only

B 1, 2 and 3 only

C 3 and 4 only

D 2, 3 and 4 only

16 *Aureomycin* is a powerful oral antibiotics that is effective against a wide range of infections.

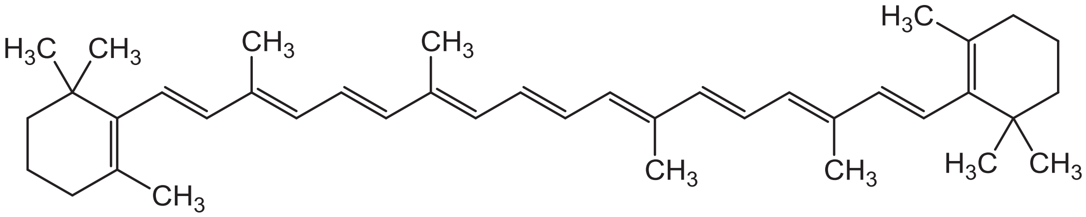


Aureomycin

Which row correctly indicates the number of chiral centres and sp^2 hybridised carbon in a molecule of *aureomycin*?

	Number of chiral centres	Number of sp^2 hybridised C
A	4	10
B	4	13
C	5	10
D	5	13

17 β-carotene is responsible for the orange colour of carrots.



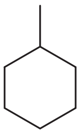
β–carotene

β-carotene is oxidised by hot, concentrated, acidified $KMnO_4$.

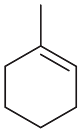
How many different products formed from the above reaction contain the ketone functional group?

A 2 **B** 4 **C** 6 **D** 8

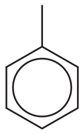
18 Which of the statements are true regarding the three compounds below?



I



II



III

1 Compounds **I** and **III** will not decolourise Br_2 in CCl_4.

2 Compounds **I** and **II** will decolourise acidified $KMnO_4$ at 298 K.

3 Compound **III** will not react with chlorine in the presence of uv light.

4 Compound **III** will react with bromine in the presence of a homogeneous catalyst.

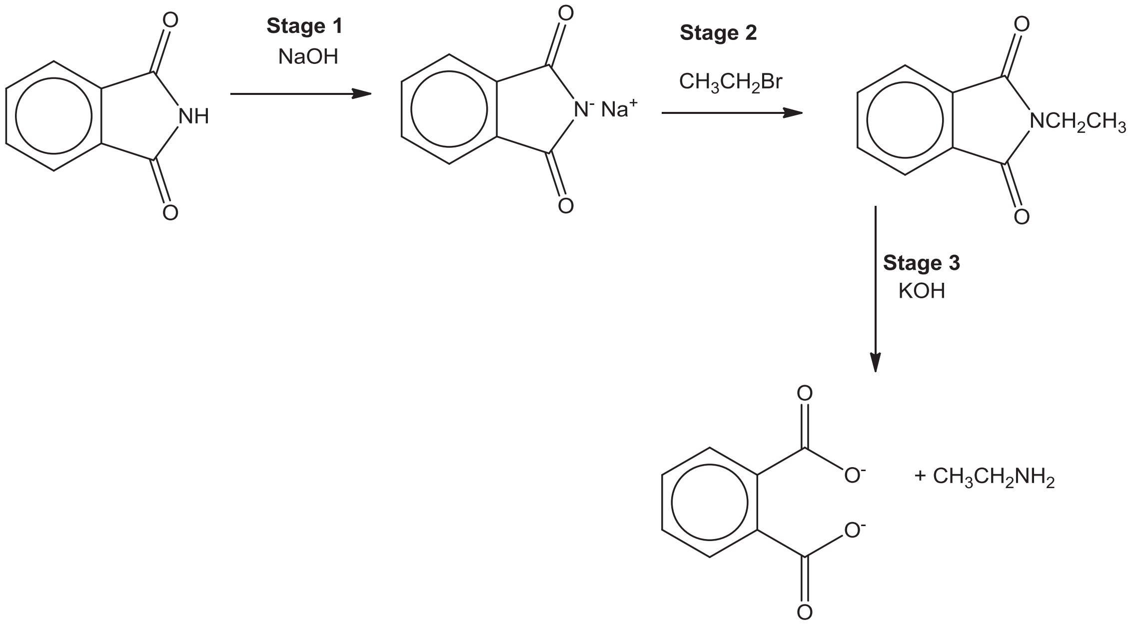
A 1 and 4 only

B 2 and 3 only

C 1, 3 and 4 only

D 1, 2, 3 and 4

19 A sequence of reactions is shown below.

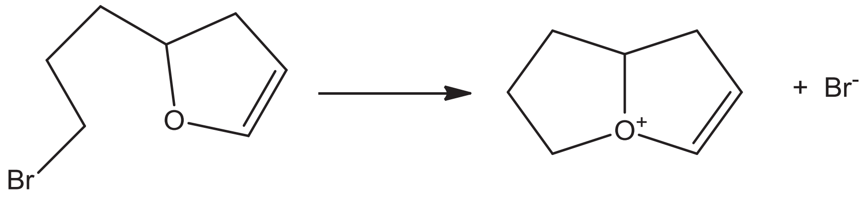


Which of the following correctly describes the type of reactions for Stages **1** to **3**?

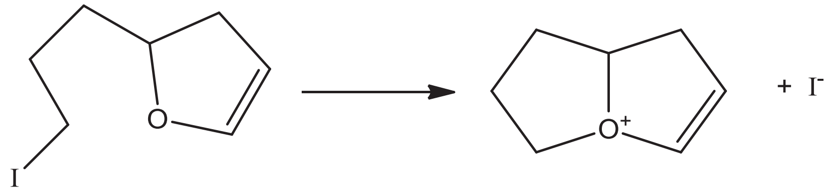
	Stage 1	Stage 2	Stage 3
A	neutralisation	electrophilic substitution	nucleophilic substitution
B	hydrolysis	nucleophilic substitution	hydrolysis
C	redox	nucleophilic addition	nucleophilic substitution
D	neutralisation	nucleophilic substitution	hydrolysis

20 The intramolecular reactions below occur via nucleophilic substitution mechanism.

Reaction 1



Reaction 2



Reaction 2 is faster than reaction 1 under identical conditions.

Which statement explains this difference?

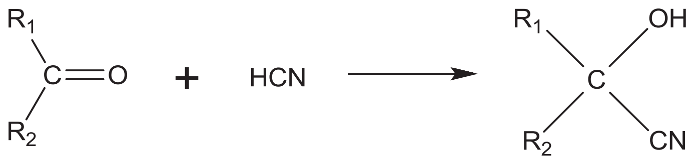
A Br is more electronegative than I.

B The I^- ion is a stronger nucleophile than Br^-.

C The C–Br bond is more polar than the C–I bond.

D The C–Br bond is stronger than the C–I bond.

21 Cyanohydrins can be made from carbonyl compounds by generating CN^- ions from HCN in the presence of a weak base.



In a similar reaction, $^-CH_2COOCH_3$ ions are generated from CH_3COOCH_3 by strong bases.

Which compound can be made from an aldehyde and CH_3COOCH_3?

A $CH_3CH(OH)COOCH_3$

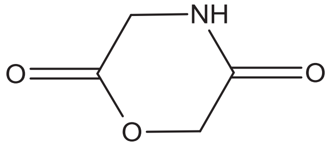
B $CH_3COOCH_2CH(OH)CH_3$

C $CH_3CH_2CH(OH)CH_2COOCH_3$

D $(CH_3)_2C(OH)CH_2COOCH_3$

[Turn over

22 The cyclic compound **X** is heated with acidified $KMnO_4$.



Compound **X**

What are the final organic products of the reaction?

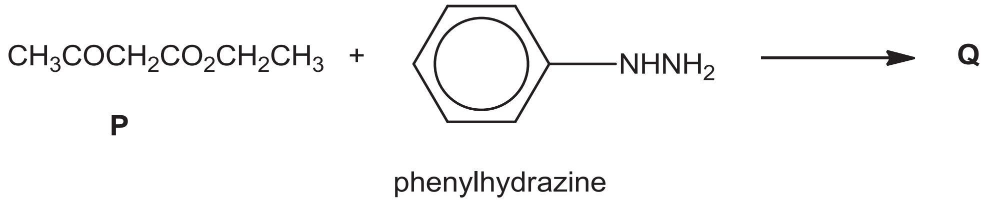
A $HOCH_2CO_2H$ and $HO_2CCH_2NH_3^+$

B $HO_2CCH_2NH_3^+$

C $HOCH_2CHO$ and $H_2NCH_2CO_2H$

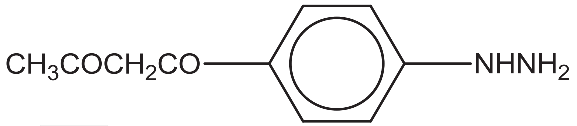
D H_2NCOCH_2OH and $HOCH_2CHO$

23 The first stage in the synthesis of *Antipyrine,* a fever medication, is the reaction between compound **P** and phenylhydrazine.

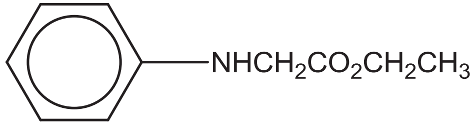


Which of the following correctly represents the structure of product **Q**?

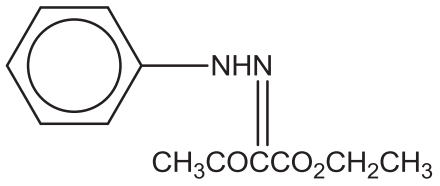
A

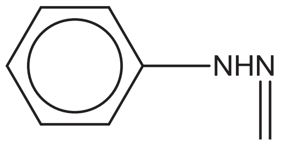


B



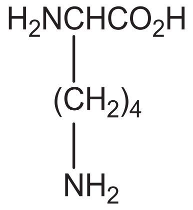
C





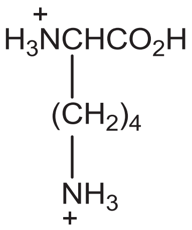
D

24 Lysine is an α-amino acid.



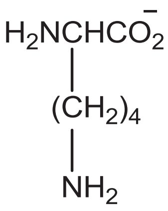
$$\begin{array}{c} H_2NCHCO_2H \\ | \\ (CH_2)_4 \\ | \\ NH_2 \end{array}$$

Which structure is predominant when lysine is in an aqueous solution of pH 9.5, given that lysine has three pK_a values of 2.2, 8.9 and 10.5?



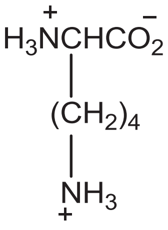
$$\begin{array}{c} H_3\overset{+}{N}CHCO_2H \\ | \\ (CH_2)_4 \\ | \\ \underset{+}{N}H_3 \end{array}$$

A



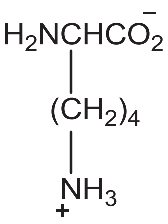
$$\begin{array}{c} H_2NCHC\overset{-}{O_2} \\ | \\ (CH_2)_4 \\ | \\ NH_2 \end{array}$$

B



$$\begin{array}{c} H_3\overset{+}{N}CHC\overset{-}{O_2} \\ | \\ (CH_2)_4 \\ | \\ \underset{+}{N}H_3 \end{array}$$

C

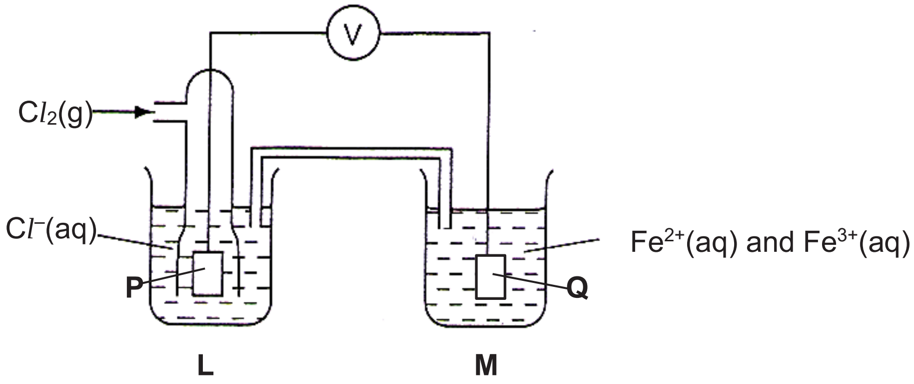


$$\begin{array}{c} H_2NCHC\overset{-}{O_2} \\ | \\ (CH_2)_4 \\ | \\ \underset{+}{N}H_3 \end{array}$$

D

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

The cell shown below is set up under standard conditions where **P** and **Q** are platinum electrodes.



Which of the following statements is correct?

A Addition of KCN to half-cell **M** will not affect $E_{cell}^{\ominus}$.

B The voltmeter will show a reading of about 2.13 V.

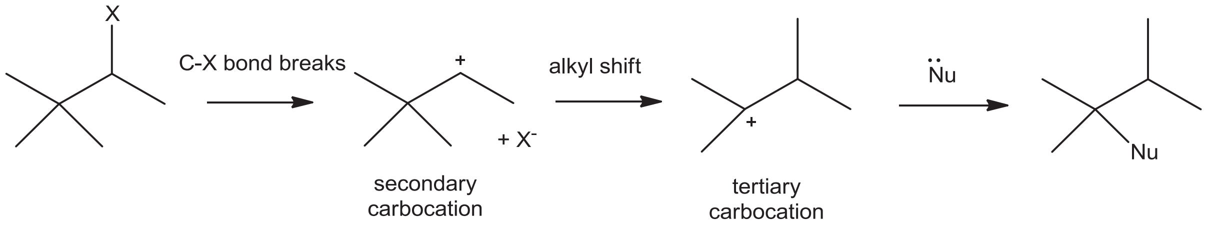
C The electrons will flow from **Q** to **P** through the voltmeter.

D **P** will be the negative electrode.

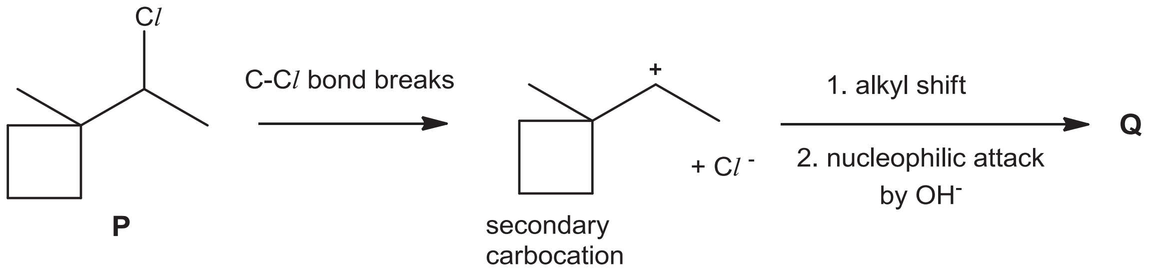
26 During electroplating, a current is passed through a cell containing aqueous silver nitrate using inert electrodes. After some time, 1.35 g of silver was deposited at one electrode. What volume of gas would be produced at the other electrode at r.t.p.?

A 70 cm^3 **B** 75 cm^3 **C** 140 cm^3 **D** 150 cm^3

27 In S_N1 reactions involving secondary halogenoalkanes, alkyl shift can sometimes occur after the breaking of C–X bond to form a more stable tertiary carbocation.

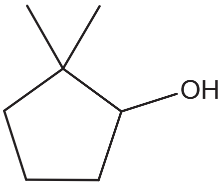


Rearrangements need not always involve methyl groups. In situation when the carbocation is formed adjacent to a strained ring, such as a cyclobutane, it is more favourable for one of the alkyl groups in the ring, rather than the methyl group, to shift so as to cause **ring expansion** and the formation of a less strained ring.

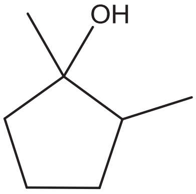


Which of the following is a possible identity of **Q**?

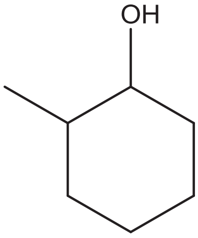
A



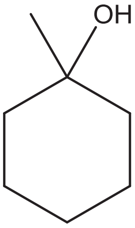
B



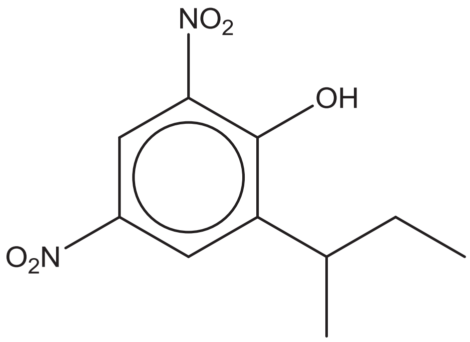
C



D



28 *Binapacryl* is used as a fungicide.



Binapacryl

Which of the following statements about *Binapacryl* are correct?

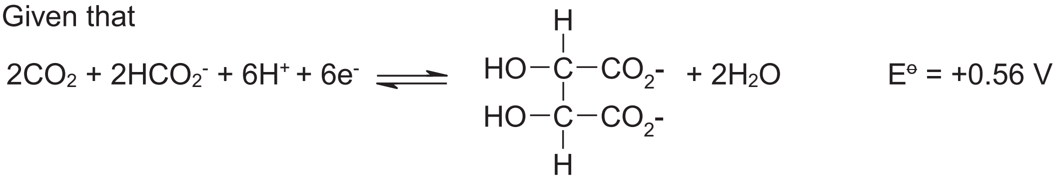
1 It dissolves in water to give a neutral solution.
2 It is inert towards acidified potassium dichromate(VI) solution.
3 It decolourises aqueous bromine to form a white precipitate.
4 It reacts with ethanoic acid in the presence of concentrated sulfuric acid to form an ester.

A 2 only
B 2 and 3 only
C 1 and 4 only
D 1, 2, 3 and 4 only

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

The reaction between peroxodisulfate(VI) ion, $S_2O_8^{2-}$, and tartrate ion, $[CH(OH)CO_2^-]_2$, is slow due to a high activation energy.

The reaction can be catalysed by a homogeneous catalyst.
Given that



$$2CO_2 + 2HCO_2^- + 6H^+ + 6e^- \rightleftharpoons \begin{array}{c} H \\ | \\ HO-C-CO_2^- \\ | \\ HO-C-CO_2^- \\ | \\ H \end{array} + 2H_2O \qquad E^\ominus = +0.56\ V$$

Which metal ion is **not** a suitable catalyst for this reaction?

A Co^{2+} **B** Cr^{2+} **C** Mn^{3+} **D** Fe^{3+}

30 Chromium forms a series of compounds with the general formula $CrCl_3 \bullet 6H_2O$. One of these compounds, **X** is violet and produces an aqueous solution from which all the chlorine can be precipitated as AgC*l* upon addition of aqueous silver nitrate.
Another compound **Y** is green and produces an aqueous solution from which only one third of the chlorine can be precipitated with silver nitrate.

Which of the following statements about **X** and **Y** is **incorrect**?

A **X** is an ionic compound consisting of $[Cr(H_2O)_6]^{3+}$ and Cl^- ions.

B **Y** is an ionic compound consisting of $[Cr(Cl)_2(H_2O)_4]^+$ and Cl^- ions.

C Oxidation number of Cr in **X** is +3 while the oxidation number of Cr in **Y** is +1.

D Oxidation number of Cr in **X** and **Y** remains unchanged during precipitation of AgC*l*.

Catholic Junior College

JC2 Preliminary Examinations
Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY **9729/02**

Paper 2 Structured Questions **18 August 2017**

2 hours

Candidates answer on the Question Paper.

Additional Materials: 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.

Answer **all** questions in the spaces provided on the Question Paper.
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.

For Examiner's Use			
Paper 1			30
Paper 2	**Q 1**	12	
	Q 2	19	
	Q 3	18	
	Q 4	9	
	Q 5	10	
	Q 6	7	75
Paper 3	**Q 1**	22	
	Q 2	20	
	Q 3	18	
	Q 4	20	
	Q 5	20	80
Total			185

This document consists of **14** printed pages and **0** blank page.

[Turn over

Answer **all** the questions.

1 Sedimentary rocks formed at the earth's surface by the accumulation of particulate matter are usually transported to the place of deposition by water, wind, or mass movement of glaciers. Dolostone, a sedimentary rock, consists of a mixture of minerals such as calcium and magnesium carbonates.

Table 1.1 below shows some properties of calcium carbonate and magnesium carbonate.

Table 1.1

	Numerical values of K_{sp} at 25 °C	Decomposition temperature / ˚C
calcium carbonate	5.0×10^{-9}	900
magnesium carbonate	1.0×10^{-5}	540

(a) **(i)** Write an expression for the solubility product, K_{sp}, of calcium carbonate.

....[1]

(ii) Calculate the solubility, in mol dm^{-3}, of calcium carbonate in water at 25 °C.

[1]

(iii) A saturated solution **X** containing calcium hydroxide and calcium carbonate has a pH of 13 at 25 °C.

Given that the K_{sp} of calcium hydroxide is 5.5×10^{-6} mol^3 dm^{-9} and using your answer in **(a)(i)**, calculate the solubility of calcium carbonate in solution **X**.

[2]

(iv) Comment on, and explain, the difference in the solubilities of calcium carbonate in water and in solution **X**.

....

....

....[2]

(v) When rainwater runs over dolostone, a chemical reaction occurs as shown below:

$$\mathbf{M}CO_3(s) + CO_2(aq) + H_2O(l) \rightleftharpoons 2HCO_3^-(aq) + \mathbf{M}^{2+}(aq)$$

where **M** is a group 2 metal

I. Suggest the source of CO_2 (aq) for the reaction.

....[1]

II. When a sample of saturated solution of $Ca(HCO_3)_2$ is heated, a reaction occurs and a precipitate is formed. Using the equation above, suggest why this happens.

....

....

....[2]

(b) Calcium carbonate can be decomposed by heating at high temperatures.

(i) Write an equation for the thermal decomposition of calcium carbonate.

....[1]

(ii) Calcium carbonate decomposes at a higher temperature than magnesium carbonate. Explain why this is so.

....

....

....

....

....[2]

[Total: 12]

[Turn over

2 **(a)** Table 2.1 gives data about some physical properties of the elements calcium and copper.

Table 2.1

physical property	calcium	copper
relative atomic mass	40.1	63.5
atomic radius (metallic) / nm	0.197	0.128
ionic radius (2+) / nm	0.099	0.069
melting point / °C	839	1085
boiling point / °C	1484	2562

(i) Explain why the atomic radius of copper is smaller than that of calcium.

....

....

....[2]

(ii) Explain why copper has a higher melting point than calcium.

....

....

....[2]

(iii) Apart from the properties given in Table 2.1, state clearly the difference in one other physical property between copper and calcium.

....

....[1]

(b) Copper, scandium and zinc are d-block elements. However, copper is a transition element while scandium and zinc are not.

(i) Define the term *transition element*.

....

....[1]

(ii) Explain why scandium is not classified as a transition element.

....

....[1]

(c) Manganese is also a transition element and shows great tendency to form stable coloured complexes with ligands.

(i) Define the term *ligand*.

....

....[1]

(ii) Draw the shape of the complex ion, $[Mn(CN)_6]^{4-}$.

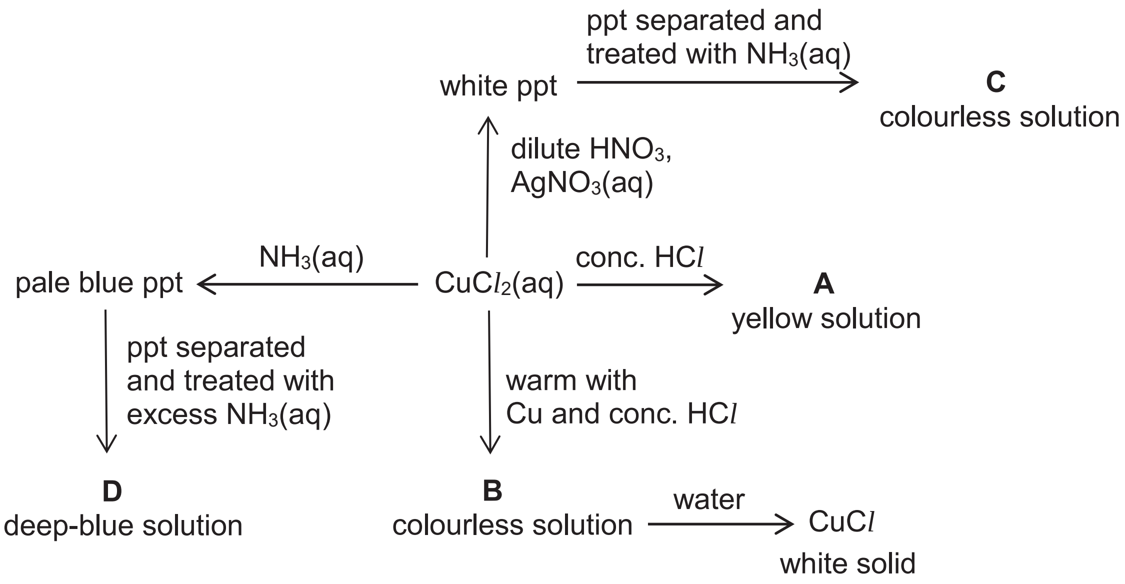
[2]

(d) Copper has more than one oxidation state and many of its compounds have colours in the blue-green-yellow part of the visible spectrum.

Write the *spdf* electronic configuration of copper(II) ions.

Cu^{2+} .... [1]

(e) Aqueous copper(II) chloride, $CuCl_2$, is a blue solution which gives the following reactions.



Both **A** and **B** contain complex ions of copper and chlorine.

(i) State the formula of compound **C**.

....[1]

[Turn over

(ii) Suggest the formula and shape of the complex ion present in **D**.

Formula .... [1]

Shape .... [1]

(iii) What type of reaction occurs when **A** is formed from $CuCl_2$(aq)?
.... [1]

(iv) Explain why **A** is yellow in colour.

....

....

....

....

....

....[3]

(v) Explain why **B** is colourless.

....

....

....[1]

[Total: 19]

3 Industrially, ethanol, CH_3CH_2OH, is manufactured by reacting ethene with steam in the presence of a catalyst. The reaction is reversible and the equation is as follows:

$$CH_2{=}CH_2(g) + H_2O(g) \rightleftharpoons CH_3CH_2OH(g)$$

At equilibrium, only 5 % of the ethene is converted into ethanol. To increase the overall yield of ethanol, ethanol is regularly removed from the equilibrium mixture as it is formed and more ethene is added into the reaction mixture. The volume of steam is not increased as this may disable the catalyst.

(a) Apart from the methods mentioned above, suggest one other method which will increase the conversion of ethene into ethanol. Explain your answer briefly.

....

....[2]

Alcoholic beverages can contain up to 40 % of ethanol. Excessive consumption of ethanol depresses the activity of the central nervous system. The blood alcohol concentration (BAC) is a good measure of the extent to which the activity of the central nervous system is depressed. It is usually defined as follows

$$\text{BAC} = \text{mg of ethanol per } 100\ \text{cm}^3 \text{ of blood}$$

Ethanol is sufficiently volatile to pass from the blood into the air in the lungs and the following equilibrium is set up:

$$CH_3CH_2OH(\text{blood}) \rightleftharpoons CH_3CH_2OH(g)$$

(b) **(i)** Suggest an expression for K_c for the equilibrium of ethanol between the blood and the air in the lungs.

[1]

(ii) Using your answer to **(b)(i)** and given that the equilibrium constant, K_c, for this process is 4.35×10^{-4}, calculate the breath alcohol concentration (in mg of ethanol / 100 cm^3 of air) which corresponds to the 80 mg / 100 cm^3 of blood legal limit for BAC.

[1]

[Turn over

(iii) Hence determine the legal limit of breath alcohol concentration in mol dm^{-3}.

[2]

(c) The handheld breathalyser contains an electrochemical cell in which ethanol is oxidised. At one electrode, atmospheric oxygen is reduced to water and the other electrode ethanol is oxidised to ethanoic acid. The electric current produced gives an approximation of the overall blood alcohol concentration (BAC).

Give the half–equation for each electrode reaction and hence give the overall equation showing the oxidation of ethanol.

....

....

....

....

....

....[2]

(d) Ethanol can be burned in excess oxygen as fuel. Complete combustion of ethanol releases 1367 kJ mol^{-1} of heat energy.

(i) Write an equation to show the standard enthalpy change of combustion of ethanol.

....[1]

(ii) Use the bond energies given in the *Data Booklet* to calculate another value for the standard enthalpy change of combustion of ethanol.

[3]

(iii) Suggest a reason for the discrepancy between this value and that quoted in **(d)**.

....

....[1]

(e) **(i)** The complete combustion of ethanoic acid, CH_3CO_2H, releases 873 kJ mol^{-1} of energy. Use this value and the enthalpy change of combustion of ethanol given in **(d)** to construct an energy cycle to calculate the enthalpy change when 1.0 mol of ethanol in the body is oxidised to ethanoic acid and water only.

[3]

(ii) The metabolism of ethanol in the human body leads to partial oxidation which releases 770 kJ mol^{-1} of energy. Assuming that ethanol is oxidised to ethanoic acid and carbon dioxide only, use your answer to **(e)(i)** and any other relevant data to calculate the proportion of ethanol metabolised to ethanoic acid and to carbon dioxide respectively.

[2]

[Total: 18]

4 **(a)** Aerosol spray is a type of dispensing system which creates an aerosol mist of liquid particles. This is used with a can that contains a product and propellant under pressure. Hair spray is a common example of an aerosol spray where butane is often used as the propellant.

(i) A typical can of hair spray has a volume of 300 ml and 70 % of which is the hair product. Given that the can has an internal pressure of 100 psi, at 27 °C, calculate the maximum amount of butane present in the can. (1 psi = 6894.76 Pa)

[2]

(ii) The can of hair spray is used such that only the propellant, butane gas, remained and the internal pressure of the can decreased to 20 psi. If the can is left in a car that reaches 50 °C on a hot afternoon, what is the new pressure in the can?

[1]

(iii) As a safety precaution, the propellant has to be completely expelled from the can prior to disposal and subsequent incineration. Using concepts from the Ideal Gas Law, explain qualitatively, why this precaution is necessary.

....

....

....

....[1]

(b) In 1873, Johannes D. van der Waals, a physicist proposed a modification to the ideal gas equation to better model real gas behaviour. The new equation, usually referred to as the van der Waals equation, has the following expression.

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

P is the observed pressure exerted by the gas.
V is the volume of the container in which the gas is contained.
The constants a and b have positive values and are characteristic of a gas.

Suggest why the term $\frac{an^2}{V^2}$ is **added** to P and the term nb is **subtracted** from V respectively.

$P + \frac{an^2}{V^2}$: ....

....

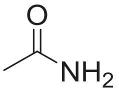
....[1]

$V - nb$: ....

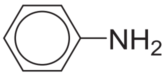
....

....[1]

(c) Arrange the following three compounds in increasing order of basicity.


ethanamide


ethylamine


phenylamine

Order of basicity:

Explain your answer.

....

....

....

....

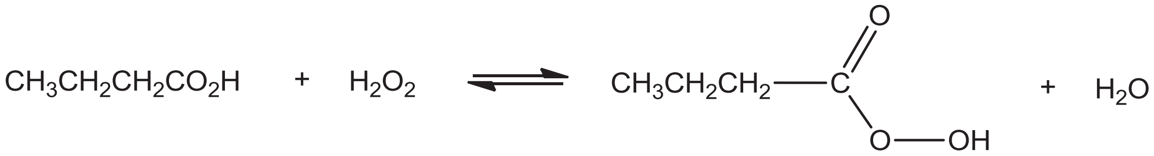
....

....[3]

[Total: 9]

[Turn over

5 **(a)** Butaneperoxoic acid, a type of peroxyacid, is produced when butanoic acid reacts with hydrogen peroxide.



$$CH_3CH_2CH_2CO_2H + H_2O_2 \rightleftharpoons CH_3CH_2CH_2C(=O)OOH + H_2O$$

butanoic acid

butaneperoxoic acid
$C_4H_8O_3$

(i) Identify the type of hybridisation involved for the C atom of O=C-O in butaneperoxoic acid and hence state its bond angle.

Hybridisation of C ……………………………………..

Bond angle …………………………………….. [2]

(ii) Non-cyclic compounds **A** and **B** are functional group isomers of butaneperoxoic acid. 1 mole of hydrogen gas is produced when 1 mole of **A** and 1 mole of **B** are reacted with Na metal separately. **A** produces yellow precipitate when reacted with aqueous alkaline iodine while **B** does not. When reacted with hot acidified $K_2Cr_2O_7$, orange $K_2Cr_2O_7$ turns green in the presence of **A** but not **B**.

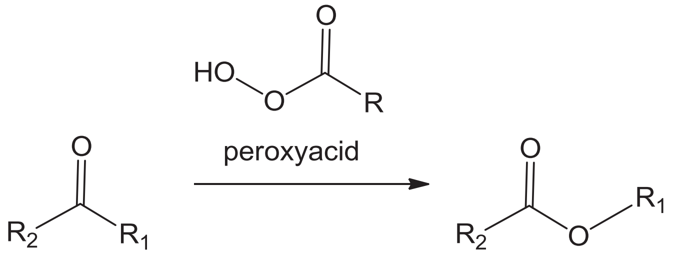
Draw the displayed formula of **A** and **B**, hence state the specific type of isomerism between **A** and **B**.

Compound **A**	Compound **B**

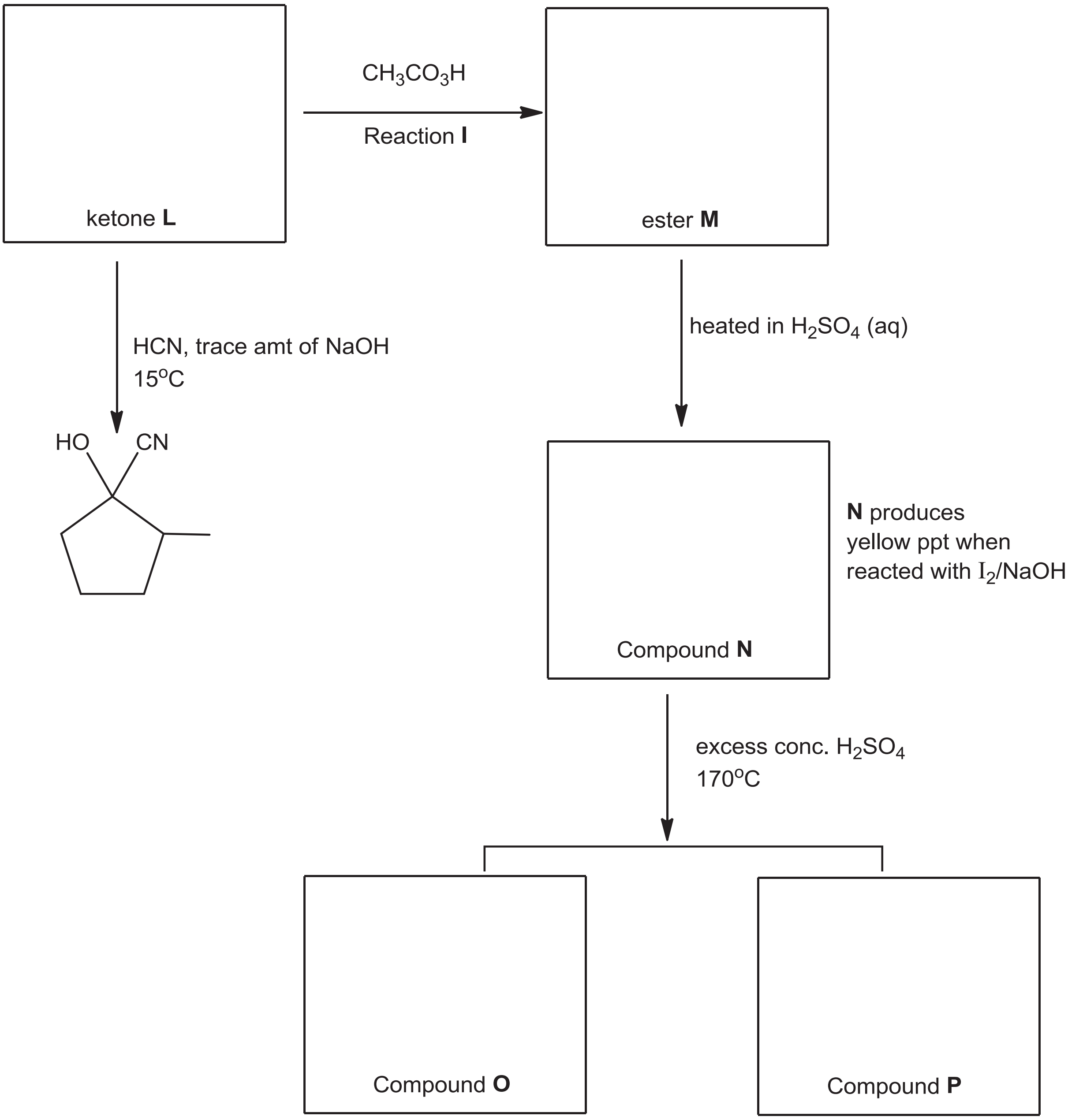
[2]

Type of isomerism between **A** and **B** ……………………………………… [1]

(b) The Baeyer-Villiger oxidation is an organic reaction that converts ketones into esters using peroxyacids.



In the following reaction scheme, reaction **I** is a Baeyer-Villiger oxidation. Give the structural formulae of compounds **L**, **M**, **N**, **O** and **P**. [5]



Both Compounds **O** and **P** decolourise aqueous bromine

[Total: 10]

[Turn over

6 2-methylbut-2-ene is reacted with bromine in an inert solvent in the absence of light.

(a) Describe the mechanism for the above reaction.

[3]

(b) **(i)** State the type of isomerism exhibited by the organic product(s) formed in the above reaction, and hence, draw the structures of the isomers.

type of isomerism ……………………………………………………………………...[1]

Structures of isomers:

[1]

(ii) It was found that the product(s) formed from **(a)** do not rotate plane of polarised light. Using the mechanism drawn in **(a)**, suggest why this is so.

....

....

....

....[2]

[Total: 7]

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.

This document consists of **14** printed pages and **0** blank page.

[Turn over

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]

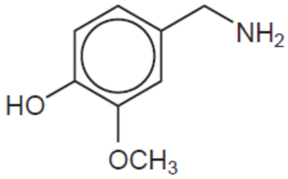
(ii) Calculate the concentration, in mol dm^{-3}, of ethanol in this brand of wine. [4]

(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)$_4$Br, 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.

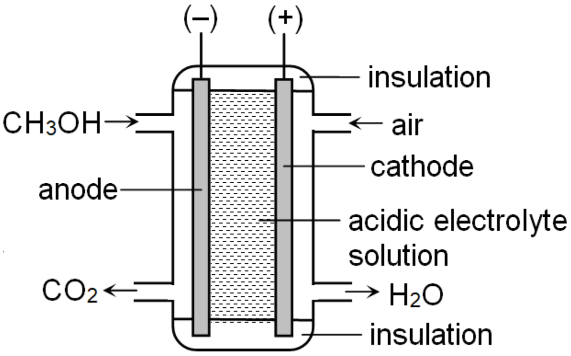


Fig. 1.1

(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]

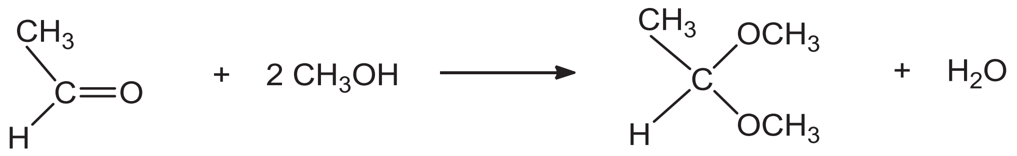
(v) Methanol could also be used as fuel in an internal combustion engine.

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

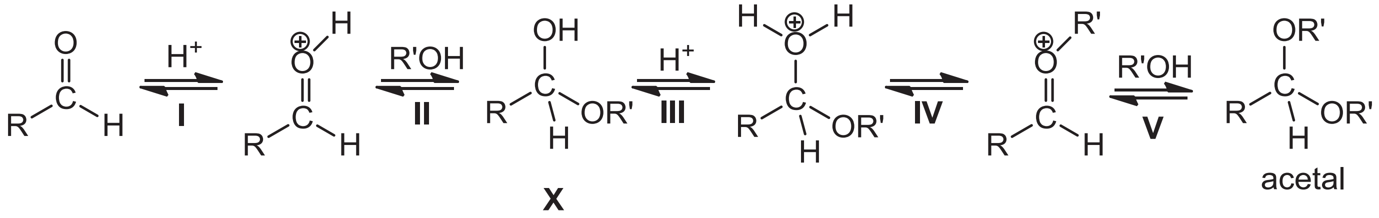
III H^+.

[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.

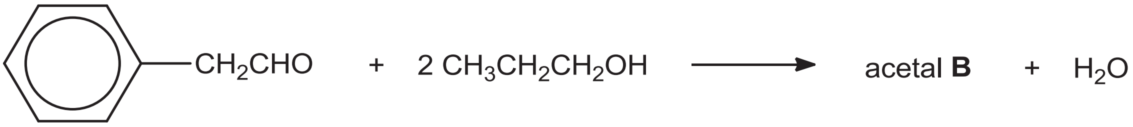


(i) The protonation of the carbonyl group in step **I** is necessary for step **II** to take place. Suggest a reason for this. [1]

(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.

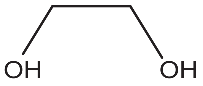


[1]

(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.

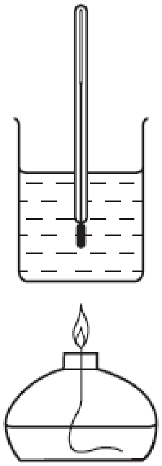
$$CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

(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]

(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]

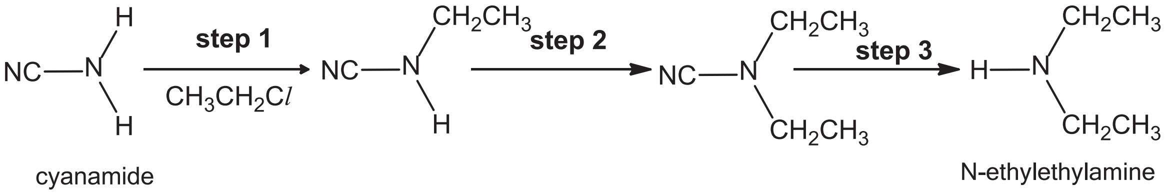
[Turn over

(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.

$N\equiv C-NH_2$

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.

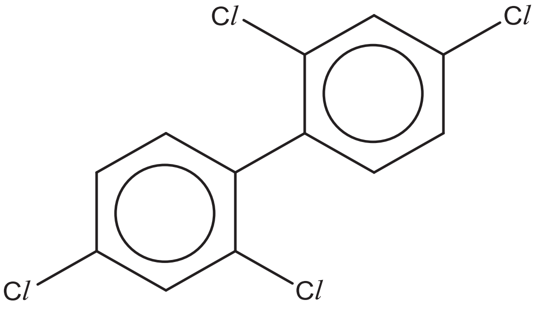


(i) Describe the mechanism for the reaction in **step 1**. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons. [4]

(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.

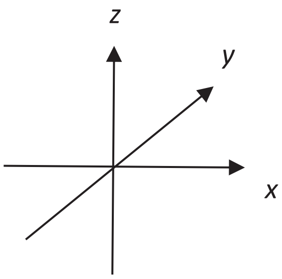


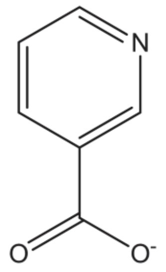
Fig. 4.1

[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]

(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.



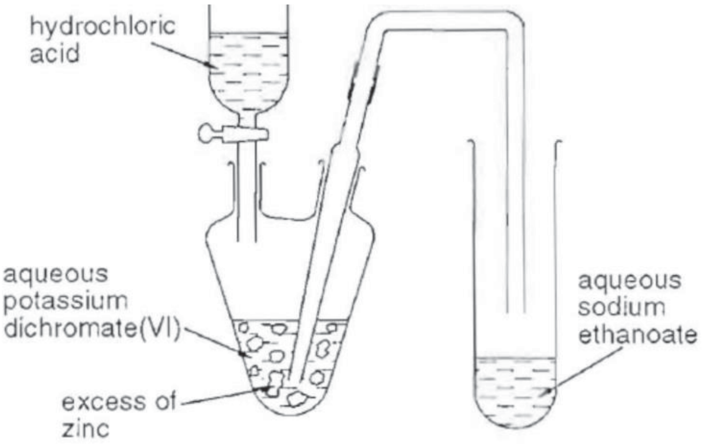
nicotinate ion

(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]

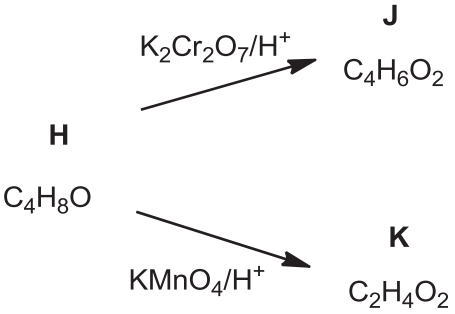
The colour of the solution in the flask subsequently changes as $Cr^{2+}(aq)$ is produced.

(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]

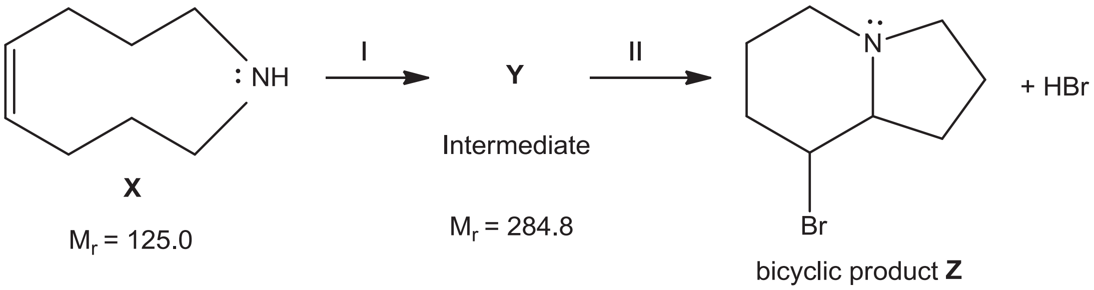
(d) Another chromium-containing compound, $K_2Cr_2O_7$, together with $KMnO_4$ are common oxidising agents used in organic synthesis. $KMnO_4$ is the more powerful of the two, as shown by the following scheme.



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]

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.

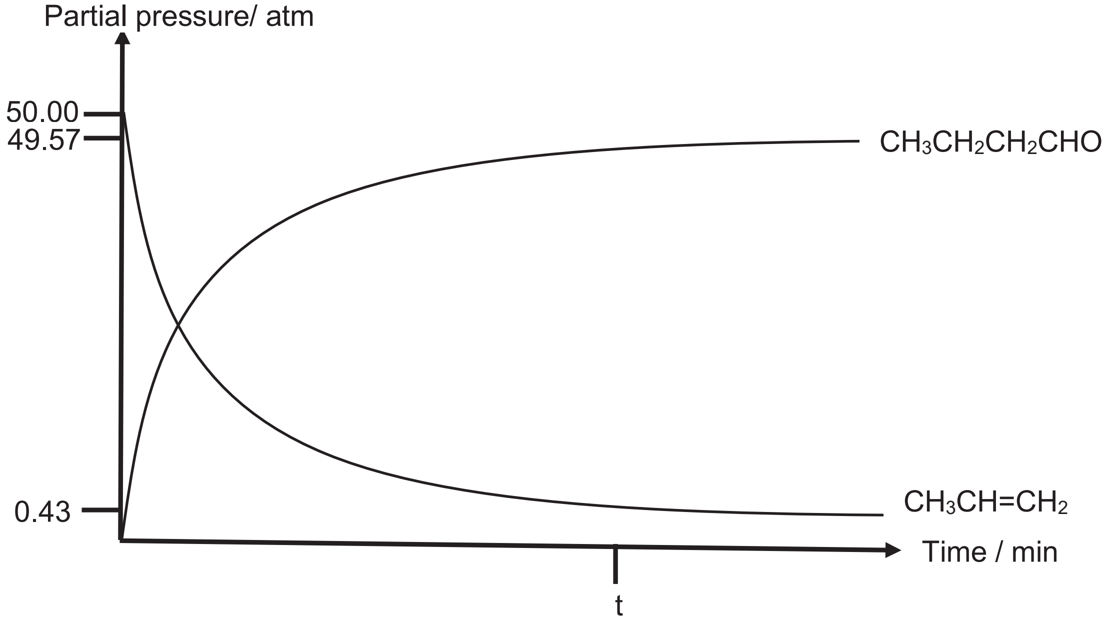


Figure 5.1

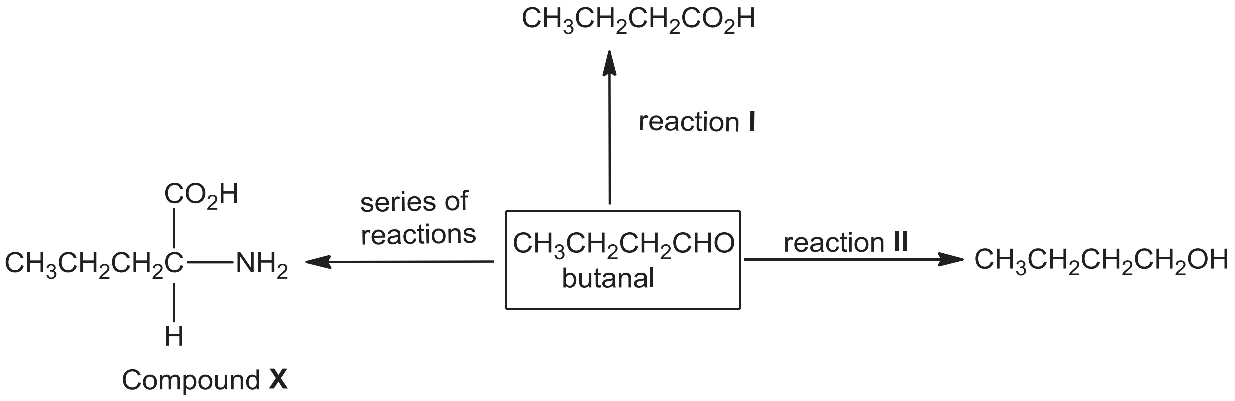
(i) Define the term *dynamic equilibrium*. [1]

(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]

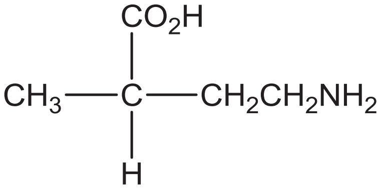
(v) Expain how the rate of the reaction in **(c)(ii)** would differ if butanone is used in place of butanal. [2]

(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]



$$\mathrm{CH_3-\overset{\overset{\displaystyle CO_2H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_2CH_2NH_2}$$

Compound **Y**

[Total: 20]

Catholic Junior College
JC2 Preliminary Examinations
Higher 2

CANDIDATE NAME	
CLASS	2T

CHEMISTRY
9729/04

Paper 4 Practical

16 August 2017

2 hour 30 minutes

Candidates answer on the Question Paper.

Additional Materials: As listed in the Confidential Instructions

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READ THESE INSTRUCTIONS FIRST

Write your name and class in the boxes above.
Give details of the practical shift and laboratory, where appropriate, in the boxes provided.
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.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 15 and 16.

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.

Shift
Laboratory

For Examiner's Use	
1	
2	
3	
Total	

This document consists of **15** printed pages and **1** blank page.

[Turn over

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

1 'Washing soda' is made from crystals of sodium carbonate, which contains 62.94 % water and 37.06 % sodium carbonate. When stored, these crystals lose some of the water in the crystals to the atmosphere.

FA 1 is solid 'washing soda', originally sodium carbonate decahydrate, $Na_2CO_3.10H_2O$.
FA 2 is 0.100 mol dm^{-3} hydrochloric acid, HCl.

In this question, you will perform a titration to determine the amount of water in **FA 1** that has been lost to the atmosphere.

(a) Method

(i) Preparation of FA 3

- Weigh the 100 cm^3 beaker provided. Record the mass in the space below.
- Tip the 'washing soda' crystals, **FA 1**, into the beaker. Weigh the beaker with **FA 1** and record the mass.
- Calculate the mass of **FA 1** used and record this in the space below.
- Add distilled water to the beaker to dissolve the crystals. Carefully transfer the solution to a 250 cm^3 graduated (volumetric) flask labelled **FA 3**. Wash the beaker twice with small quantities of water and add these washings to the volumetric flask.
- Make the solution up to the mark using distilled water. Stopper the flask and invert a number of times to ensure thorough mixing.

[1]

(ii) Titration of FA 3 against FA 2

- Fill the burette with **FA 2**.
- Pipette 25.0 cm^3 of **FA 3** into a conical flask and add a few drops of the indicator provided.
- Titrate the solution with **FA 2**. Record your results in the space provided on page **3**. Make certain that the recorded results show the precision of your practical work.
- Repeat the titration until consistent results are obtained.

Titration Results:

[6]

(iii) From your titrations, obtain a suitable volume of **FA 2** to be used in your calculations. Show clearly how you obtained this volume.

volume of **FA 2** = ……………............…. [1]

(b) **(i)** Calculate the amount of hydrochloric acid run from the burette.

amount of HC*l* =…………….………...…. [1]

(ii) Sodium carbonate reacts with hydrochloric acid as follows.

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$

Calculate the amount of sodium carbonate, Na_2CO_3, in 250 cm^3 of **FA 3**.

amount of Na_2CO_3 in 250 cm^3 of **FA 3** =…………….………...…. [2]

(iii) Calculate the mass of sodium carbonate, Na_2CO_3, dissolved in 250 cm^3 of **FA 3**.
[A_r: C, 12.0; O, 16.0; Na, 23.0]

mass of Na_2CO_3 in 250 cm^3 of **FA 3** =…………….……….....… [1]

(iv) Calculate the mass of water present in the washing soda crystals.

mass of water =…………….……….....… [1]

(v) Hence calculate the percentage of water in the sodium carbonate crystals, **FA 1**.

percentage of water in **FA 1** =…………….……….....… [1]

(c) The maximum error for a 25 cm^3 pipette commonly used in schools is ±0.06 cm^3.
The maximum error in any single burette reading is ±0.05 cm^3.

Calculate the maximum percentage error in each of the following.

(i) The volume of **FA 3** pipetted into the conical flask.

maximum percentage error in pipette volume =…………….……….....… %

(ii) The titre volume calculated in **(a)(iii)**.

maximum percentage error in titre volume =…………….……….....… %

[2]

[Total: 16]

2 The enthalpy change for the reaction of sodium carbonate, Na_2CO_3, with water and carbon dioxide to form sodium hydrogencarbonate, $NaHCO_3$ cannot be determined directly. However both Na_2CO_3(s) and $NaHCO_3$(s) react with dilute hydrochloric acid.

Reaction 1 $NaHCO_3(s) + HCl(aq) \rightarrow NaCl\ (aq) + H_2O(l) + CO_2(g)$ ΔH_1

Reaction 2 $Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl\ (aq) + H_2O(l) + CO_2(g)$ ΔH_2

In this experiment you will determine the enthalpy change ΔH_1 for **reaction 1** and ΔH_2 for **reaction 2**, and then use your results to calculate ΔH_3 for the reaction:

$$Na_2CO_3(s) + H_2O(l) + CO_2(g) \rightarrow 2NaHCO_3(s) \qquad \Delta H_3$$

FA 4 is sodium hydrogen carbonate, $NaHCO_3$.
FA 5 is sodium carbonate, Na_2CO_3.
FA 6 is 2.0 mol dm^{-3} hydrochloric acid, HC*l*.

(a) Method

(i) Experiment 1: $NaHCO_3(s) + HCl(aq) \rightarrow NaCl\ (aq) + H_2O(l) + CO_2(g)$

- Use a measuring cylinder to transfer 25 cm^3 of the acid, **FA 6**, into the plastic cup supported in a 250 cm^3 beaker. The acid is in excess.
- Weigh the container with **FA 4** and record the balance reading.
- Place the thermometer in the acid and record its temperature at 1 minute interval for the first two minutes.
- At 2½ minutes, carefully tip all the **FA 4**, in small portions, into the acid and stir to dissolve.
- Record the temperature of the solution at 1 minute interval from 3 minutes up to 8 minutes.
- Reweigh the container with any residual **FA 4** and record the balance reading and the mass of **FA 4** used.
- Rinse out the plastic cup and shake it to remove excess water.

Results

Record **all** weighings and temperature readings in the space below.

[5]

(ii) Plot on the grid below, a graph of temperature on the *y*-axis against time on the *x*-axis. The scale for the temperature should extend at least 1°C below the lowest recorded temperature.

Draw two straight lines of best fit and extrapolate the two lines to 2½ minutes. Determine the change in temperature at this time.

temperature change at 2½ minutes = ... °C

[4]

(iii) **Experiment 2**: $Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$

- Use a measuring cylinder to transfer 25 cm^3 of the acid, **FA 6**, into the plastic cup supported in a 250 cm^3 beaker. The acid is in excess.
- Weigh the container with **FA 5** and record the balance reading.
- Place the thermometer in the acid and record its initial temperature.
- Carefully tip all the **FA 5**, in small portions, into the acid and stir to dissolve.
- Record the highest temperature reached.
- Reweigh the container with any residual **FA 5** and record the balance reading and the mass of **FA 5** used.

Results

Record **all** weighings and temperature readings in the space below.

[3]

(b) **(i)** Using your answer to **2(a)(ii)**, calculate the heat energy absorbed when **FA 4** was added to the acid in **Experiment 1**.
[Assume that 4.3 J of heat energy changes the temperature of 1.0 cm^3 of solution by 1.0 °C.]

heat energy absorbed =…………..…. J [1]

(ii) Calculate the enthalpy change, in kJ mol^{-1}, when 1 mol of **FA 4**, $NaHCO_3$, reacts with the acid. [A_r: H, 1.0; C, 12.0; O, 16.0; Na, 23.0]

enthalpy change, ΔH_1 = ... kJ mol^{-1} [1]

(iii) Using your results in **2(a)(iii)**, calculate the heat energy produced when **FA 5** was added to the acid in **Experiment 2**.
[Assume that 4.3 J of heat energy changes the temperature of 1.0 cm^3 of solution by 1.0 °C.]

heat energy produced =…………..…. J [1]

(iv) Calculate the enthalpy change, in kJ mol^{-1}, when 1 mol of **FA 5**, Na_2CO_3, reacts with the acid. [A_r: C, 12.0; O, 16.0; Na, 23.0].

enthalpy change, ΔH_2 = ... kJ mol^{-1} [1]

(v) Using your answers to **2(b)(ii)** and **2(b)(iv)** and the equations for **Experiment 1** and **Experiment 2**, determine the enthalpy change for the reaction:

$$Na_2CO_3(s) + H_2O(l) + CO_2(g) \rightarrow 2NaHCO_3(s)$$

enthalpy change, ΔH_3 = ... kJ mol^{-1} [3]

(c) Planning

You are provided with **FA 4**, solid sodium hydrogencarbonate, $NaHCO_3$, distilled water and apparatus commonly found in the school laboratory.

Using only these materials, you are to plan an additional experiment to determine a further enthalpy change, ΔH_4, which can be put together with those from **Experiment 1** and **Experiment 2** to determine the enthalpy change for the reaction:

$$Na_2CO_3(s) + H_2O(l) + CO_2(g) \rightarrow 2NaHCO_3(aq) \qquad \Delta H_5$$

In your plan, you should include details of:

- the quantity of reactants and apparatus that you would use,
- the procedure you would follow,
- the measurements you would take, and
- an outline of how you would use your results to determine ΔH_5.

DO NOT CARRY OUT YOUR PLAN.

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[5]

[Total: 24]

3 Qualitative Analysis

In this question, you will carry out tests, make observations and come to conclusions about the compounds.

If the evolution of a gas is observed at any stage, the gas should be tested and identified. Details of the test carried out, the observations from the test and the identity of the gas should be given with the observations.

If it appears that no reaction has taken place, this should be clearly recorded

(a) **FA 7** is an organic solid. Carry out the tests described in Table 3.1 and use the observations to identify two functional groups present in **FA 7**.

Table 3.1

tests	*observations*
Add 10 cm^3 of ethanol to your **FA 7** in a boiling tube. Stopper the boiling tube and shake to dissolve the solid. Then add 10 cm^3 of deionised water. Shake again to ensure complete mixing. Divide the solution into four clean test-tubes and use a fresh tube for each of the following tests:	
(i) add a piece of magnesium ribbon to the solution	
(ii) add solid sodium carbonate to the solution	
(iii) add a few drops of aqueous iron(III) chloride to the solution	
(iv) add 2 cm depth of bromine water. (Take care: bromine water is corrosive.)	

[4]

(v) Complete Table 3.2, using the observations in Table 3.1 to identify the two functional groups present in **FA 7**. In each case, give evidence to support your conclusion.

Table 3.2

functional group	*evidence*

[2]

(b) Plan

You are provided with four solutions, labelled **FA 8**, **FA 9**, **FA 10** and **FA 11**.

Each solution contains one of the following compounds.

- lead nitrate, $Pb(NO_3)_2$
- sodium chloride, NaC*l*
- sodium hydroxide, NaOH
- zinc sulfate, $ZnSO_4$

The order in the list of solutions does **not** correspond to the **FA** numbers.

(i) Using the *Qualitative Analysis Notes* on page 14, complete Table 3.3 to show the expected observations when pairs of the solutions are mixed. Solutions should be added a little at a time, with shaking, until no further change is observed.

Expected observations for $Pb(NO_3)_2$ have already been recorded in Table 3.3.

Table 3.3

	NaC*l*	**NaOH**	**$ZnSO_4$**
$Pb(NO_3)_2$	white ppt.	white ppt. soluble in excess NaOH	white ppt.
NaC*l*			
NaOH			

Explain how you could use the expected observations in Table 3.3 to identify **each** of the solutions.

....

....

....

....

....

.... [5]

(ii) Carry out the experiment using **FA 8**, **FA 9**, **FA 10** and **FA 11** and record your results in a suitable table.

[3]

(iii) Identify the substance present in each of the solutions.

FA 8 ....

FA 9 ....

FA 10 ....

FA 11 ....

[1]

[Total: 15]

Qualitative Analysis Notes

[*ppt. = precipitate*]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, A*l* $^{3+}$(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

ion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and A*l* foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and A*l* foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

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Catholic Junior College

JC 2 Preliminary Examinations

Higher 2

CHEMISTRY

9729/01

Paper 1 Multiple Choice

29 August 2017

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, HT group and NRIC/FIN number on the Answer Sheet in the spaces provided.
Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

MARK SCHEME

This document consists of **25** printed pages and **1** blank page.

For each question there are ***four*** possible answers, ***A***, ***B***, ***C*** and ***D***. Choose the **one** you consider to be correct.

1 When an unknown organic compound is burned completely in excess oxygen, 90 cm^3 of gaseous products is collected. When cooled to room temperature, the gaseous volume decreased to 50 cm^3. A further decrease of 40 cm^3 in the gaseous volume was observed when the gaseous mixture is passed through aqueous potassium hydroxide.

What is the possible identity of the organic compound?

1 CH_2CH_2

2 CH_3CO_2H

3 $CH_3CH_2CH_3$

4 CH_2CHCH_2OH

A 1 and 3 only

B 1 and 4 only

C 1, 2 and 4 only

D 2 and 4 only

Concept: MCS: rxn stoichiometry, molar volume of gas at r.t.p,

Start with volume of CO_2 given and use the equation to work out the mole ratio.

Answer: C

First reduction of gaseous vol due to cooling

→ hot $H_2O(g)$ has condensed to form $H_2O(l)$ at r.t.p.

→ thus, vol of $H_2O(g)$ = 90 – 50 = 40 cm^3

Second reduction of gaseous vol due to reaction with KOH(aq)

→ $CO_2(g)$ is an acidic gas and reacts with KOH(aq) via acid-base reaction

→ vol of $CO_2(g)$ = 40 cm^3

Thus, $CO_2(g) : H_2O(g)$ → Thus, C : H
= 40 : 40 = 1 : 2
= 1 : 1

Thus the organic compound must have a ratio C : H = 1: 2.

1 CH_2CH_2 → C_2H_4 → correct
2 CH_3CO_2H → $C_2H_4O_2$ → correct
3 $CH_3CH_2CH_3$ → C_3H_8 → incorrect
4 CH_2CHCH_2OH → C_3H_6O → correct

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

A vanadium salt of unknown oxidation state was dissolved in water to form a solution of 0.500 mol dm^{-3}. It was found that 20.4 cm^3 of this solution will react with 1.00 g of zinc powder to form vanadium(II) solution.

What is the possible identity of the vanadium salt used?

A V^{2+} **B** V^{3+} **C** VO^{2+} **D** VO_2^+

Concept: Redox: determination of oxidation state

Answer: D

Let the vanadium salt of unknown oxidation state be V^{x+}

Amt of zinc used = 1 ÷ 65.4 = 0.0153 mol

Amt of V^{x+} reacted = $\frac{20.4}{1000}$ × 0.500 = 0.0102 mol

Ratio of Zn : V^{x+} = 0.0153 : 0.0102

= 3 : 2

Given that $Zn \rightarrow Zn^{2+} + 2e^-$,

3 mol of Zn will donate 6 mol of e^- and 2 mol of V^{x+} will accept 6 mol of e^-.

Therefore, 1 mol of V^{x+} will accept 3 mol of e^-.

Since V^{x+} is reduced to V^{2+}, its original oxidation state is +5.

species	V^{2+}	V^{3+}	VO^{2+}	VO_2^+
Oxidation state	+2	+3	+4	+5

Thus, only VO_2^+ is the possible identities of the unknown salt solution.

3 The table below gives some data about four ions.

ions	number of neutrons	number of nucleons
$\mathbf{Q}^-$	16	33
$\mathbf{R}^+$	19	39
$\mathbf{S}^{2-}$	17	33
$\mathbf{T}^{2+}$	18	35

Which of the following pairs consists of ions that are isoelectronic?

A $\mathbf{Q}^-$ and $\mathbf{S}^{2-}$

B $\mathbf{R}^+$ and $\mathbf{S}^{2-}$

C $\mathbf{S}^{2-}$ and $\mathbf{T}^{2+}$

D $\mathbf{Q}^-$ and $\mathbf{T}^{2+}$

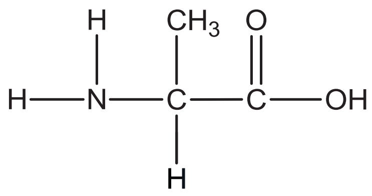
Concept: Atomic Structure: determination of no. of protons and electrons from given species, isoelectronic species

Isoelectronic species have the same number of electrons.

particle	number of neutrons	number of nucleons	number of protons	number of electrons
$\mathbf{Q}^-$	16	33	33 – 16 = 17	17 + 1 = **18**
$\mathbf{R}^+$	19	39	39 – 19 = 20	20 – 1 = 19
$\mathbf{S}^{2-}$	17	33	33 – 17 = 16	16 + 2 = **18**
$\mathbf{T}^{2+}$	18	35	35 – 18 = 17	17 – 2 = 15

ANS: A

4 Which bond angle is present in a molecule of alanine, $H_2NCH(CH_3)CO_2H$, but is **not** present in its zwitterion?



$H{-}N(H){-}C(CH_3)(H){-}C({=}O){-}OH$

alanine

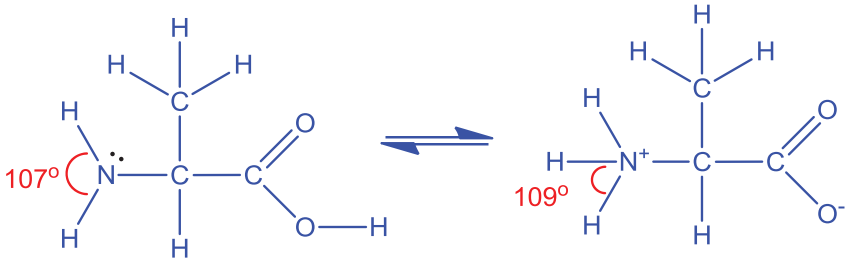
A 90° **B** 107° **C** 109° **D** 120°

Concept: Chemical Bonding: Structure of zwitterion of amino acid

Predict bond angles based on number of bond and lone pairs, and shape around central atom.

Answer: B

Zwitterion of alanine is $^{+}H_3NCH(CH_3)COO^{-}$



alanine

3 bp, 1 lp around N
bond angle = 107°

zwitterion of alanine

4 bp, 0 lp around N
bond angle = 109°

In the zwitterion, $-NH_2$ group (trigonal pyramidal about N, bond angle = 107°) becomes $-NH_3^{+}$ (tetrahedral about N, bond angle = 109°) and $-CO_2H$ (trigonal planar about sp^2 hybridised carbon, 120°) group becomes CO_2^{-} (trigonal planar about sp^2 hybridised carbon, 120°).
Option A: bond angle of 90° is not present in both alanine and its zwitterion.

5 What are the types of chemical bonds present in solid phenylammonium chloride, $C_6H_5NH_3Cl$?

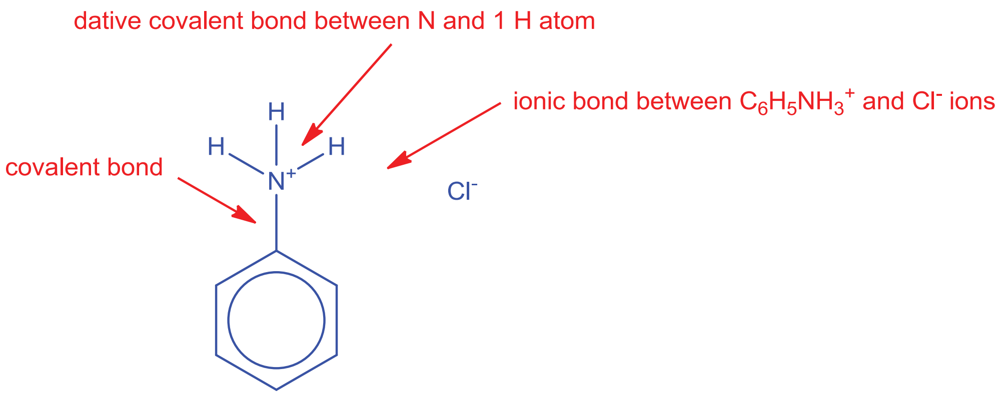
1 dative covalent bonds
2 ionic bonds
3 hydrogen bonds

A 2 only
B 1 and 2 only
C 2 and 3 only
D 1, 2 and 3

Concept: Chemical Bonding: Identify type of chemical bonds within an ionic compound, consisting of polyatomic ions.

Identify structure to be giant ionic, with covalent bonds within the polyatomic cation, $C_6H_5NH_3^{+}$

Answer: B



phenylammonium chloride

absence of hydrogen bond; absence of lone electron pair on N

$C_6H_5NH_3Cl$ is an ionic compound, consisting of polyatomic cations, $C_6H_5NH_3^+$ and Cl^-. Hence ionic bonds exist between $C_6H_5NH_3^+$ and Cl^- ions while covalent bond and dative covalent bonds exist between the C, N and H atoms within the $C_6H_5NH_3^+$ cation. Hydrogen bonds are not present as no lone electron pair is present on N atom in $C_6H_5NH_3^+$.

6 Which one of the following shows the standard enthalpy change of formation of carbon monoxide?

A $C(s) + ½O_2(g) \rightarrow CO(g)$

B $C(s) + CO_2(g) \rightarrow 2CO(g)$

C $C(g) + ½O_2(g) \rightarrow CO(g)$

D $C(g) + CO_2(g) \rightarrow 2CO(g)$

Concept: Chemical Energetics, Definition of enthalpy change of formation.

Answer: A

The **standard enthalpy change of formation,** $\Delta H_f^{\ominus}$, of a substance (usually a compound) is defined as the enthalpy change when one mole of the substance is formed **(Hence options B and D are incorrect as 2 moles of CO are formed)** from its elements under standard conditions of 298 K and 1 bar. (Elements must be in most stable physical form.) **The most stable physical form of carbon is graphite (solid). Hence option C is incorrect and the answer is option A.**

7 Nitrogen dioxide, NO_2, has an unpaired electron and dimerises to form N_2O_4.

$$2NO_2(g) \rightarrow N_2O_4(g)$$

Which of the following statements about the spontaneity of the reaction is true?

A The reaction is only spontaneous at low temperatures.

B The reaction is only spontaneous at high temperatures.

C The reaction is spontaneous at all temperatures.

D The reaction is non-spontaneous at all temperatures.

ΔH of the reaction is negative since the reaction involves bond formation which is exothermic.

ΔS of the reaction is negative as there is a decrease in the number of moles of gaseous particles.

$\Delta G = \Delta H - T\Delta S$
Since ΔH is negative and $-T\Delta S$ is positive, a higher temperature would cause ΔG to become more positive and less spontaneous. Hence the reaction is only spontaneous at low temperatures.

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

Gas canisters used in camping stoves contain partially liquefied hydrocarbon. A canister was connected to a gas syringe and the valve opened slightly to allow some gas into the syringe. 0.200 g of the gas occupied a volume of 96.0 cm^3 at a temperature of 30.0 °C and a pressure of 101 kPa.

What is the average M_r of the gas mixture?

A 31 **B** 52 **C** 479 **D** 519

Concept: Gaseous State; application of Ideal gas equation, pV = nRT & unit conversion

Rearrange pV = nRT equation to solve for M_r

Answer: B

$pV = nRT$

$$= \frac{m}{M_r}RT \qquad \therefore M_r = \frac{mRT}{pV} = \frac{(0.200)(8.31)(30+273)}{(101 \times 10^3)(96.0 \times 10^{-6})} = 52$$

[Turn over

9 At a certain temperature, three gases N_2, O_2 and HC*l* were mixed and the following reaction occurred:

$$2N_2(g) + 3O_2(g) + 4HCl(g) \rightleftharpoons 4NOCl(g) + 2H_2O(g)$$

The initial partial pressures of N_2, O_2 and HC*l* are 0.800 atm, 0.800 atm and 0.400 atm respectively. After equilibrium has been established, it is found that the partial pressure of steam is 0.15 atm.

What is the numerical value of K_p for this reaction at this temperature?

A 1.20 **B** 22.7 **C** 0.0217 **D** 0.0251

Concept: Chemical Equilibria, Finding equilibrium values and calculating *K*p, keeping in mind the stoichiometric ratios reacted / formed while achieving equilibrium.

Answer: B

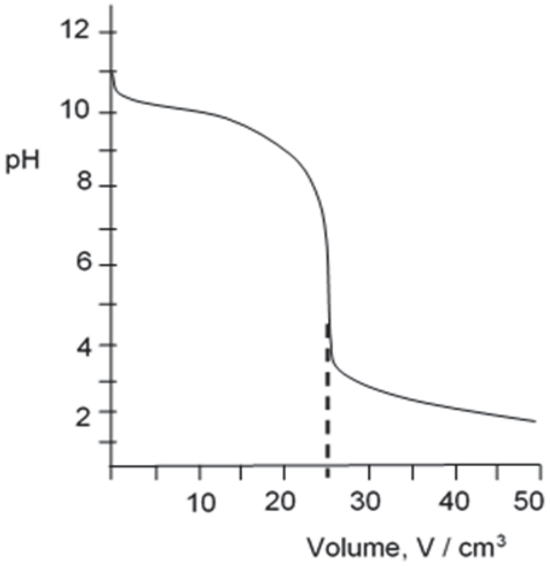
To find the pressures at equilibrium, the ICE table can be drawn.

	$2N_2(g)$	+ $3O_2(g)$	+ $4HCl(g)$	$\rightleftharpoons$ $4NOCl(g)$	+ $2H_2O(g)$
Initial p / atm	0.800	0.800	0.400	0	0
Change in p / atm	- (0.15)	-3/2(0.15)	-2(0.15)	+2(0.15)	+0.15
Eqm p / atm	0.65	0.575	0.100	0.300	0.15

$$K_p = \frac{pNOCl^4\, pH_2O^2}{pN_2{}^2 pO_2{}^3 pHCl^4} = \frac{(0.300)^4(0.15)^2}{(0.65)^2(0.575)^3(0.100)^4} = 22.7\text{atm}^{-3}$$

10 In an acid-base titration, a 0.10 mol dm^{-3} solution of an acid is added to a 25 cm^{3} of a 0.10 mol dm^{-3} solution of a base.

The pH value of the solution is plotted against the volume, V, of acid added as shown in the diagram.



Which of the following statements is **incorrect**?

A The titration involved a strong acid and a weak base.

B The pair of solutions could have been HC*l*(aq) and CH_3NH_2(aq).

C Methyl orange is a suitable indicator for the above titration.

D When concentration of acid is doubled, the end point volume of the titration would be halved while the pH at equivalence point would remain unchanged.

Concept: Chemistry of Aqueous Solutions, interpreting titration curve

Using equivalence point pH to determine type of acid-base reaction

Answer: D

pH at equivalence point < 7; implies presence of acidic salt. Hence strong acid-weak base titration has occurred. Hence Option A is correct.

As the stoichiometry of acid: base = 1:1, hence the solutions involved should be a monoprotic base and a monobasic acid. Hence Option B is correct.

For strong acid-weak base titration, methyl orange is a suitable indicator. Hence Option C is correct too.

When concentration of acid is doubled, the amount of salt formed at equivalence point is fixed though total volume of the solution is now lower.

Compared to $[salt]_{original}$ = 25.0 x 0.1 / (25+25) = 0.05 mol dm^{-3}

$[salt]_{new}$ = 12.5 x 0.2 / (12.5 + 25) = 0.0667 mol dm^{-3}

Since $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

And $[H^+] = \sqrt{Ka} \times [acidic\ salt]$

when [salt] is higher, new $[H^+]$ will work out to be higher, hence new equivalence pH will decrease.

11 The following two reactions are examples of acid-base reactions.

Reaction 1: $HNO_3 + H_2SO_4 \rightleftharpoons H_2NO_3^+ + HSO_4^-$

Reaction 2: $NH_3 + BF_3 \rightarrow NH_3BF_3$

Which of the following correctly describes the behaviour of each species?

	Brønsted acid	Brønsted base	Lewis acid	Lewis base
A	HNO_3	NH_3	H_2SO_4	HSO_4^-
B	H_2SO_4	HNO_3	BF_3	NH_3
C	HSO_4^-	NH_3	BF_3	$H_2NO_3^+$
D	$H_2NO_3^+$	HSO_4^-	NH_3BF_3	NH_3

Concept: Definition of Bronsted acids and bases, Lewis acids and bases

For Reaction 1

HNO_3 donated a proton to form $H_2NO_3^+$. HNO_3 is a Brønsted base whereas $H_2NO_3^+$ is the conjugate acid.

H_2SO_4 donated a proton to form HSO_4^- and is a Brønsted acid, whereas HSO_4^- is the conjugate base.

For Reaction 2

NH_3 has a lone pair of electrons on N and donates a pair of electrons to B in BF_3 (which is electron-deficient). NH_3 thus acts as a Lewis base whereas BF_3 acts as the Lewis acid.

12 The decomposition of hydrogen peroxide is known to be a first order reaction.

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

The rate constant is found to be 4.95 x 10^{-2} min^{-1}. If the initial concentration of H_2O_2 is 4.00 mol dm^{-3}, what will be the concentration of H_2O_2 after 64 min?

A 0.50 mol dm^{-3}

B 0.20 mol dm^{-3}

C 0.17 mol dm^{-3}

D 0.13 mol dm^{-3}

Concept: Calculations involving first order reactions, making use of the formula t1/2 = ln 2 / k

Half life = ln 2 / (4.95 x 10^{-2}) = 14 min
Number of half-lives = 64 / 14 = 4.57

$$\frac{Ct}{Co} = (\frac{1}{2})^{n}$$

$$\frac{Ct}{4} = (\frac{1}{2})^{4.57}$$

C_t = 0.168 mol dm^{-3}

13 The rate equation for the reaction 2**W** + **X** → **Y** + **Z** is given as rate = k[**W**][**X**]. In an experiment to study the kinetics of the reaction, the initial concentration of **W** used is 0.20 mol dm^{-3} and the initial concentration of **X** used is 0.001 mol dm^{-3}.

Which of the following statements regarding the experiment is correct?

A The half-life for the [**X**] against time curve is approximately constant.

B The mechanism for the above reaction involves one step.

C The units of the rate constant is $mol^{-2}dm^{6}s^{-1}$.

D Doubling the initial concentration of **W** to 0.40 mol dm^{-3} will not affect the half-life of **X**.

Concept: relationship of mechanism to rate equation and overall equation, interpretation of units for rate constant

The concentration of **W** is 200 times larger than **X**, hence the reaction is pseudo zero order wrt **W** and the reaction becomes overall pseudo first-order.

Rate = k' [**X**], where k' = k [**W**]

Therefore half-life of **X** will be approximately constant having a value of $t_{½} = \frac{\ln 2}{0.2\ k}$

D: when initial [**W**] is doubled, $t_{½}$ will be halved.

B: Since stoichiometry shows that 2 W are involved, the reaction will have more than one step as the slow step involves only 1W and 1X leaving the other W molecule/ion to be involved in the fast step.

C: Since rate = k[**W**][**X**], and units of rate = $moldm^{-3}s^{-1}$, the units for k = $mol^{-1}dm^{3}s^{-1}$

14 The oxide and chloride of an element **E** are mixed separately with water. The two resulting solutions have the same effect on litmus.

What is element **E**?

A Mg **B** A*l* **C** Si **D** P

Concept: Trends across Period 3, and oxides and chlorides of Period 3

Answer: D
For Option B and C
Note that both SiO_2 and Al_2O_3 are insoluble in water. The resulting solution would thus be neutral. Both $SiCl_4$ and $AlCl_3$ will give undergo hydrolysis to give acidic solutions.

PCl_5 undergoes hydrolysis to form H_3PO_4 and HC*l*, which causes the resulting solution to be acidic and turn blue litmus red. P_4O_{10} would also undergo hydrolysis to give H_3PO_4 which is an acidic solution.

MgO is gives $Mg(OH)_2$ in water which is weakly basic whereas $MgCl_2$ is weakly acidic.

15 Which of the following statements about iodine or its compounds are correct?

1 A crystal of iodine contains covalent bonds and instantaneous dipole-induced dipole forces of attraction.
2 When aqueous chlorine is added to potassium iodide and the aqueous mixture shaken with tetrachloromethane, a purple organic layer is obtained.
3 The first ionisation energy of iodine is less than that of bromine.
4 The thermal stability of hydrogen iodide is higher than that of hydrogen bromide.

A 1 and 3 only
B 1, 2 and 3 only
C 3 and 4 only
D 2, 3 and 4 only

Concept: Group 17 Halogen and Halide properties

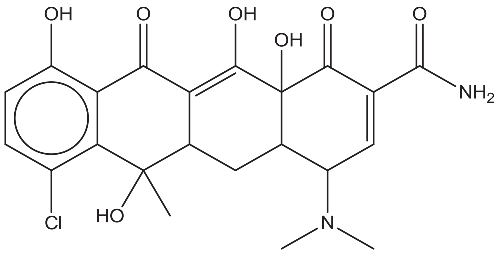
1: I_2 is a non-polar simple covalent molecule. Thus, there are strong covalent bonds between I atoms and instantaneous dipole-induced dipole forces of attraction between iodine molecules.

2: Cl_2 can oxidise KI to form I_2 which is purple in the organic layer.
Ecell = 1.36 – 0.54 > 0 V (thus the reaction is spontaneous)

3: Ionisation energy decreases down the group. I_2 has a lower first ionisation energy than Br_2.

4: H- I bond is longer and weaker than H-Br and thus HI has a lower thermal stability.

16 *Aureomycin* is a powerful oral antibiotics that is effective against a wide range of infections.



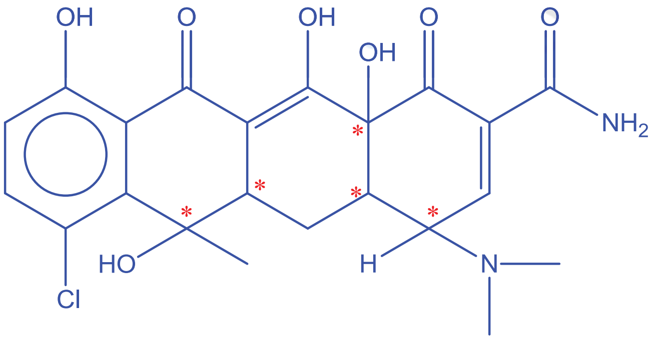
Aureomycin

Which row correctly indicates the number of chiral centres and sp^2 hybridised carbon in a molecule of *aureomycin*?

	Number of chiral centres	Number of sp^2 hybridised C
A	4	10
B	4	13
C	5	10
D	5	13

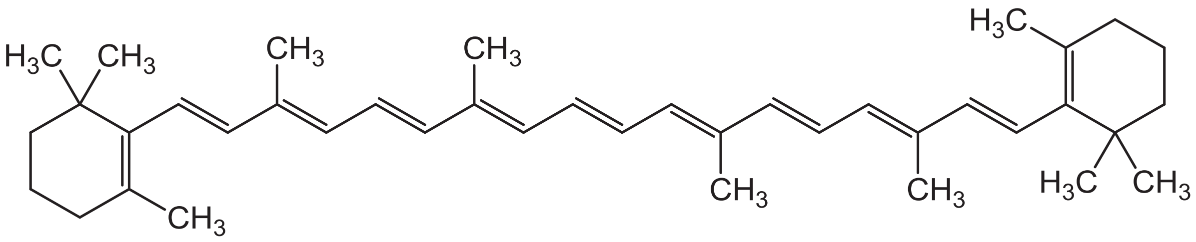
Concept: Introduction to Organic Chem; identification of chiral C & hybridisation

Answer: D



5 chiral centres
13 sp^2 C

17 β-carotene is responsible for the orange colour of carrots.



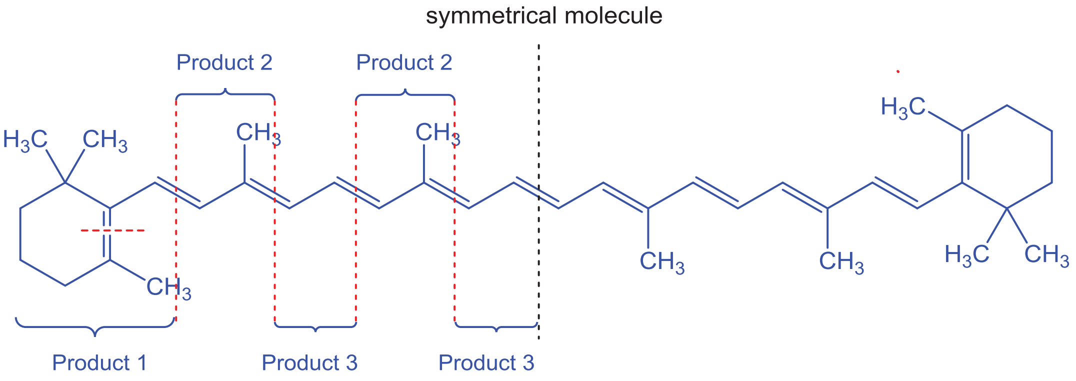
β–carotene

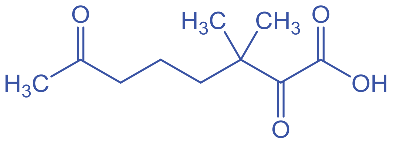
β-carotene is oxidised by hot, concentrated, acidified $KMnO_4$.

How many different products formed from the above reaction contain the ketone functional group?

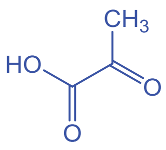
A 2 **B** 4 **C** 6 **D** 8

Concept: oxidative cleavage of C=C and identifying the ketone functional group

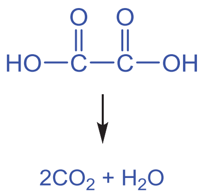




Product 1



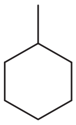
Product 2



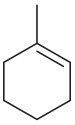
Product 3

Since the molecule is symmetrical, there are only 2 different products that contained ketone groups.

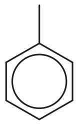
18 Which of the statements are true regarding the three compounds below?



I



II



III

1 Compounds **I** and **III** will not decolourise Br_2 in CCl_4.

2 Compounds **I** and **II** will decolourise acidified $KMnO_4$ at 298 K.

3 Compound **III** will not react with chlorine in the presence of uv light.

4 Compound **III** will react with bromine in the presence of a homogeneous catalyst.

A 1 and 4 only

B 2 and 3 only

C 1, 3 and 4 only

D 1, 2, 3 and 4

Concept: Chemical properties of Hydrocarbons

Reagents and conditions of Free Radical Substitution, Electrophilic Addition and Electrophilic Substitution

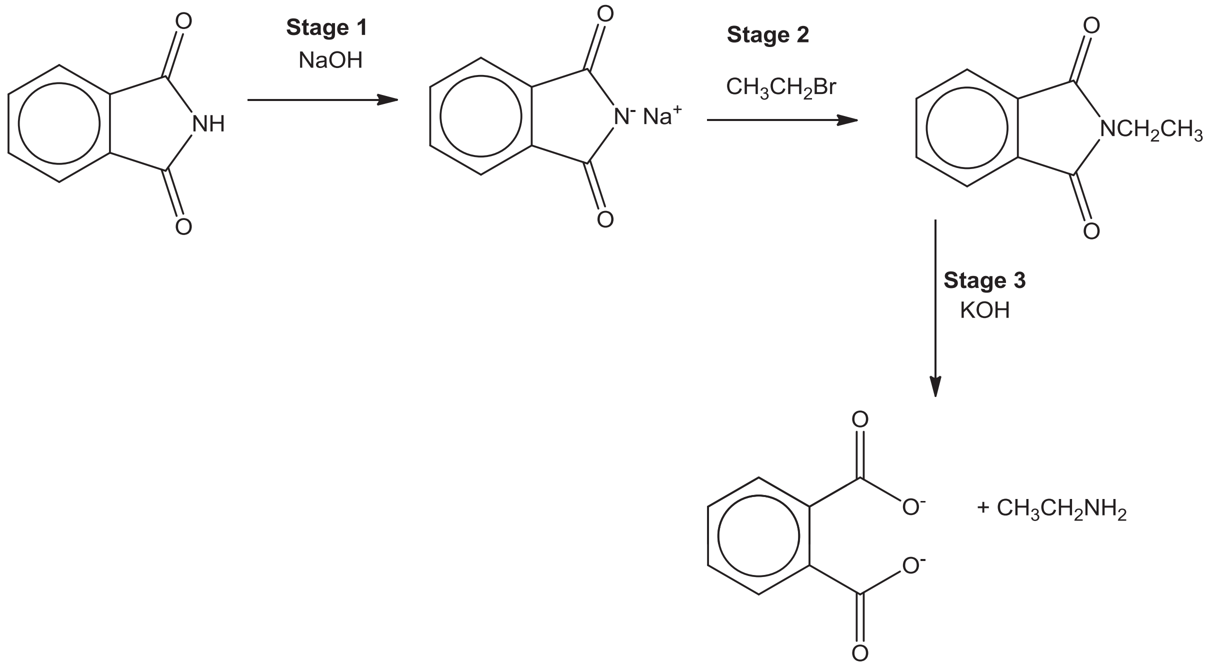
addition. Thus, both compounds **I** and **III** will not decolourise Br_2.

Statement 2: False. Compound **I** will not decolourise purple $KMnO_4$ at room temp.

Statement 3: False. The alkyl side-chain of compound **III** will be able to undergo free radical substitution with Cl_2 gas when exposed to uv light.

Statement 4: True. Compound **III** requires $FeBr_3$ catalyst for electrophilic substitution to occur.

19 A sequence of reactions is shown below.



Which of the following correctly describes the type of reactions for Stages **1** to **3**?

Stage 1 **Stage 2** **Stage 3**

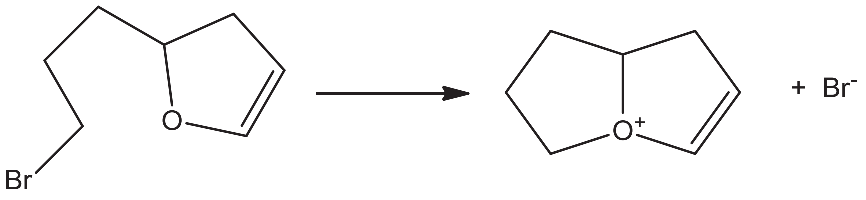
A	neutralisation	electrophilic substitution	nucleophilic substitution
B	hydrolysis	nucleophilic substitution	hydrolysis
C	redox	nucleophilic addition	nucleophilic substitution
D	neutralisation	nucleophilic substitution	hydrolysis

Concept: identifying types of reaction for organic compounds

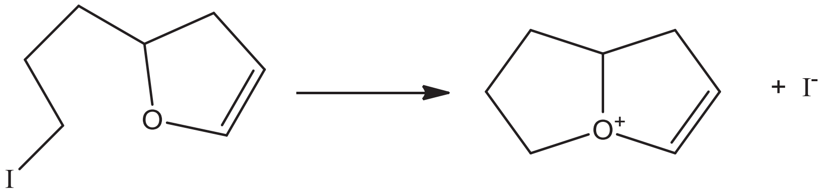
Stage 1: The diamide donated a proton and is a Bronsted acid. The OH^- accepted a H^+ to form H_2O. Thus this is an acid-base reaction.
Stage 2: Bromoethane undergoes nucleophilic substitution, with the negatively charged ion acting as the nucleophile.
Stage 3: The amide undergoes base-catalysed hydrolysis.

20 The intramolecular reactions below occur via nucleophilic substitution mechanism.

Reaction 1



Reaction 2



Reaction 2 is faster than reaction 1 under identical conditions.

Which statement explains this difference?

A Br is more electronegative than I.

B The I^- ion is a stronger nucleophile than Br^-.

C The C–Br bond is more polar than the C–I bond.

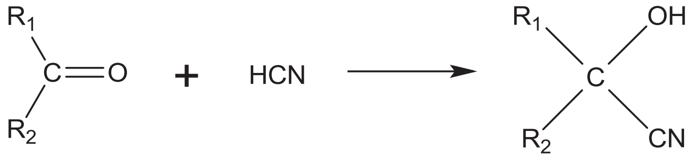
D The C–Br bond is stronger than the C–I bond.

Concept: Halogen Derivatives; effect of C-Hal bond strength on reactivity towards nucleophilic substitution

To recall weaker C-Hal bond leads to faster substitution by nucleophile

Answer: D
C-Br bond is stronger than C-I bond, hence rate of S_N2 nucleophilic substitution in reaction 1 is slower.

21 Cyanohydrins can be made from carbonyl compounds by generating CN^- ions from HCN in the presence of a weak base.



In a similar reaction, $^-CH_2COOCH_3$ ions are generated from CH_3COOCH_3 by strong bases.

Which compound can be made from an aldehyde and CH_3COOCH_3?

A $CH_3CH(OH)COOCH_3$
B $CH_3COOCH_2CH(OH)CH_3$
C $CH_3CH_2CH(OH)CH_2COOCH_3$
D $(CH_3)_2C(OH)CH_2COOCH_3$

Concept: Pattern identification and interpreting condensed structural formula

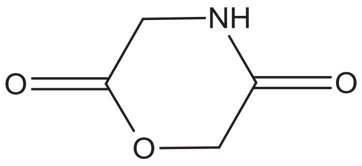
A is incorrect. The nucleophile used is $^-COOCH_3$.

B is incorrect. The nucleophile used is $CH_3COOCH_2^-$.

C is correct. The nucleophile used is $^-CH_2COOCH_3$ and it reacts with an aldehyde CH_3CH_2CHO.

D is incorrect. The nucleophile used is $^-CH_2COOCH_3$ but it reacts with a ketone CH_3COCH_3

22 The cyclic compound **X** is heated with acidified $KMnO_4$.



Compound **X**

What are the final organic products of the reaction?

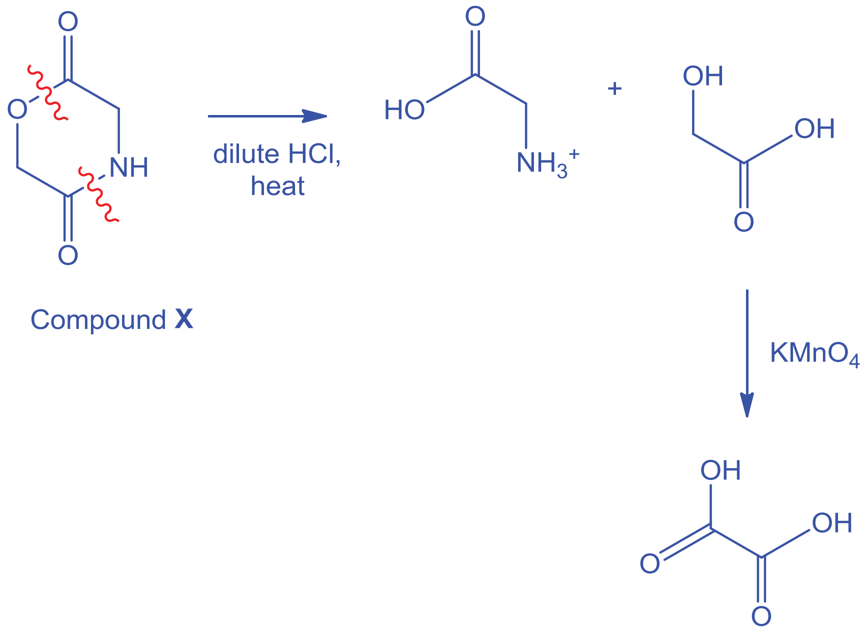
A $HOCH_2CO_2H$ and $HO_2CCH_2NH_3^+$

B $HO_2CCH_2NH_3^+$

C $HOCH_2CHO$ and $H_2NCH_2CO_2H$

D H_2NCOCH_2OH and $HOCH_2CHO$

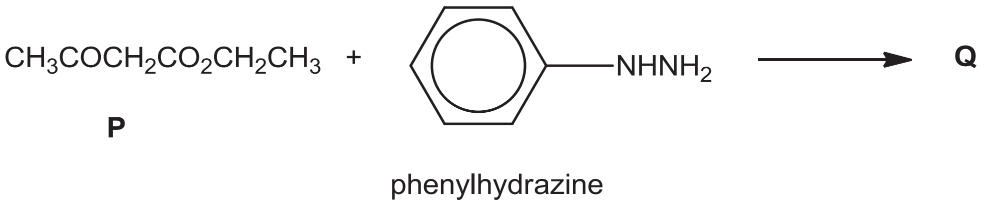
Concept: hydrolysis of amides and esters



Compound **X**

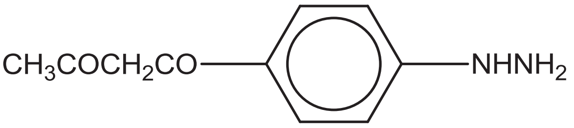
ethanedioic acid undergoes further oxidation to give CO_2 and H_2O

23 The first stage in the synthesis of *Antipyrine,* a fever medication, is the reaction between compound **P** and phenylhydrazine.

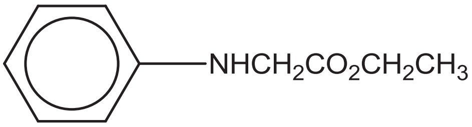


Which of the following correctly represents the structure of product **Q**?

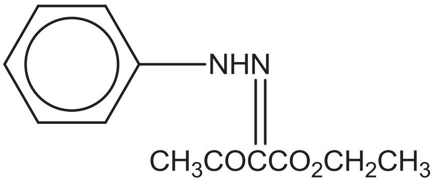
A



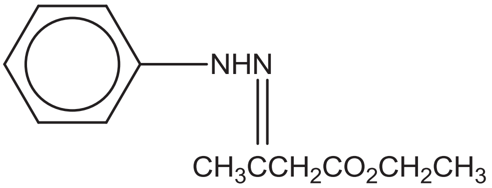
B



C



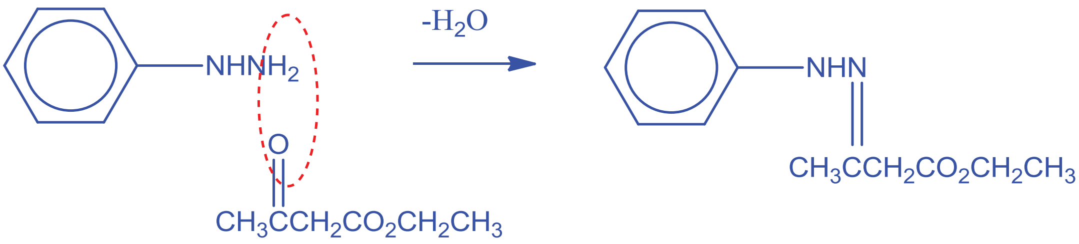
D



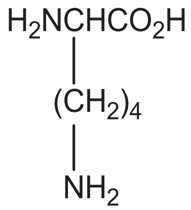
Concept: Carbonyl Compounds & Carboxylic acids derivatives

Predicting product formed from condensation reaction between a ketone and phenylhydrazine (extension of knowledge from reaction between carbonyl compounds and 2,4-DNPH.

Answer: D

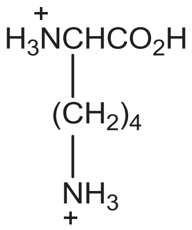


24 Lysine is an α-amino acid.



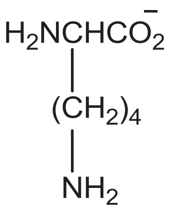
$$\begin{array}{c}\mathrm{H_2NCHCO_2H}\\ |\\ \mathrm{(CH_2)_4}\\ |\\ \mathrm{NH_2}\end{array}$$

Which structure is predominant when lysine is in an aqueous solution of pH 9.5, given that lysine has three pK_a values of 2.2, 8.9 and 10.5?



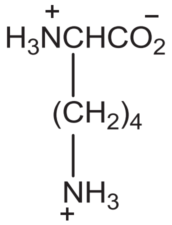
$$\begin{array}{c}\mathrm{\overset{+}{H_3N}CHCO_2H}\\ |\\ \mathrm{(CH_2)_4}\\ |\\ \mathrm{\underset{+}{NH_3}}\end{array}$$

A



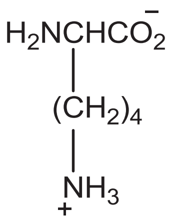
$$\begin{array}{c}\mathrm{H_2NCHCO_2^-}\\ |\\ \mathrm{(CH_2)_4}\\ |\\ \mathrm{NH_2}\end{array}$$

B



$$\begin{array}{c}\mathrm{\overset{+}{H_3N}CHCO_2^-}\\ |\\ \mathrm{(CH_2)_4}\\ |\\ \mathrm{\underset{+}{NH_3}}\end{array}$$

C



$$\begin{array}{c}\mathrm{H_2NCHCO_2^-}\\ |\\ \mathrm{(CH_2)_4}\\ |\\ \mathrm{\underset{+}{NH_3}}\end{array}$$

D

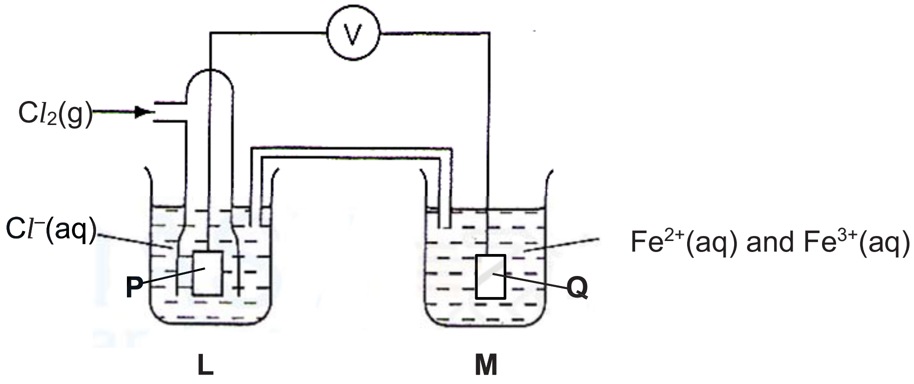
Concept: Nitrogen Compounds; assigning pK_a values, determining predominant structure of amino acid in alkaline solution.

Answer: D

Side-chain -NH_3+ group will not dissociate as its pK_a value (10.5) is above pH 9.5.

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

The cell shown below is set up under standard conditions where **P** and **Q** are platinum electrodes.



Which of the following statements is correct?

A Addition of KCN to half-cell **M** will not affect $E_{cell}^{\ominus}$.

B The voltmeter will show a reading of about 2.13 V.

C The electrons will flow from **Q** to **P** through the voltmeter.

D **P** will be the negative electrode.

Concept: Electrochemical cell setup, determining cell emf.

Answer: C

A. Wrong. By introducing CN^- Ligands, the E(Fe^{3+}/Fe^{2+}) changes and therefore the cell emf will change. , it will participate in reaction.

B. Wrong. Cell emf = 1.36 – 0.77 = 0.59 V

C. Correct. Half-cell **M** is undergoing oxidation (loss of electrons) since the E(Fe^{3+}/Fe^{2+}) is less positive than E(Cl_2/Cl^-).

D. Wrong. In electrochemical cell, the half-cell where reduction takes place, the electrode will have positive polarity. Oxidation is taking place in half-cell **M**.

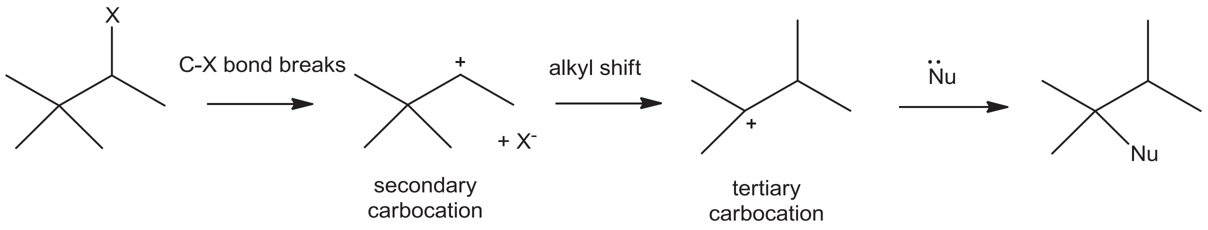
26 During electroplating, a current is passed through a cell containing aqueous silver nitrate using inert electrodes. After some time, 1.35 g of silver was deposited at one electrode. What volume of gas would be produced at the other electrode at r.t.p.?

A 70 cm^3 **B** 75 cm^3 **C** 140 cm^3 **D** 150 cm^3

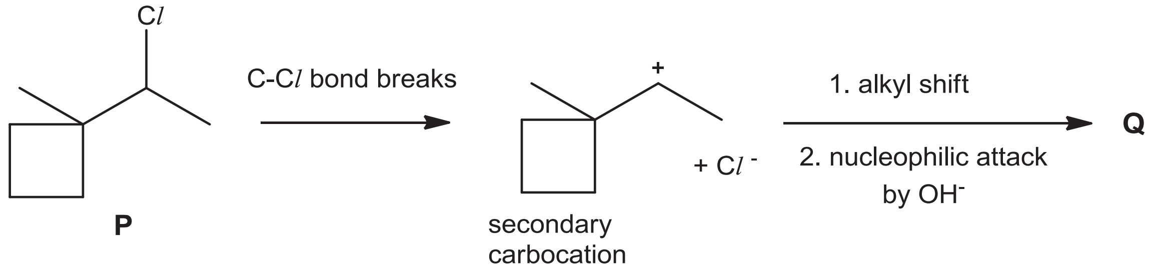
Concept: Electrolytic calculations via half-cell reactions.

Answer: B
$Ag^+ + e^- \rightarrow Ag$ is formed at the cathode
1 mol of Ag requires 1 mol of electrons
No. of mole of electrons = 1.35/108 = 0.0125 mol
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
1 mol O_2 give 4 mol of electrons
No. of mole of oxygen formed = 0.0125/4 = 0.003125 mol
Volume of oxygen = 0.03125 x 24000 = 75 cm^3

27 In S_N1 reactions involving secondary halogenoalkanes, alkyl shift can sometimes occur after the breaking of C–X bond to form a more stable tertiary carbocation.

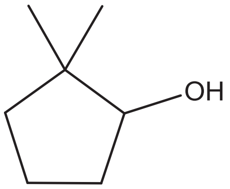


Rearrangements need not always involve methyl groups. In situation when the carbocation is formed adjacent to a strained ring, such as a cyclobutane, it is more favourable for one of the alkyl groups in the ring, rather than the methyl group, to shift so as to cause **ring expansion** and the formation of a less strained ring.

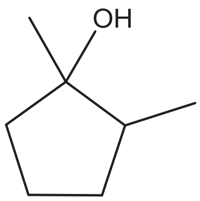


Which of the following is a possible identity of **Q**?

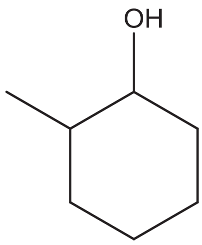
A



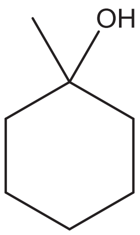
B



C

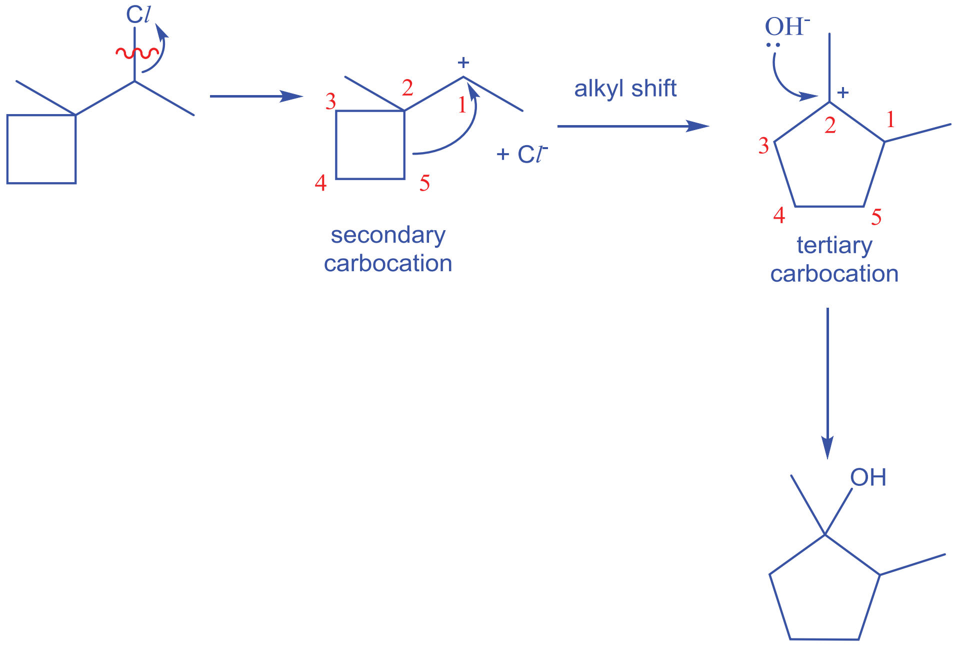


D

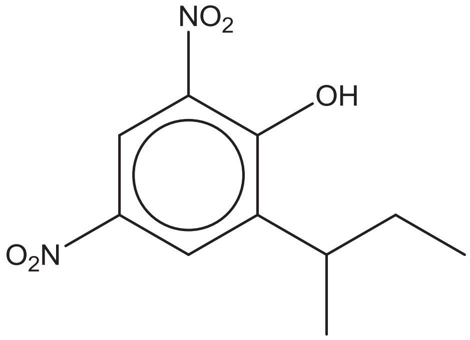


Concept: Pattern recognition of novel reaction; predicting structure of product

Answer: B



28 *Binapacryl* is used as a fungicide.



Binapacryl

Which of the following statements about *Binapacryl* are correct?

1 It dissolves in water to give a neutral solution.

2 It is inert towards acidified potassium dichromate(VI) solution.

3 It decolourises aqueous bromine to form a white precipitate.

4 It reacts with ethanoic acid in the presence of concentrated sulfuric acid to form an ester.

A 2 only

B 2 and 3 only

C 1 and 4 only

D 1, 2, 3 and 4 only

Concept: Hydroxy compounds (phenols); reactions of phenols; chirality.

Answer: A

1 It dissolves in water to give a neutral solution. **False; Binapacryl is not soluble in water.**

2 It is inert towards acidified potassium dichromate solution. **True; acidified $K_2Cr_2O_7$ is not strong enough to oxidise the alkyl side-chain.**

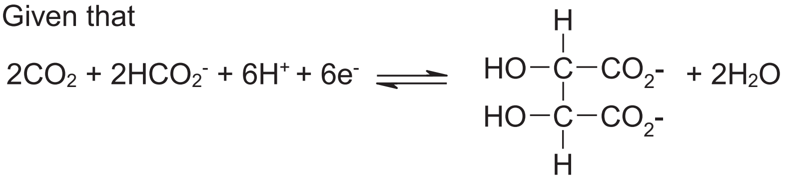
3 It decolourises aqueous bromine to form a white precipitate. **False; phenolic group in Binapacryl is already 2, 4 substituted. Hence will not be able to undergo further electrophilic substitution with aq. Br_2.**

4 It reacts with ethanoic acid in the presence of concentrated sulphuric acid to form an ester. **False; phenol and ethanoic acid are both weak acids; no reaction between both compounds. To form ester with phenol, acyl chloride is required instead.**

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

The reaction between peroxodisulfate(VI) ion, $S_2O_8^{2-}$, and tartrate ion, $[CH(OH)CO_2^-]_2$, is slow due to a high activation energy.

The reaction can be catalysed by a homogeneous catalyst.
Given that



$$2CO_2 + 2HCO_2^- + 6H^+ + 6e^- \rightleftharpoons \mathrm{HO{-}CH(CO_2^-){-}CH(CO_2^-){-}OH} + 2H_2O \qquad E^\ominus = +0.56\ V$$

Which metal ion is **not** a suitable catalyst for this reaction?

A Co^{2+}

B Cr^{2+}

C Mn^{3+}

D Fe^{3+}

Concept tested: Transition metal ions as suitable homogeneous catalyst

From data booklet, $E^\ominus$ ($S_2O_8^{2-}$ / SO_4^{2-}) = +2.01V
Hence $E^\ominus$ value of suitable catalyst should be between +0.56 V and +2.01 V

$E^\ominus$ (Co^{3+}/Co^{2+}) = +1.89 V
$E^\ominus$ (Mn^{3+}/Mn^{2+}) = +1.54 V
$E^\ominus$ (Fe^{3+}/Fe^{2+}) = +0.77 V
$E^\ominus$ (Cr^{3+}/Cr^{2+}) = -0.41 V

Hence Cr^{3+} is not a suitable catalyst for this reaction.
Answer: B

30 Chromium forms a series of compounds with the general formula $CrCl_3 \bullet 6H_2O$. One of these compounds, **X** is violet and produces an aqueous solution from which all the chlorine can be precipitated as AgC*l* upon addition of aqueous silver nitrate.
Another compound **Y** is green and produces an aqueous solution from which only one third of the chlorine can be precipitated with silver nitrate.

Which of the following statements about **X** and **Y** is **incorrect**?

A **X** is an ionic compound consisting of $[Cr(H_2O)_6]^{3+}$ and Cl^- ions.

B **Y** is an ionic compound consisting of $[Cr(Cl)_2(H_2O)_4]^+$ and Cl^- ions.

C Oxidation number of Cr in **X** is +3 while the oxidation number of Cr in **Y** is +1.

D Oxidation number of Cr in **X** and **Y** remains unchanged during precipitation of AgC*l*.

Concept: Introduction to Transition Elements; complex ion formation and oxidation number of central metal ion.

Determining formula of Cr-containing complex ions and oxidation number of central metal ion based on given information.

Answer: C

A **X** is an ionic compound consisting of $[Cr(H_2O)_6]^{3+}$ and Cl^- ions. **True; since all chlorine can be precipitated, it implies all chlorine exists as free Cl- ions in the aqueous solution.**

B **Y** is an ionic compound consisting of $[Cr(Cl)_2(H_2O)_4]^+$ and Cl^- ions. **True; since only 1/3 of the chlorine can be precipitated, it implies 2/3 of the chlorine are bonded to the Cr in the complex ion.**

C Oxidation number of Cr in **X** is +3 while the oxidation number of Cr in **Y** is +1. **False; Oxidation number of Cr in both X and Y is +3.**

D Oxidation number of Cr in **X** and **Y** remains unchanged during precipitation of AgC*l*; **True; precipitation is not a redox reaction.**

Catholic Junior College
JC2 Preliminary Examinations
Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY
9729/02

Paper 2 Structured Questions

18 August 2017

2 hours

Candidates answer on the Question Paper.

Additional Materials: 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.

Answer **all** questions in the spaces provided on the Question Paper.
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.

For Examiner's Use			
Paper 1			30
Paper 2	**Q 1**	12	
	Q 2	19	
	Q 3	18	
	Q 4	9	
	Q 5	10	
	Q 6	7	75
Paper 3	**Q 1**	22	
	Q 2	20	
	Q 3	18	
	Q 4	20	
	Q 5	20	80
Total			185

Suggested Solutions

This document consists of **14** printed pages.

[Turn over

1 Sedimentary rocks formed at the earth's surface by the accumulation of particulate matter are usually transported to the place of deposition by water, wind, or mass movement of glaciers. Dolostone, a sedimentary rock, consists of a mixture of minerals such as calcium and magnesium carbonates.

Table 1.1 below shows some properties of calcium carbonate and magnesium carbonate.

	Numerical values of K_{sp} at 25 °C	Decomposition temperature / ˚C
calcium carbonate	5.0×10^{-9}	900
magnesium carbonate	1.0×10^{-5}	540

Table 1.1

(a) **(i)** Write an expression for the solubility product, K_{sp}, of calcium carbonate.

$K_{sp} = [Ca^{2+}]\ [CO_3^{2-}]$

.... [1]

(ii) Calculate the solubility, in mol dm^{-3}, of calcium carbonate in water at 25 °C.

Let solubility of $CaCO_3$ be x
$[Ca^{2+}] = [CO_3^{2-}] = x$
$K_{sp} = [Ca^{2+}][CO_3^{2-}]$
$x^2 = 5.0 \times 10^{-9}$
$x = \underline{7.07 \times 10^{-5}\ mol\ dm^{-3}}$

[1]

(iii) A saturated solution **X** containing calcium hydroxide and calcium carbonate has a pH of 13 at 25 °C.

Given that the K_{sp} of calcium hydroxide is 5.5×10^{-6} mol^3 dm^{-9} and using your answer in **(a)(i)**, calculate the solubility of calcium carbonate in solution **X**.

pOH = 14 - 13
$[OH^-] = 10^{-(14-13)} = 0.100\ mol\ dm^{-3}$
$[Ca^{2+}][OH^-]^2 = 5.5 \times 10^{-6}$
$[Ca^{2+}] = 5.5 \times 10^{-4}\ mol\ dm^{-3}$
$[Ca^{2+}][CO_3^{2-}] = 5.0 \times 10^{-9}$
$[CO_3^{2-}] = 5.0 \times 10^{-9} / 5.5 \times 10^{-4}$
$[CO_3^{2-}] = 9.09 \times 10^{-6}\ mol\ dm^{-3}$
Since mol $CaCO_3$ dissolved ≡ CO_3^{2-} in saturated solution
Solubility of $CaCO_3$= = $\underline{9.09 \times 10^{-6}\ mol\ dm^{-3}}$

[2]

(iv) Comment on, and explain, the discrepancy in the solubilities of calcium carbonate in water and in solution **X**.

Solubility of calcium carbonate in solution X is lower . Presence of common ion, Ca^{2+}, shifts position of equilibrium (1) to the left by Le Chatelier's Principle.

....[2]

$CaCO_3\,(s) \rightleftharpoons Ca^{2+}\,(aq) + CO_3^{2-}\,(aq)$ ---------(1)

(v) When rainwater runs over dolostone, a chemical reaction occurs as shown below:

$$\mathbf{M}CO_3(s) + CO_2(aq) + H_2O(l) \rightleftharpoons 2HCO_3^-(aq) + \mathbf{M}^{2+}(aq)$$

where **M** is a group 2 metal

I. Suggest the source of CO_2 (aq) for the reaction.

Air containing CO_2 that is dissolved in the rainwater. [1]

II. When a sample of saturated solution of $Ca(HCO_3)_2$ is heated, a reaction occurs and a precipitate is formed. Using the equation above, suggest why this happens.

Boiling causes CO_2 to be released from the solution. Based on Le Chatelier's Principle, position of equilibrium of above equation shifts left, which results in the precipitation of $CaCO_3$ (s).

....[2]

(b) Calcium carbonate can be decomposed by heating at high temperatures.

(i) Write an equation for the thermal decomposition of calcium carbonate.

$CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)$ [1]

(ii) Calcium carbonate decomposes at a higher temperature than magnesium carbonate. Explain why this is so.

Ca^{2+} has a larger ionic size than Mg^{2+}, thus charge density of Ca^{2+} is lower, leading to lower polarising power of the cation Ca^{2+} compared to Mg^{2+}. As a result, the CO_3^{2-} ion is polarised (or distorted) to a smaller extent and the C-O bond is weakened to a larger extent. Hence, decomposition of the $CaCO_3$ occurs with greater difficulty and at higher temperature compared to $MgCO_3$. [2]

[Total: 12]

2 **(a)** Table 2.1 gives data about some physical properties of the elements calcium and copper.

physical property	calcium	copper
relative atomic mass	40.1	63.5
atomic radius (metallic) / nm	0.197	0.128
ionic radius (2+) / nm	0.099	0.069
melting point / °C	839	1085
boiling point / °C	1484	2562

Table 2.1

(i) Explain why the atomic radius of copper is smaller than that of calcium.

$_{29}$Cu: [Ar] $3d^{10}$ $4s^1$ $_{20}$Ca:[Ar] $4s^2$

Copper has more protons and hence higher nuclear charge than calcium. Since the 3d electrons in copper provide poor shielding, the shielding effect is similar. Hence, the atomic radius of copper is smaller than that of calcium. [2]

(ii) Explain why copper has a higher melting point than calcium.

Copper has more electrons available for delocalisation (3d and 4s electrons) than calcium (only 4s electrons). In copper, the metal cation has a smaller ionic radius (or higher charge density) than in calcium. Hence there is stronger metallic bonding between the metal cations and 'sea' of delocalised electrons, and more energy required to break. [2]

(iii) Apart from the properties given in Table 2.1, state clearly the difference in one other physical property between copper and calcium.

Copper has higher density than calcium.
Or
Copper has higher electrical conductivity than calcium. [1]

(b) Copper, scandium and zinc are d-block elements. However, copper is a transition element while scandium and zinc are not.

(i) Define the term *transition element*.

A transition element is a d-block element which forms one or more stable ions with partially filled d subshells. [1]

(ii) Explain why scandium is not classified as a transition element.

Sc is not a transition element as it only forms Sc^{3+} ion which has empty d subshell.

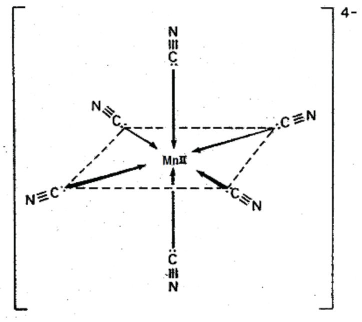
[1]

(c) Manganese is also a transition element and shows great tendency to form stable coloured complexes with ligands.

(i) Define the term *ligand*.

A ligand is an ion or molecule that has at least one lone pair of electrons available for donation to the central metal atom/ion. [1]

(ii) Draw the shape of the complex ion, $[Mn(CN)_6]^{4-}$.



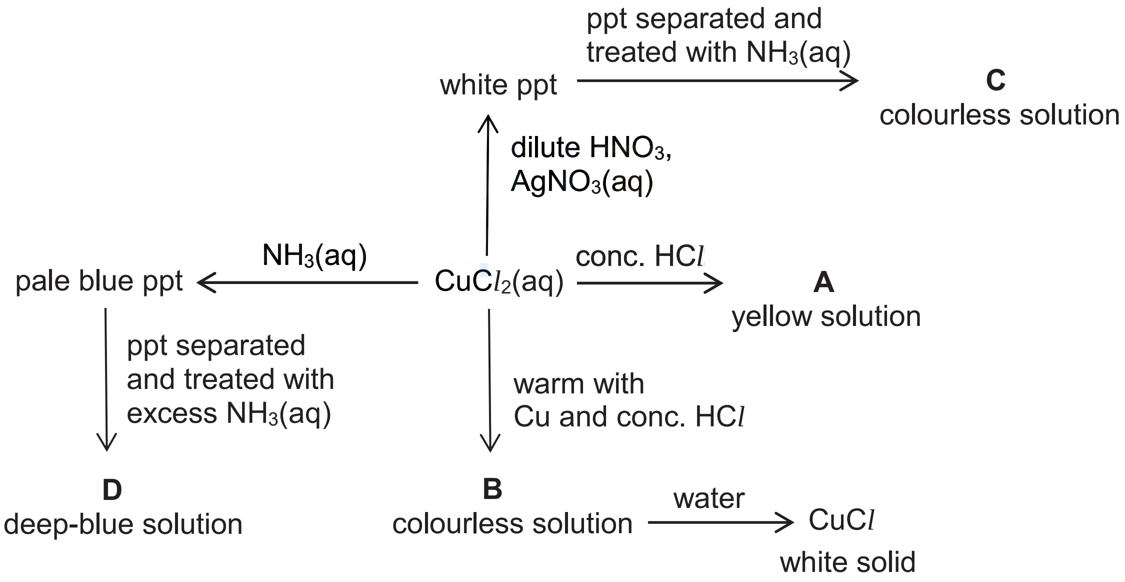
[2]

(d) Copper has more than one oxidation state and many of its compounds have colours in the blue-green-yellow part of the visible spectrum.

Write the *spdf* electronic configuration of copper(II) ions.

Cu^{2+} **$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$** [1]

(e) Aqueous copper(II) chloride, $CuCl_2$, is a blue solution which gives the following reactions.



Both **A** and **B** contain complex ions of copper and chlorine.

[Turn over

(i) State the formula of compound **C**.

$[Ag(NH_3)_2]Cl$ ....[1]

(ii) Suggest the formula and shape of the complex ion present in **D**.

Formula $[Cu(NH_3)_4]^{2+}$ / $[Cu(NH_3)_4(H_2O)_2]^{2+}$ .... [1]

Shape square planar / distorted octahedral .... [1]

(iii) What type of reaction occurs when **A** is formed from $CuCl_2(aq)$?

Ligand exchange / ligand displacement .... [1]

(iv) Explain why **A** is yellow in colour.

In the presence of Cl^- ligands, the partially filled degenerate d orbitals of Cu^{2+} ions split into two groups of non-degenerate d orbitals with a small energy gap. When exposed to visible light, d electron absorb energy in the violet region and is promoted to a higher energy d* orbital from a lower energy d orbital. This process is called *d-d** *electronic transition* . The complementary colour i.e. yellow is not absorbed and thus seen as the colour of the complex. [3]

(v) Explain why **B** is colourless.

Cu^+ in B has a fully filled d subshell (d^{10} configuration).

No d-d* electronic transition is possible.

..................[1]

[Total: 19]

3 Industrially, ethanol, CH_3CH_2OH, is manufactured by reacting ethene with steam in the presence of a catalyst. The reaction is reversible and the equation is as follows:

$$CH_2{=}CH_2(g) + H_2O(g) \rightleftharpoons CH_3CH_2OH(g)$$

At equilibrium, only 5 % of the ethene is converted into ethanol. To increase the overall yield of ethanol, ethanol is regularly removed from the equilibrium mixture as it is formed and more ethene is added into the reaction mixture. The volume of steam is not increased as this may disable the catalyst.

(a) Apart from the methods mentioned above, suggest one other method which will increase the conversion of ethene into ethanol. Explain your answer briefly.

By Le Chatelier's Principle, **increasing the pressure** will shift the position of equilibrium to favour the production of **fewer number of moles of gas molecules**. Hence the equilibrium shifts forward and more ethanol is produced. [2]

Alcoholic beverages can contain up to 40 % of ethanol. Excessive consumption of ethanol depresses the activity of the central nervous system. The blood alcohol concentration (BAC) is a good measure of the extent to which the activity of the central nervous system is depressed. It is usually defined as follows

BAC = mg of ethanol per 100 cm^3 of blood

Ethanol is sufficiently volatile to pass from the blood into the air in the lungs and the following equilibrium is set up:

$$CH_3CH_2OH(blood) \rightleftharpoons CH_3CH_2OH(g)$$

(b) **(i)** Suggest an expression for K_c for the equilibrium of ethanol between the blood and the air in the lungs.

$$K_c = \frac{[C_2H_5OH_{(g)}]}{[C_2H_5OH_{(blood)}]}$$

State symbols are required in the K_c expression to distinguish between ethanol in blood and ethanol in one's breath.

[1]

(ii) Using your answer to **(b)(i)** and given that the equilibrium constant, K_c, for this process is 4.35×10^{-4}, calculate the breath alcohol concentration (in mg of ethanol / 100 cm^3 of air) which corresponds to the 80 mg / 100 cm^3 of blood legal limit for BAC.

$[C_2H_5OH\ (g)] = 4.35 \times 10^{-4} \times 80 = 0.0348$ mg/ 100 cm^3 of air

[1]

(iii) Hence determine the legal limit of breath alcohol concentration in mol dm^{-3}.

[C_2H_5OH (g)] in g/ 100cm^3 = 3.48 x 10^{-5} g / 100 cm^3 of air
[C_2H_5OH (g)] in g/ dm^3 = 3.48 x 10^{-4} g / dm^3 of air

$$[C_2H_5OH\ (g)]\ \text{in mol/ dm}^3 = \frac{3.48 \times 10^{-4}}{46.0} = 7.56 \times 10^{-6}\ \text{mol dm}^{-3}$$

[2]

(c) The handheld breathalyser contains an electrochemical cell in which ethanol is oxidised. At one electrode, atmospheric oxygen is reduced to water and the other electrode ethanol is oxidised to ethanoic acid. The electric current produced gives an approximation of the overall blood alcohol concentration (BAC).

Give the half–equation for each electrode reaction and hence give the overall equation showing the oxidation of ethanol.

anode: $CH_3CH_2OH(g) + H_2O(l) \rightarrow CH_3CO_2H(l) + 4H^+(aq) + 4e^-$

cathode, atmospheric oxygen is reduced:

$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

The overall reaction is the oxidation of ethanol to ethanoic acid and water.

$CH_3CH_2OH(l) + O_2(g) \rightarrow CH_3CO_2H(aq) + H_2O(l)$

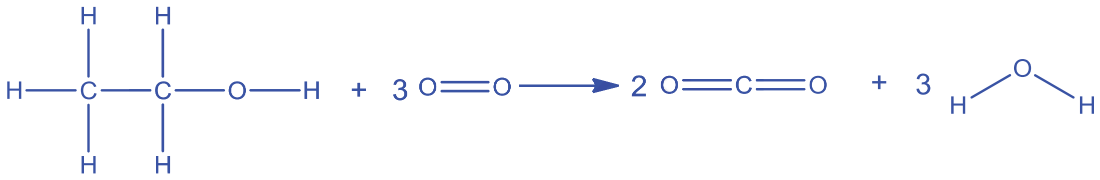
[2]

(d) Ethanol can be burned in excess oxygen as fuel. Complete combustion of ethanol releases 1367 kJ mol^{-1} of heat energy.

(i) Write an equation to show the standard enthalpy change of combustion of ethanol.

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ [1]

(ii) Use the bond energies given in the *Data Booklet* to calculate another value for the standard enthalpy change of combustion of ethanol.



Bonds broken	kJ mol^{-1}	Bonds formed	kJ mol^{-1}
5(C-H)	5(410)	4(C=O)	-4(805)
1(C-C)	(350)	6(O-H)	-6(460)
1(C-O)	(360)		
1(O-H)	(460)		
3(O=O)	3(496)		
Total:	+4708	Total:	-5980

Enthalpy change = +4708 – 5980 = -1272 kJ mol^{-1} = -1270 kJ mol^{-1} (3 sf)

[3]

(iii) Suggest a reason for the discrepancy between this value and that quoted in **(d)**.

The values in *the Data Booklet* were average values and hence the calculated value is an approximation.

OR [1]

Bond energies are based on calculations from reaction in the gas phase, but at standard state, ethanol and water are liquids.

(e) **(i)** The complete combustion of ethanoic acid, CH_3CO_2H, releases 873 kJ mol^{-1} of energy. Use this value and the enthalpy change of combustion of ethanol given in **(d)** to construct an energy cycle to calculate the enthalpy change when 1.0 mol of ethanol in the body is oxidised to ethanoic acid and water only.

$$\begin{tikzcd}
C_2H_5OH + O_2 \arrow[rr, "\Delta H_{reaction}"] \arrow[dr, "\Delta H_c \text{ of } C_2H_5OH = -1367 \text{ kJ mol}^{-1}"'] & & CH_3CO_2H + H_2O \arrow[dl, "\boldsymbol{\Delta H_c} \textbf{ of } \boldsymbol{CH_3CO_2H = -873} \textbf{ kJ mol}^{\boldsymbol{-1}}"] \\
& 2CO_2 + 3H_2O &
\end{tikzcd}$$

Using Hess' Law,
$\Delta H_{reaction} + \Delta H_c$ of $CH_3CO_2H = \Delta H_c$ of C_2H_5OH

$\Delta H_{reaction} = -1367 - (-873) = -494$ kJ mol^{-1}

[3]

(ii) The metabolism of ethanol in the human body leads to partial oxidation which releases 770 kJ mol^{-1} of energy. Assuming that ethanol is oxidised to ethanoic acid and carbon dioxide only, use your answer to **(e)(i)** and any other relevant data to calculate the proportion of ethanol metabolised to ethanoic acid and to carbon dioxide respectively.

Energy released when 1 mole of ethanol is oxidised to CO_2 and CH_3CO_2H = 770 kJ
Let % of ethanol oxidised to CH_3CO_2H be x
% of ethanol oxidised to CO_2 = 100 –x

$$770 \text{ kJ} = \frac{x}{100} \times \Delta H_{reaction} \text{ (answer in } \mathbf{(e)}\text{(i))} + \frac{100-x}{100} \times \Delta H_c \text{ of } C_2H_5OH$$

$$770000 = 494x + (100-x)(1367)$$

$$x = 68.4\%$$

Proportion of ethanol metabolized to CO_2 is 31.6% while proportion of ethanol metabolised to CH_3COOH is 68.4%

[2]

[Total: 18]

[Turn over

4 **(a)** Aerosol spray is a type of dispensing system which creates an aerosol mist of liquid particles. This is used with a can that contains a product and propellant under pressure. Hair spray is a common example of an aerosol spray where butane is often used as the propellant.

(i) A typical can of hair spray has a volume of 300 ml and 70 % of which is the hair product. Given that the can has an internal pressure of 100 psi, at 27 °C, calculate the maximum amount of butane present in the can. (1 psi = 6894.76 Pa)

pV = nRT

$(100 \times 6894.76)(300 \times 10^{-6} \times 30\%) = n(8.31)(273 + 27)$

n = 0.0249 mol of butane

[2]

(ii) The can of hair spray is used such that only the propellant, butane gas, remained and the internal pressure of the can decreased to 20 psi. If the can is left in a car that reaches 50 °C on a hot afternoon, what is the new pressure in the can?

Since V is constant

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\frac{20}{273 + 27} = \frac{P_2}{273 + 50}$$

P_2 = 21.5 psi or 148 kPa

[1]

(iii) As a safety precaution, the propellant has to be completely expelled from the can prior to disposal and subsequent incineration. Using concepts from the Ideal Gas Law, explain qualitatively, why this precaution is necessary.

As the can will be incinerated, it will be subjected to high temperatures. Given that volume of the can is constant, pressure of butane increases when temperature increases.

....[1]

(b) In 1873, Johannes D. van der Waals, a physicist proposed a modification to the ideal gas equation to better model real gas behaviour. The new equation, usually referred to as the van der Waals equation, has the following expression.

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

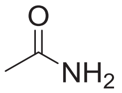
P is the observed pressure exerted by the gas.
V is the volume of the container in which the gas is contained.
The constants a and b have positive values and are characteristic of a gas.

Suggest why the term $\frac{an^2}{V^2}$ is **added** to P and the term nb is **subtracted** from V respectively.

$P + \frac{an^2}{V^2}$: **Real gas particles have significant forces of attraction, the pressure exerted by a real gas is smaller than expected for an ideal gas. Thus, a term is added to P.** [1]

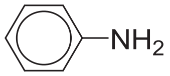
$V - nb$: **As real gas particles have a significant volume compared to the volume of the container, the volume of space in which the gas particles can move about is smaller than that of the container. Thus a term is subtracted** [1] **from V.**

(c) Arrange the following three compounds in increasing order of basicity.



ethanamide

ethylamine



phenylamine

Order of basicity:

ethanamide < phenylamine < ethylamine

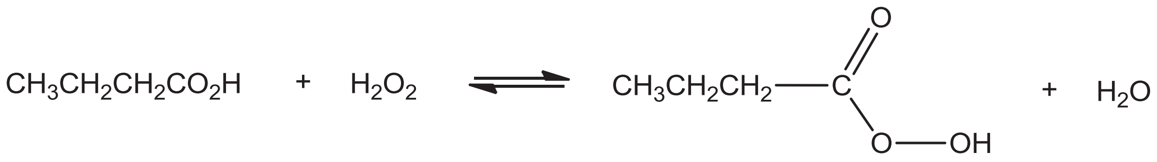
Explain your answer.

Ethanamide is an amide and the lone pair of electrons on N is delocalised into the π bond of C=O, thus it is not available to accept H^+, making ethanamide neutral and less basic than phenylamine and ethylamine. Ethylamine is more basic than phenylamine as it has an electron-donating ethyl group. Thus the lone pair of electrons on N is more available to accept H^+ compared to phenylamine.

OR Ethylamine is the most basic. Phenylamine is less basic than ethylamine due to the lone pair of electrons on N being delocalised into the benzene ring. [3] **Thus, the lone pair of electron is less available to accept H^+. Ethanamide is neutral (least basic among the three) as lone pair of electrons on N is delocalised into the π bond of C=O, thus it is not available to accept H^+.**

[Total: 9]

5 **(a)** Butaneperoxoic acid, a type of peroxyacid, is produced when butanoic acid reacts with hydrogen peroxide.



butanoic acid

butaneperoxoic acid
$C_4H_8O_3$

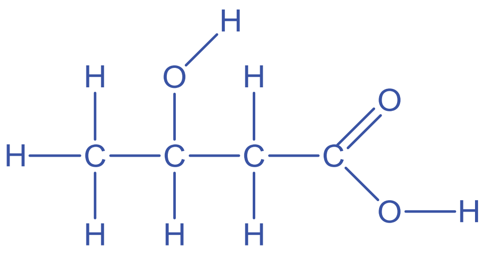
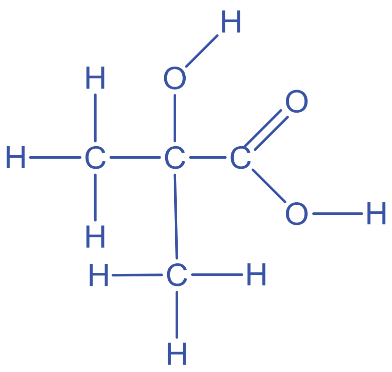
(i) Identify the type of hybridisation involved for the C atom of O=C-O in butaneperoxoic acid and hence state its bond angle.

Hybridisation of C ..sp^2......................................

Bond angle ..120°...................................... [2]

(ii) Non-cyclic compounds **A** and **B** are functional group isomers of butaneperoxoic acid. 1 mole of hydrogen gas is produced when 1 mole of **A** and 1 mole of **B** are reacted with Na metal separately. **A** produces yellow precipitate when reacted with aqueous alkaline iodine while **B** does not. When reacted with hot acidified $K_2Cr_2O_7$, orange $K_2Cr_2O_7$ turns green in the presence of **A** but not **B**.

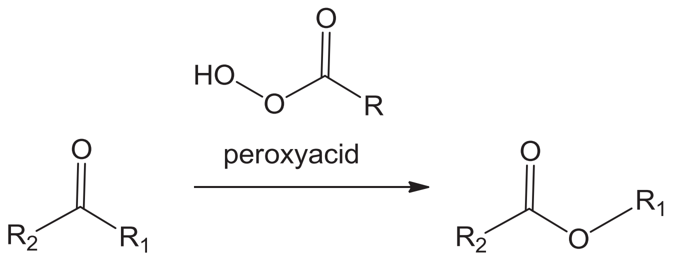
Draw the displayed formula of **A** and **B**, hence state the specific type of isomerism between **A** and **B**.

 Compound **A**	 Compound **B**

[2]

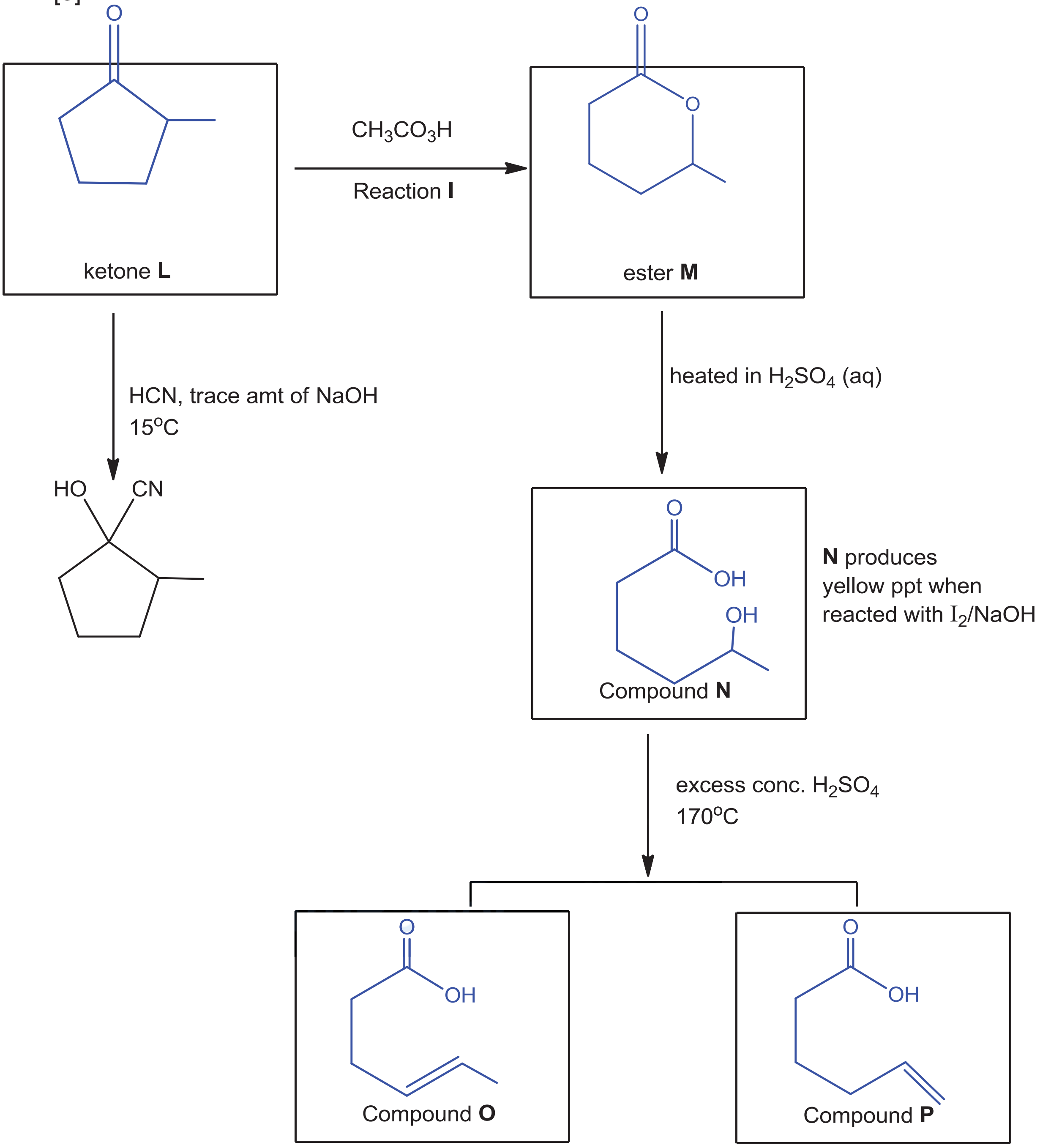
Type of isomerism between **A** and **B** .....Chain isomerism..................... [1]

(b) The Baeyer-Villiger oxidation is an organic reaction that converts ketones into esters using peroxyacids.



In the following reaction scheme, reaction **I** is a Baeyer-Villiger oxidation. Give the structural formulae of compounds **L**, **M**, **N**, **O** and **P**.

[5]



N produces yellow ppt when reacted with I_2/NaOH

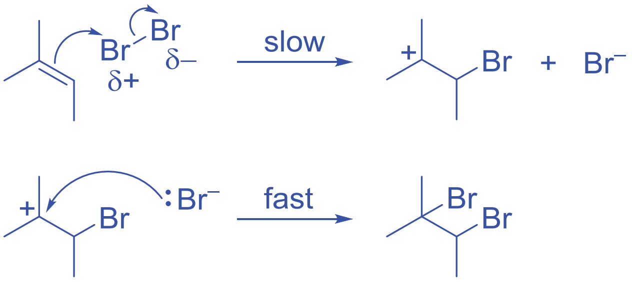
Both Compounds **O** and **P** decolourise aqueous bromine

[Total: 10]

6 2-methylbut-2-ene is reacted with bromine in an inert solvent in the absence of light.

(a) Describe the mechanism for the above reaction.

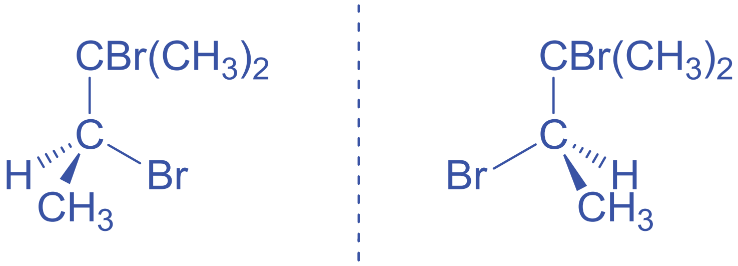
Electrophilic addition



[3]

(b) State the type of isomerism exhibited by the organic product(s) formed in the above reaction, and hence, draw the structures of the isomers.

Enantiomerism [1]



[1]

(ii) It was found that the product(s) formed from **(a)** do not rotate plane of polarised light. Using the mechanism drawn in **(a)**, suggest why this is so.

Since the C in the C=C is sp^2 hybridised and thus has a trigonal planar shape about C, the δ+ Br electrophile has a 50% chance to attack the electron rich C from either side of the plane, resulting in racemic mixture. Thus the products do not rotate plane of polarised light. [2]

[Total: 7]

Catholic Junior College

JC2 Preliminary Examinations

Higher 2

CHEMISTRY 9729/03

Paper 3 Free Response **25 August 2017**

Candidates answer on separate paper. **2 hours**

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.

Suggested Solutions

[Turn over

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]

$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

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

mol of excess $Cr_2O_7^{2-}$ = $\frac{1}{6} \times$ mol of Fe^{2+} used in titration

$= \frac{1}{6} \times 0.118 \times \frac{12.25}{1000}$

$= 2.41 \times 10^{-4}$ mol

mol of $Cr_2O_7^{2-}$ added initially = cV = $0.156 \times \frac{25.0}{1000}$

$= 3.90 \times 10^{-3}$ mol

mol of $Cr_2O_7^{2-}$ that react with CH_3CH_2OH = $(3.90 \times 10^{-3}) - (2.41 \times 10^{-4})$

$= 3.66 \times 10^{-3}$ mol

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

mol of CH_3CH_2OH in 25.0 cm^3 of diluted soln = $\frac{3}{2} \times$ mol of $Cr_2O_7^{2-}$ reacted

$= \frac{3}{2} \times 3.66 \times 10^{-3}$

$= 5.49 \times 10^{-3}$ mol

mol of CH_3CH_2OH in 250 cm^3 of diluted soln = $\frac{250}{25.0} \times 5.49 \times 10^{-3}$

= 0.0549 mol

Since 10.0 cm^3 of the sample of spirit was diluted to 250 cm^3,

$\therefore$ mol of CH_3CH_2OH in 10.0 cm^3 of spirit = 0.0549 mol

$\Rightarrow$ [CH_3CH_2OH] in the brand of spirit = $\frac{1000}{10.0} \times 0.0549$

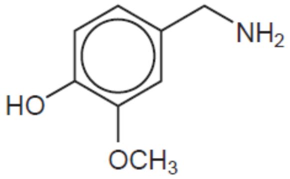
= 5.49 mol dm^{-3}

(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.

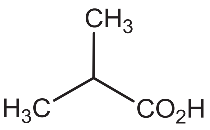
(i) What observations and deductions could be made from the reaction of **A**, **C** and **D** with aqueous sodium carbonate? [2]

effervescence of CO_2 ; A, C and D are acidic/contains $–CO_2H$ group.

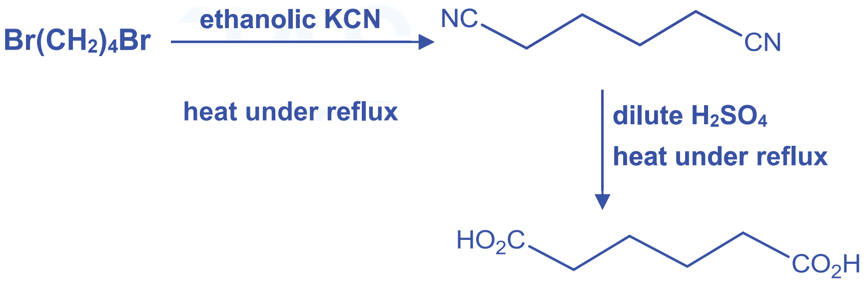
(ii) Draw the structural formula of **D** and state the reagents and conditions required for its preparation from $(CH_3)_2CHCH_2OH$. [2]

$K_2Cr_2O_7$ + dil. H_2SO_4; heat under reflux

D is



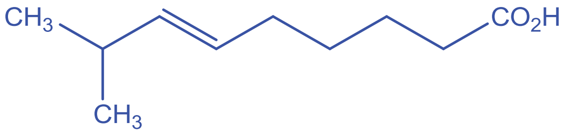
(iii) Show how compound **C** can be prepared from $Br(CH_2)_4Br$, stating clearly the reagents and conditions required for each step, and give the structural formulae of **C** and the intermediate formed. [4]



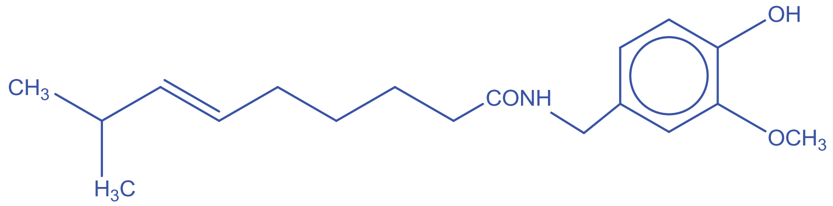
C

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

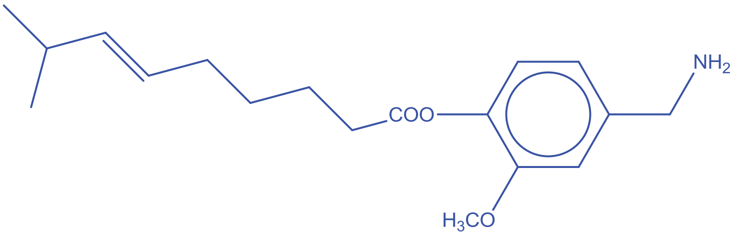
A is



capsaicin is



and



(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.

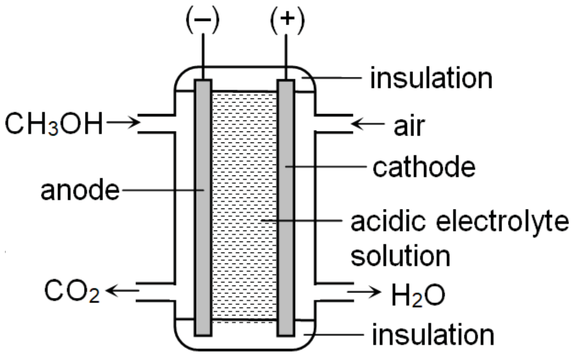


Fig. 1.1

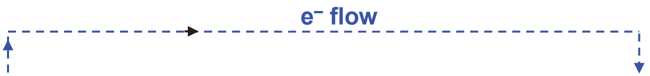
(i) Write balanced equations for the half reactions at each electrode and for the overall cell reaction. [2]

Cathode: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

Anode: $CH_3OH(l) + H_2O \rightarrow CO_2(g) + 6H^+ + 6e^-$

Overall reaction: $2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$

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



Pt(s) | $CH_3OH(l)/CO_2(g)$ // $O_2(g)/H_2O(l)$, $H^+(aq)$ | Pt(s)

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

In an acidic medium, $E^\ominus_{O_2/H_2O} = +1.23\text{ V}$

In an alkaline medium, $E^\ominus_{O_2/OH^-} = +0.40\text{ V}$

Acidic electrolyte is preferred because oxygen is a stronger oxidising agent in an acidic medium.

(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]

Using a film of solid H^+ ion-conducting polymer as electrolyte would eliminate the possibility of acid leakage from the fuel cell.

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

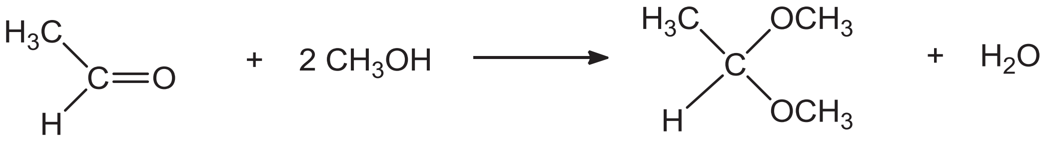
Suggest one advantage of the methanol fuel cell over such an internal combustion engine that uses methanol. [1]

In the methanol fuel cell, there is complete combustion of CH_3OH and so, no C nor CO (atmospheric pollutants) is produced.

[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

By inspection
Using experiments 1 and 2,
when [CH_3CHO] increased by 0.25/0.20 = 1.25 times and the concentration of other reactants remain constant, the relative rate increases by 1.25 times.
Order of reaction wrt ethanal = 1

II methanol and

By inspection
Using experiments 2 and 3,
when [CH_3OH] increased by 0.32/0.1 = 3.2 times and the concentration of other reactants remain constant, the relative rate increases by 4.00/1.25 = 3.2 times.
Order of reaction wrt ethanal = 1

III H^+.

[3]

By inspection
Using experiments 1 and 4,
when [CH_3CHO] is halved and [CH_3OH] is increased by 0.16/0.1 = 1.6 times, relative rate should be 0.8 since orders of reaction wrt ethanal and methanol are 1. However, the relative rate is 1.60 which means when the [H^+] is doubled, rate is doubled.
Order of reaction wrt H^+ = 1

Alternatively, mathematical method
Let n be the order of reaction wrt H^+
$\text{rate}_{\text{exp1}} = k[\text{ethanal}]_{\text{exp1}}[\text{methanol}]_{\text{exp1}}[H^+]^n$

$1.00 = k(0.20)(0.10)(0.05)^n$---- (1)
$\text{rate}_{exp2} = k[\text{ethanal}]_{exp2}[\text{methanol}]_{exp2}[H^+]^n$
$1.60 = k(0.10)(0.16)(0.10)^n$---- (2)
(2) ÷ (1)
$1.6 = (0.5)(1.6)(2)^n$
$n = 1$

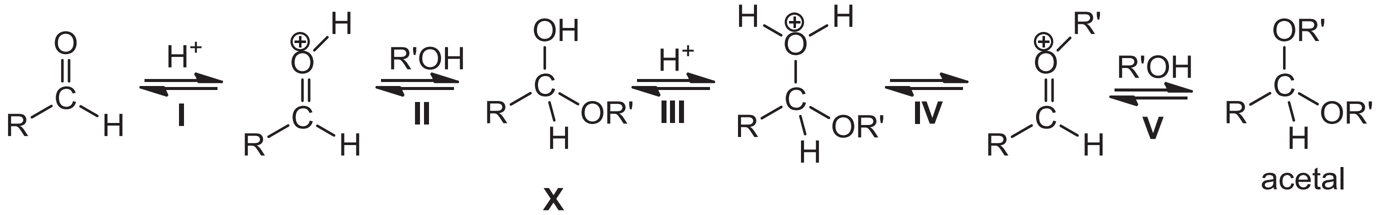
(ii) Use your results from **(a)(i)** to write the rate equation for the reaction. [1]

rate = $k[CH_3CHO][CH_3OH][H^+]$

(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]

rate will be 2 × 4 = 8 times as fast as reaction 1 (i.e. relative rate = 8)

(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]

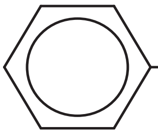
The protonation of the carbonyl group makes the carbonyl carbon more electron deficient (greater partial positive charge on carbonyl carbon) and thus more susceptible for the alcohol to attack.

(ii) Using your answer to **(a)(ii)**, state with reasons, which one is the rate-determining step of the reaction mechanism. [2]
Step II
Based on the rate equation, the slow step should involve 1 molecule of the carbonyl compound, 1 H^+ ion and 1 alcohol molecule

(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]
H^+ is a catalyst as H^+ is regenerated in steps II and V

X is an intermediate as it is being produced in step II but used in step III .

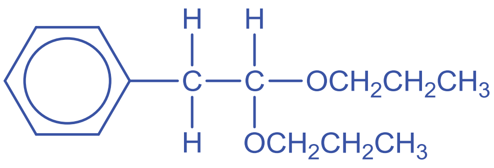
(c) Draw the structure of the acetal **B** formed from the reaction between phenylethananl and propan-1-ol.



$-CH_2CHO + 2\ CH_3CH_2CH_2OH \longrightarrow$ acetal **B** + H_2O

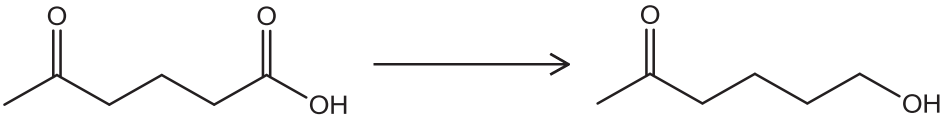
[1]

[Turn over

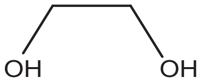


(d) Acetal formation is useful in organic synthesis. When an aldehyde or ketone is converted to an acetal, the carbonyl group is protected from attack by reagents such as bases and reducing agents. The acetal can later be hydrolysed by a strong acid to form the original aldehyde or ketone since the formation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

Suggest a suitable synthesis route for the following conversion

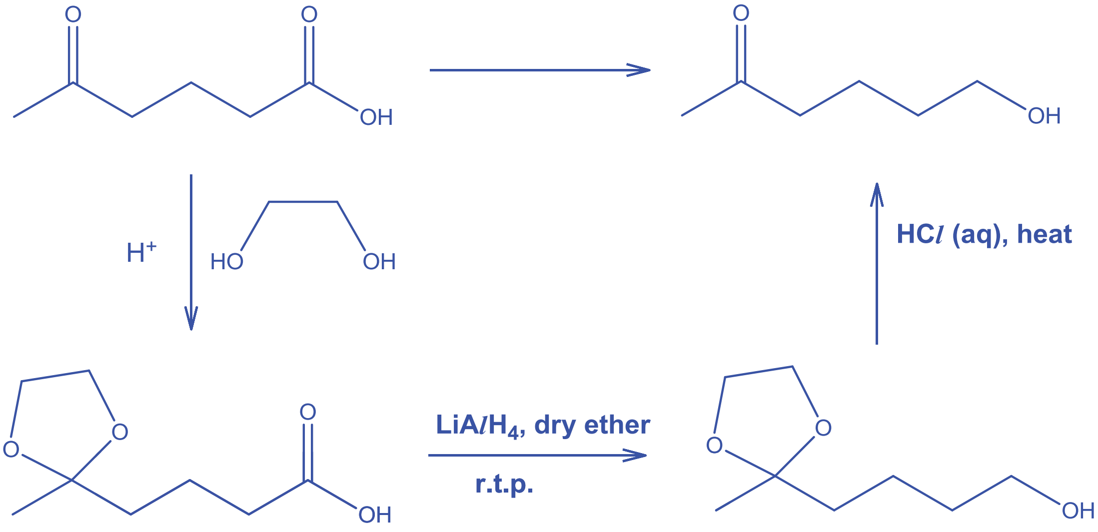


which involves the initial formation of an acetal group using ethane-1,2-diol,



.

[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

$\Delta S_c^\ominus$ $CH_3OH(l)$ = $S^\ominus_{products} - S^\ominus_{reactants}$

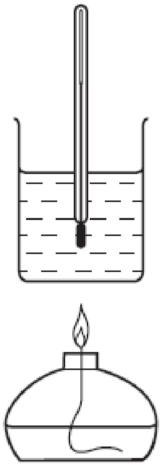
= 213.6 + 2 x 69.9 – (126.8 + 3/2 x 205)

= – 80.9 J K^{-1} mol^{-1}

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

The standard entropy change of combustion reaction has a negative sign. Since the amount of gaseous particles produced is less than the initial amount, there is a decrease in the number of ways to arrange the gaseous particles, giving rise to a decrease in disorder.

(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]

(Experimental) Heat absorbed by water = (150 – 50)(4.18)(48.2 – 25)

[Turn over

= 9697.6J

Theoretical heat evolved by combustion of methanol = 726 000 x $\frac{0.5}{32}$ = 11343J

% of heat evolved used to heat up the water = 9697.6 / 11343 x 100 = 85.5%

(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]

$\Delta G_c^o = \Delta H_c^o - T\Delta S_c^o$

$= -726 - (298)(-80.9/1000)$

$= -702$ kJmol^{-1}

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

$\Delta G = \Delta H - T\Delta S$

ΔH is negative while $-T\Delta S$ is positive. Increasing the temperature increases the magnitude of $-T\Delta S$ and ΔG becomes more positive.
Thus, reaction becomes less spontaneous .

[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]

$ClO^- + H_2O \rightleftharpoons HClO + OH^-$

(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]

Disproportionation reaction

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

+4 +1 +5

(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]

No. of moles of $S_2O_3^{2-}$ $= \frac{12.30}{1000} \times 0.001$

$= 1.23 \times 10^{-5}$ mol

Since $I_2 \equiv 2S_2O_3^{2-}$,

No. of moles of I_2 formed $= \frac{1}{2} \times 1.23 \times 10^{-5}$

$= 6.15 \times 10^{-6}$ mol

[Turn over

Since $Cl_2 \equiv I_2$,

$$\text{Concentration of } Cl_2 = \frac{1000}{250} \times 6.15 \times 10^{-6}$$

$$= 2.46 \times 10^{-5} \text{ mol dm}^{-3}$$

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

calcium chlorate(I) is a solid which makes it easier and safer to handle compared to chlorine gas.

or calcium chlorate(I) is more soluble in water than chlorine.

(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]

$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl$
[white ppt & white fumes observed]

$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$
[white fumes observed]

(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]

$AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$

$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H_3O^+$

pH 3

$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

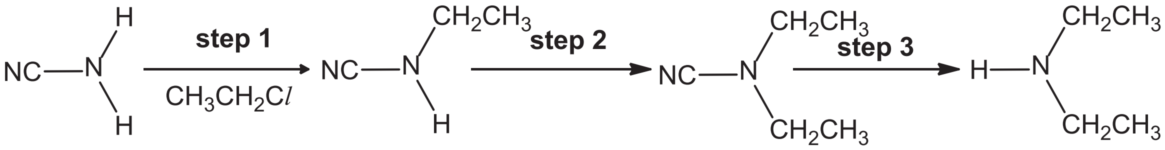
pH 1-2

(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.

$$N\equiv C-NH_2$$

cyanamide

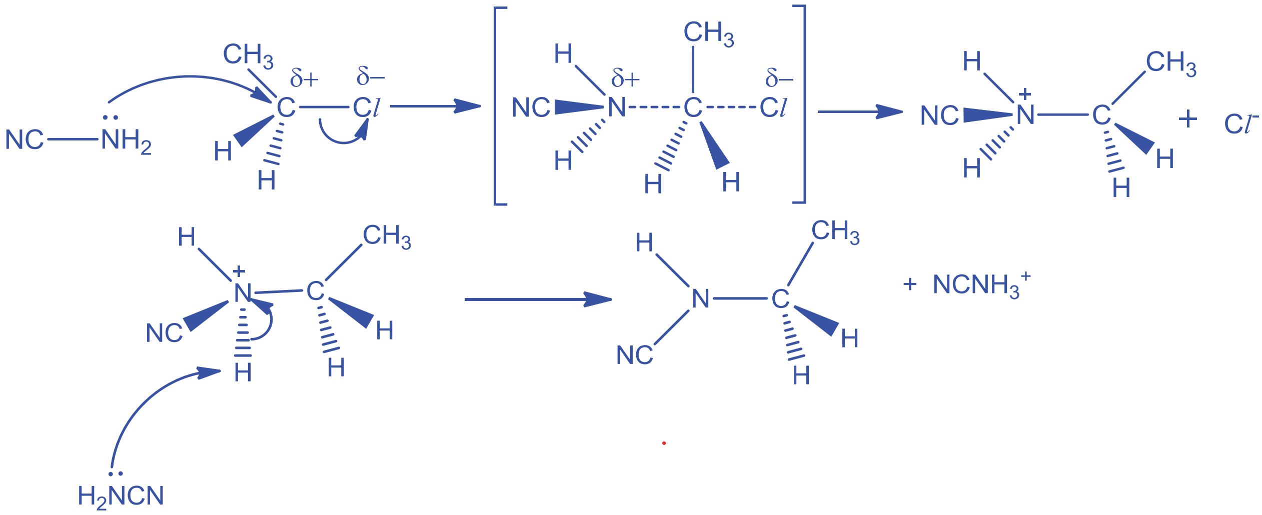
Cyanamide is a useful precursor for the synthesis of secondary amines with a relatively high yield. Below is the sequence of steps for the synthesis of N-ethylethylamine.



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]

Mechanism: Nucleophilic substitution reaction (S_N2)



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

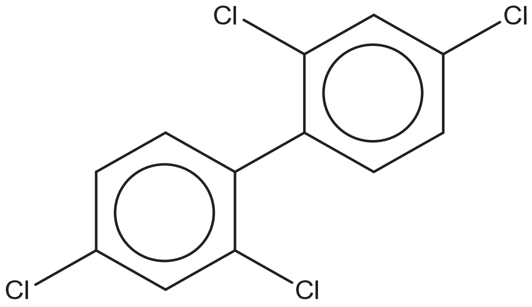
Nucleophile and Base

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

Excess CH_3CH_2Cl

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

[Turn over



2,2',4,4'-tetrachlorobiphenyl

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

The p-orbital of the chlorine atoms overlap with the π electron cloud system of the benzene rings. The lone pair of electrons on each C*l* atom is delocalised into the benzene rings. This results in the C–C*l* bond having a partial double-bond character which makes the C–C*l* bond stronger and less ready to undergo reaction.

The C of the C–C*l* bond also has a lower partial positive charge and is less susceptible to nucleophilic attacks.

The π-electron cloud of the benzene ring will repel the lone pair of electrons of an incoming nucleophile, rendering attack of the nucleophile difficult.

[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.

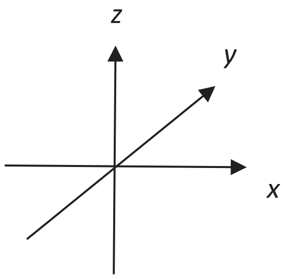
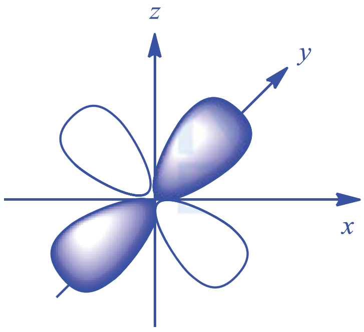
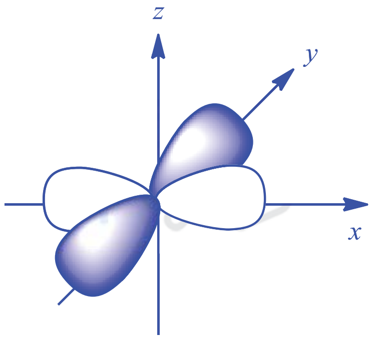


Fig. 4.1

[2]



lower d-orbital



upper d-orbital

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

During formation of an octahedral complex, the ligands would approach the central metal ion with partially filled d-subshell along the x, y and z axes.

As the ligands would approach the $d_{x^2-y^2}$ and d_{z^2} orbitals 'head-on' (along the x, y and z axes), the inter-electronic repulsion is stronger between the ligands and the d_{z^2} and $d_{x^2-y^2}$ orbitals.

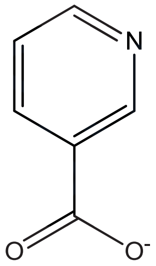
The ligands approach the d_{xy}, d_{xz} and d_{yz} orbitals between the orbital lobes (between the x, y and z axes). Hence the inter-electronic repulsion is not as strong between the ligands and the d_{xy}, d_{xz} and d_{yz} orbitals.

Hence the splitting of the degenerate d orbitals into two slightly different energy levels with a small energy gap will occur.

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

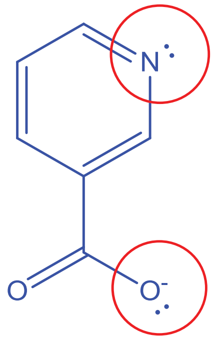
$[Cr(OH)_6]^{3-}$ complex has a different d-d* energy gap from $[Cr(NH_3)_6]^{3+}$ complex, hence visible light of different wavelength / frequency is absorbed during d-d* transition in both complexes.

(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]



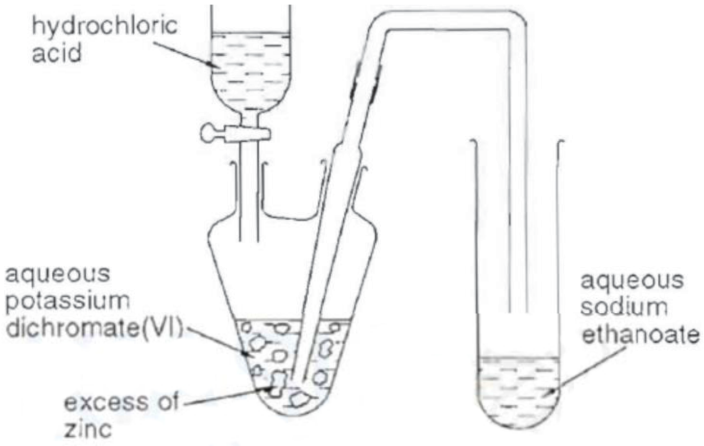
Presence of lone pairs of electrons on both N and O$^-$ which allows nicotinate ion to donate two lone pairs of electrons to form a stable 6-membered ring structure with the central Cr^{3+} ion.

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

0 / no charge

(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]

[Turn over

$Zn + 2HCl \rightarrow ZnCl_2 + H_2$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$(Zn \rightarrow Zn^{2+} + 2e^-) \times 3$

--

$Cr_2O_7^{2-} + 3Zn + 14H^+ \rightarrow 2Cr^{3+} + 3Zn^{2+} + 7H_2O$

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]

$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$ $E^\ominus = -0.41$ V (less negative)

$Zn^{2+} + 2e^- \rightleftharpoons Zn$ $E^\ominus = -0.76$ V

Since $E^\ominus_{Cr3+/Cr2+}$ is less negative than $E^\ominus_{Zn2+/Zn}$,

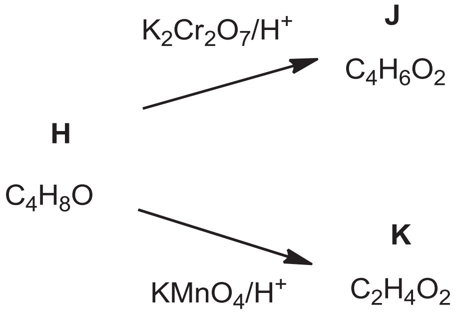
$E^\ominus_{cell} = -0.41 - (-0.76) = +0.35$ V > 0 (spontaneous reaction)

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]

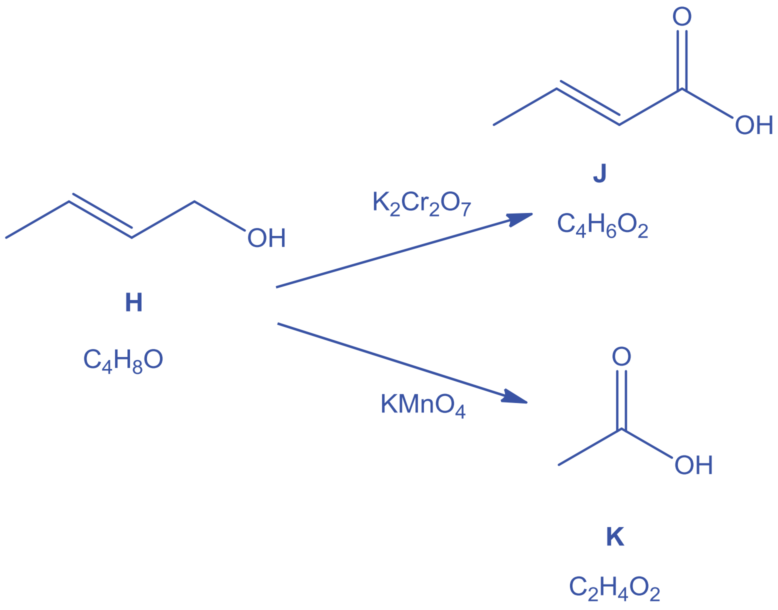
Build-up of pressure from the formation of H_2(g) caused liquid to be forced over.

(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.

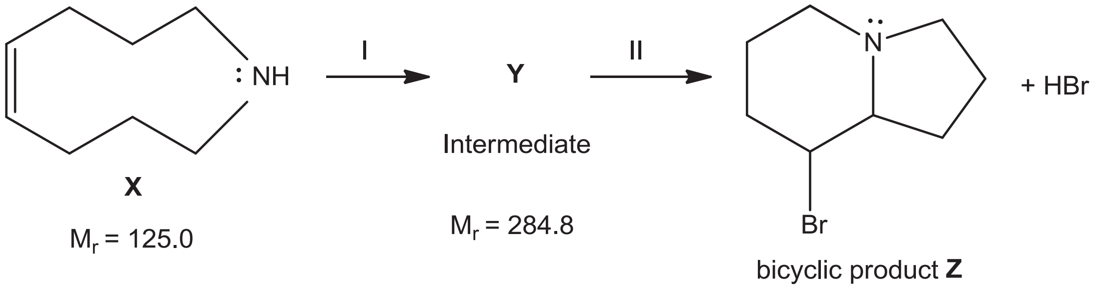


All three compounds, **H**, **J** and **K** react with sodium metal. **J** and **K** react with Na_2CO_3, but **H** does not. **H** and **J** decolourise aqueous bromine.

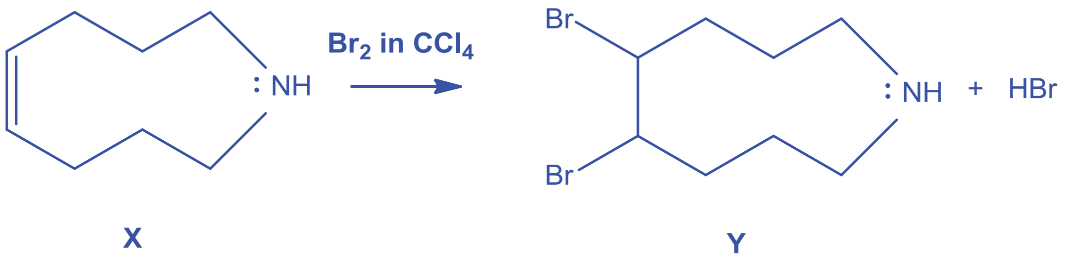
Suggest structures for **H**, **J** and **K**. [3]



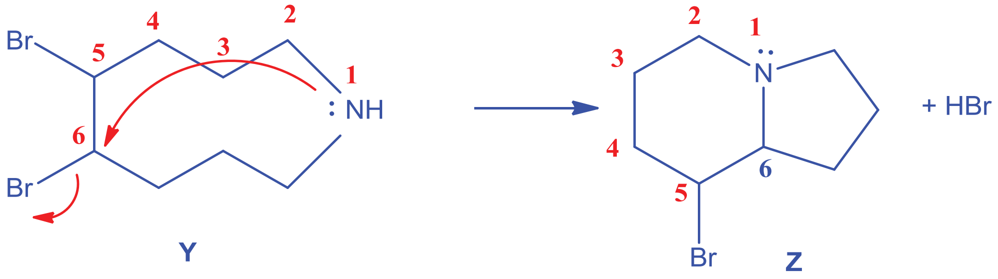
(e) The bicyclic product **Z** shown below can be formed from **X** in the following scheme:



(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]



intramolecular **nucleophilic substitution** occurs

[Total: 20]

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.

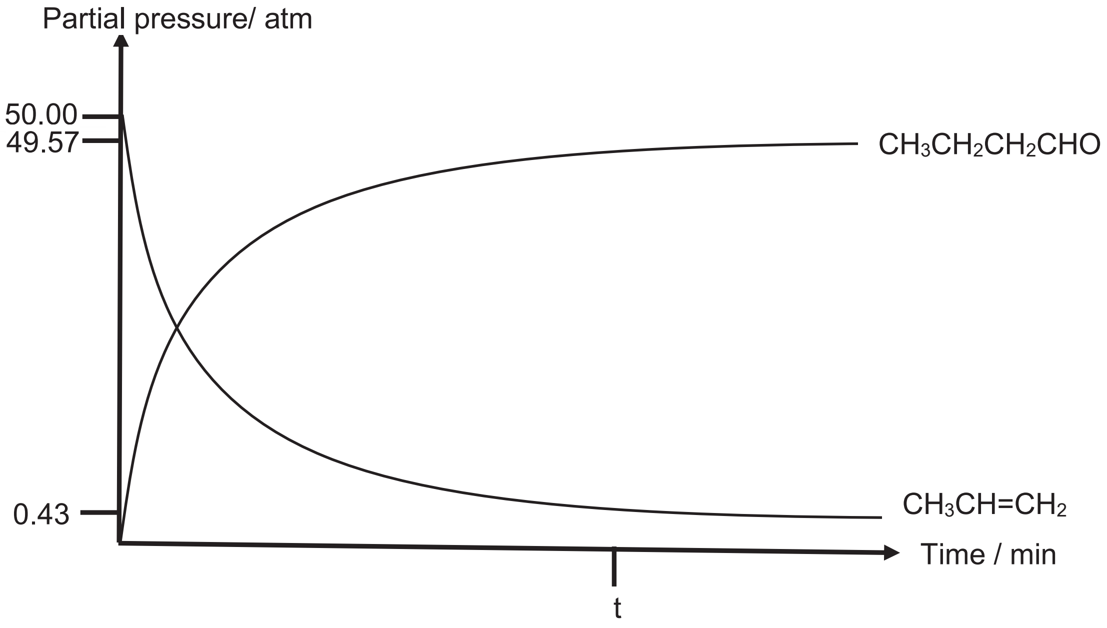


Figure 5.1

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

Dynamic equilibrium refers to a reversible reaction in which the rates of forward and reverse reactions have become equal and there is no change in the concentration of the reactants and the products.

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

$$K_p = \frac{P_{CH3CH2CH2CHO}}{(P_{CH3CH=CH2})(P_{CO})(P_{H2})}$$

[Turn over

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

	$CH_3CH{=}CH_2(g)$ +	$CO(g)$ +	$H_2(g)$	$\rightleftharpoons$	$CH_3CH_2CH_2CHO(g)$
Initial Partial Pressure/ atm	**50**	**50**	**50**		**0**
Change in partial pressure/ atm	**- 49.57**	**- 49.57**	**- 49.57**		**+ 49.57**
Equilibrium Partial Pressure/ atm	**0.43**	**0.43**	**0.43**		**49.57**

$$K_p = \frac{49.57}{(0.43)(0.43)(0.43)} = 623.46 \text{ atm}^{-2}$$

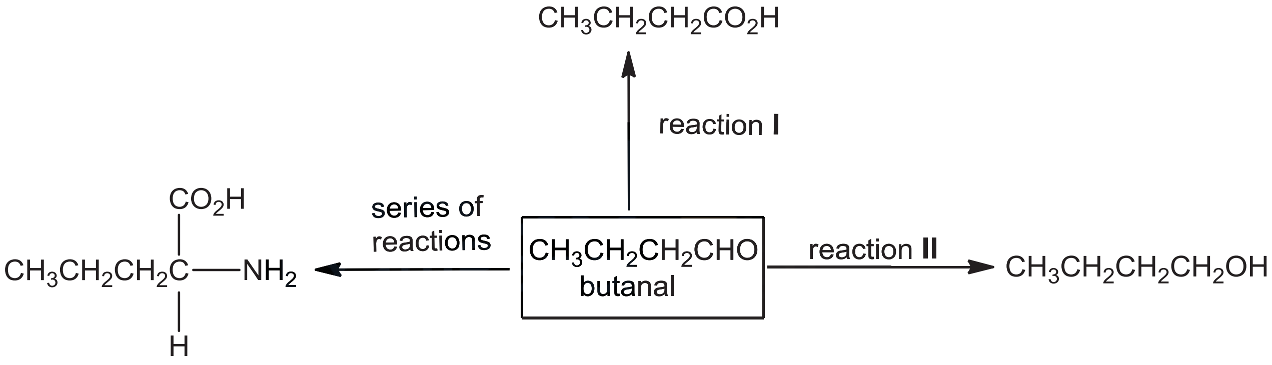
$$= 623 \text{ atm}^{-2}$$

(iv) State 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]

The gradients of the graphs will be steeper Or the equilibrium will be established at a shorter time (before time t).

The equilibrium partial pressure of $CH_3CH_2CH_2CHO$ would decrease while the equilibrium partial pressure of $CH_3CH{=}CH_2$ will increase.

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



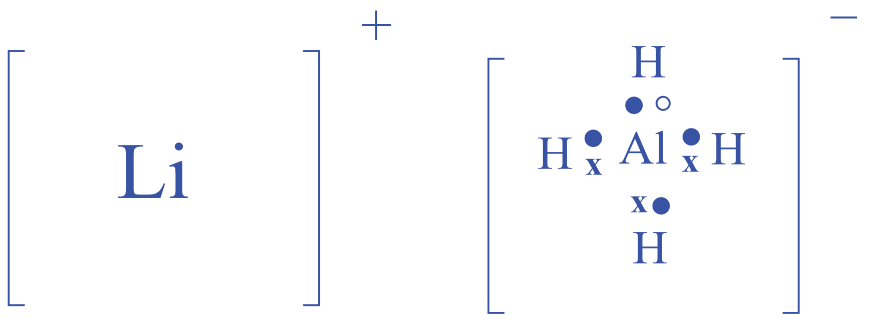
Compound **X**

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

Butanoic acid <u>is more soluble</u> than butanal. Butanoic acid molecules contains both electron deficient H atoms as well as highly electronegative O atoms with lone pair of electrons, therefore they are able to <u>form more extensive hydrogen bonds with water molecules on average</u> as compared to butanal molecules which only contains highly electronegative O atoms with lone pair of electrons.

(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.

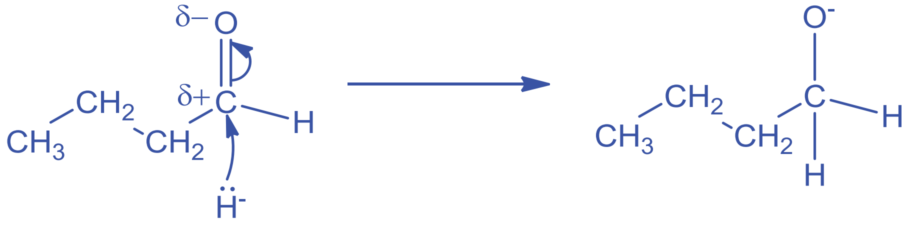
(i) Given that $LiAlH_4$ exist as $Li^+[AlH_4]^-$, draw the dot-and-cross diagram for $LiAlH_4$. [1]



(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]

The size of Al atom is larger compared to B and the orbital overlap of Al and H is less effective. Thus the <u>bond length of Al–H bond is longer than that of B–H bond</u> and less energy is required to break the <u>weaker Al–H bond</u>, resulting in a greater ease of generating the H^- nucleophile. Or There <u>is greater electronegativity difference</u> between Al and H than B and H, therefore the tendency of forming H^- is higher in $LiAlH_4$ than $NaBH_4$.

[Turn over

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

The electron rich C=C will not attract the H^- nucleophiles.

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

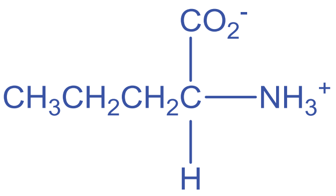
The rate of reaction will be slower with butanone.

In butanone, there are two electron-donating alkyl groups directly attached to the carbonyl carbon. Hence the partial positive charge on the carbonyl carbon in butanone is less pronounced than that in butanal which only has 1 alkyl group.

Or

The presence of 2 alkyl groups in butanone contributes to greater steric hindrance.

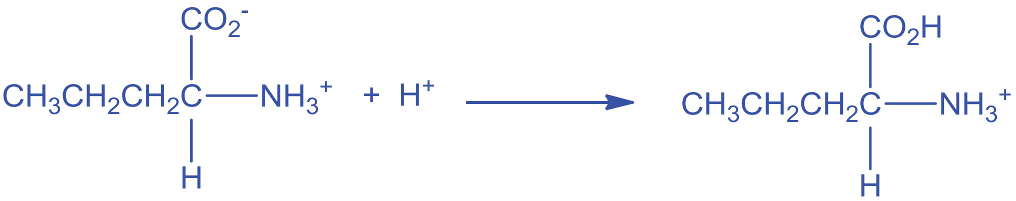
(d) Draw the structure of the predominant form produced when compound **X** is in an aqueous solution of pH 7. [1]



$$CH_3CH_2CH_2\overset{CO_2^-}{\underset{H}{C}}-NH_3^+$$

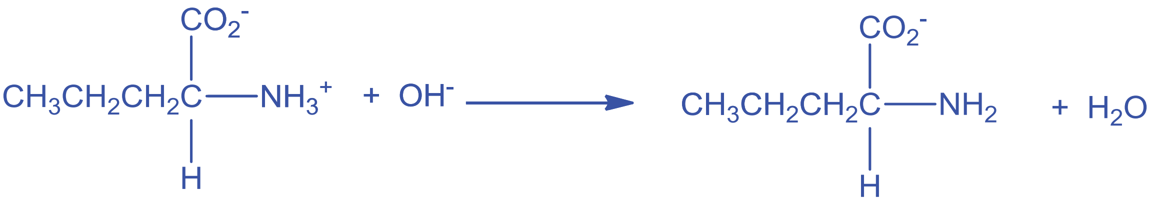
(e) Write two equations to show how the solution in **(d)** is able to resist the change in pH upon addition of small amounts of acid and base. [2]

When small amounts of acid is added,



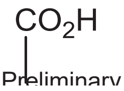
$$CH_3CH_2CH_2\overset{CO_2^-}{\underset{H}{C}}-NH_3^+ + H^+ \longrightarrow CH_3CH_2CH_2\overset{CO_2H}{\underset{H}{C}}-NH_3^+$$

When small amounts of base is added,



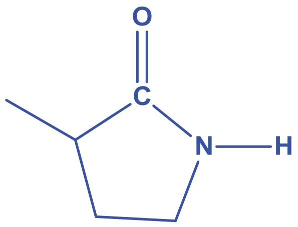
$$CH_3CH_2CH_2\overset{CO_2^-}{\underset{H}{C}}-NH_3^+ + OH^- \longrightarrow CH_3CH_2CH_2\overset{CO_2^-}{\underset{H}{C}}-NH_2 + H_2O$$

(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]



CO_2H

Final product formed:



[Total: 20]

[Turn over

Catholic Junior College
JC2 Preliminary Examinations
Higher 2

CANDIDATE NAME	
CLASS	2T

CHEMISTRY
9729/04

Paper 4 Practical

16 August 2017

2 hour 30 minutes

Candidates answer on the Question Paper.

Additional Materials: As listed in the Confidential Instructions

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READ THESE INSTRUCTIONS FIRST

Write your name and class in the boxes above.
Give details of the practical shift and laboratory, where appropriate, in the boxes provided.
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.

Shift
Laboratory

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 15 and 16.

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.

For Examiner's Use	
1	
2	
3	
Total	

Suggested Solutions

This document consists of **15** printed pages and **1** blank page.

[Turn over

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

1 'Washing soda' is made from crystals of sodium carbonate, which contains 62.94 % water and 37.06 % sodium carbonate. When stored, these crystals lose some of the water in the crystals to the atmosphere.

FA 1 is solid 'washing soda', originally sodium carbonate decahydrate, $Na_2CO_3.10H_2O$.
FA 2 is 0.100 mol dm^{-3} hydrochloric acid, HC*l*.

In this question, you will perform a titration to determine the amount of water in **FA 1** that has been lost to the atmosphere.

(a) Method

(i) Preparation of FA 3

- Weigh the 100 cm^3 beaker provided. Record the mass in the space below.
- Tip the 'washing soda' crystals, **FA 1**, into the beaker. Weigh the beaker with **FA 1** and record the mass.
- Calculate the mass of **FA 1** used and record this in the space below.
- Add distilled water to the beaker to dissolve the crystals. Carefully transfer the solution to a 250 cm^3 graduated (volumetric) flask labelled **FA 3**. Wash the beaker twice with small quantities of water and add these washings to the volumetric flask.
- Make the solution up to the mark using distilled water. Stopper the flask and invert a number of times to ensure thorough mixing.

mass of beaker + **FA1** / g	**21.138**
mass of beaker / g	**17.746**
mass of **FA 1** used / g	**3.392**

[1]

(ii) Titration of FA 3 against FA 2

- Fill the burette with **FA 2**.
- Pipette 25.0 cm^3 of **FA 3** into a conical flask and add a few drops of the indicator provided.
- Titrate the solution with **FA 2**. Record your results in the space provided on page **3**. Make certain that the recorded results show the precision of your practical work.
- Repeat the titration until consistent results are obtained.

Titration Results:

	1	2
final burette reading / cm^3	28.50	30.50
initial burette reading / cm^3	3.00	5.00
volume of FA 2 used / cm^3	25.50	25.50
	✓	✓

[6]

(iii) From your titrations, obtain a suitable volume of **FA 2** to be used in your calculations. Show clearly how you obtained this volume.

average titre = $\frac{25.50+25.50}{2}$

= 25.50 cm^3

volume of **FA 2** = ……25.50 cm^3……… [1]

(b) **(i)** Calculate the amount of hydrochloric acid run from the burette.

mol of HC*l* = *cV* = 0.100 × $\frac{25.50}{1000}$

= 2.55 x 10^{-3} mol

amount of HC*l* =…2.55 x 10^{-3} mol…… [1]

(ii) Sodium carbonate reacts with hydrochloric acid as follows.

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$

Calculate the amount of sodium carbonate, Na_2CO_3, in 250 cm^3 of **FA 3**.

mol of Na_2CO_3 in 25.0 cm^3 of FA3 = $\frac{1}{2}$ × mol of HC*l*

= $\frac{1}{2}$ × 2.55 x 10^{-3}

= 1.275 x 10^{-3} mol

mol of Na_2CO_3 in 250 cm^3 of FA 3 = $\frac{250}{25.0}$ × 1.275 x 10^{-3}

= 1.275 x 10^{-2} mol

amount of Na_2CO_3 in 250 cm^3 of **FA 3** =…1.275 x 10^{-2} mol…… [2]

(iii) Calculate the mass of sodium carbonate, Na_2CO_3, dissolved in 250 cm^3 of **FA 3**.
[A_r: C, 12.0; O, 16.0; Na, 23.0]

M_r of Na_2CO_3 = 2(23.0) + 12.0 + 3(16.0) = 106.0

mass of Na_2CO_3 in 250 cm^3 FA 3 = nM_r = (1.275 x 10^{-2}) x 106.0
= 1.351 g

mass of Na_2CO_3 in 250 cm^3 of **FA 3** =……**1.351 g**…………...… [1]

(iv) Calculate the mass of water present in the washing soda crystals.

mass of water = mass of FA 1 – mass of Na_2CO_3 in 250 cm^3 of FA 3
= 3.392 – 1.351
= 2.041 g

mass of water =……**2.041 g**…………...… [1]

(v) Hence calculate the percentage of water in the sodium carbonate crystals, **FA 1**.

% of water = $\frac{2.041}{3.392}$ x 100
= 60.2 %

percentage of water in **FA 1** =……**60.2 %**…………...… [1]

(c) The maximum error for a 25 cm^3 pipette commonly used in schools is ±0.06 cm^3.
The maximum error in any single burette reading is ±0.05 cm^3.

Calculate the maximum percentage error in each of the following.

(i) The volume of **FA 3** pipetted into the conical flask.

max % error = $\frac{0.06}{25.0}$ × 100 = 0.240 %

maximum percentage error in pipette volume =……**0.240**…………...… %

(ii) The titre volume calculated in **(a)(iii)**.

max % error = $\frac{(2\times0.05)}{25.50}$ × 100 = 0.392 %

maximum percentage error in titre volume =……**0.392**…………...… %
[2]

[Total: 16]

2 The enthalpy change for the reaction of sodium carbonate, Na_2CO_3, with water and carbon dioxide to form sodium hydrogencarbonate, $NaHCO_3$ cannot be determined directly. However both $Na_2CO_3(s)$ and $NaHCO_3(s)$ react with dilute hydrochloric acid.

Reaction 1 $NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l) + CO_2(g)$ ΔH_1

Reaction 2 $Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$ ΔH_2

In this experiment you will determine the enthalpy change ΔH_1 for **reaction 1** and ΔH_2 for **reaction 2**, and then use your results to calculate ΔH_3 for the reaction:

$$Na_2CO_3(s) + H_2O(l) + CO_2(g) \rightarrow 2NaHCO_3(s) \qquad \Delta H_3$$

FA 4 is sodium hydrogen carbonate, $NaHCO_3$.
FA 5 is sodium carbonate, Na_2CO_3.
FA 6 is 2.0 mol dm^{-3} hydrochloric acid, HCl.

(a) Method

(i) Experiment 1: $NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l) + CO_2(g)$

- Use a measuring cylinder to transfer 25 cm^3 of the acid, **FA 6**, into the plastic cup supported in a 250 cm^3 beaker. The acid is in excess.
- Weigh the container with **FA 4** and record the balance reading.
- Place the thermometer in the acid and record its temperature at 1 minute interval for the first two minutes.
- At 2½ minutes, carefully tip all the **FA 4**, in small portions, into the acid and stir to dissolve.
- Record the temperature of the solution at 1 minute interval from 3 minutes up to 8 minutes.
- Reweigh the container with any residual **FA 4** and record the balance reading and the mass of **FA 4** used.
- Rinse out the plastic cup and shake it to remove excess water.

Results

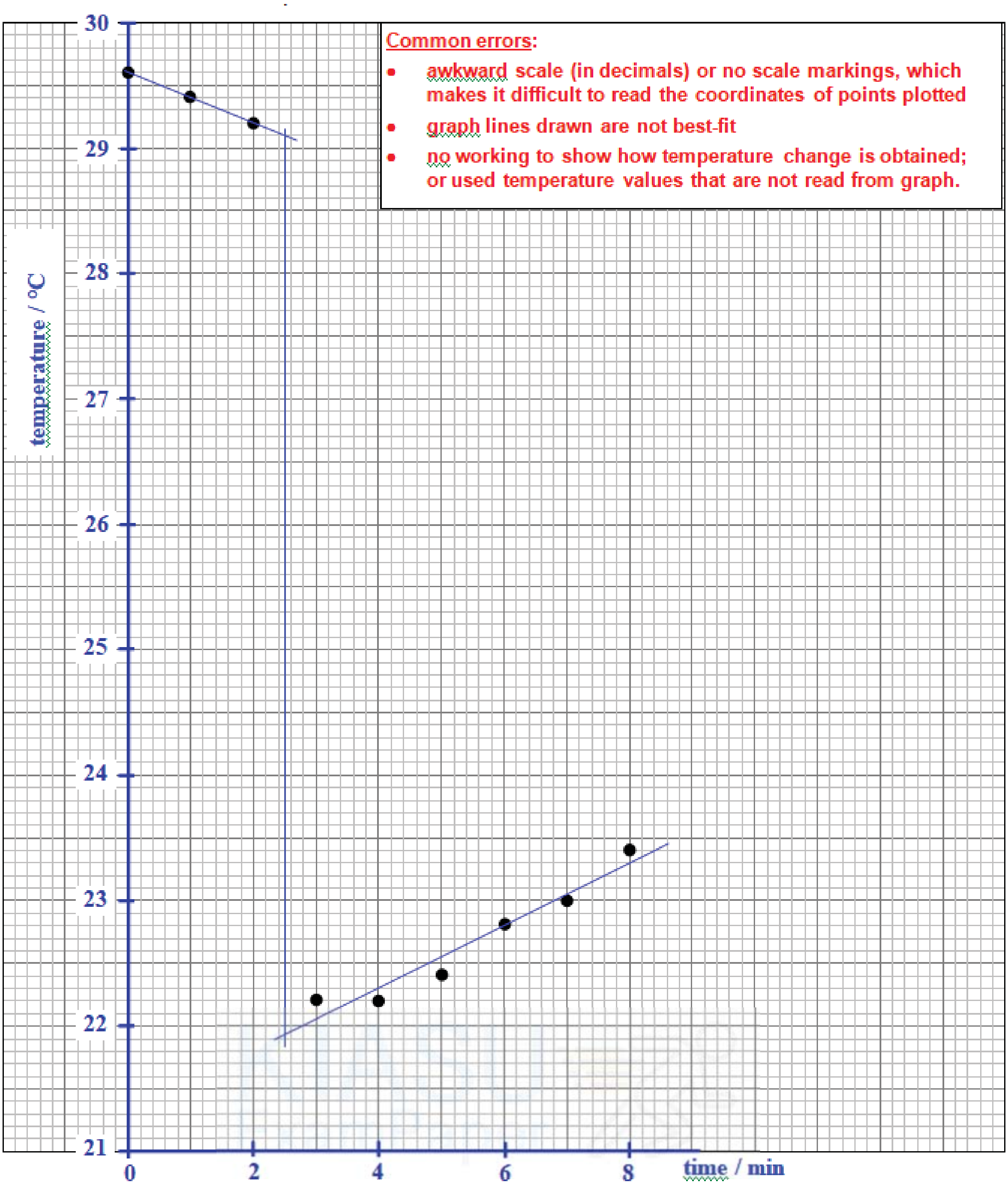
Record **all** weighings and temperature readings in the space below.

mass of container + **FA 4** / g	**5.976**
mass of container + residual **FA 4** / g	**3.489**
mass of **FA 4** used / g	**2.487**

time / min	0	1	2	3	4	5	6	7	8
temperature / °C	29.6	29.4	29.2	22.2	22.2	22.4	22.8	23.0	23.4

[5]

(ii) Plot on the grid below, a graph of temperature on the *y*-axis against time on the *x*-axis. The scale for the temperature should extend at least 1°C below the lowest recorded temperature.



Common errors:

- awkward scale (in decimals) or no scale markings, which makes it difficult to read the coordinates of points plotted
- graph lines drawn are not best-fit
- no working to show how temperature change is obtained; or used temperature values that are not read from graph.

Draw two straight lines of best fit and extrapolate the two lines to 2½ minutes. Determine the change in temperature at this time.

temperature change = 29.10 – 21.95 = 7.15 °C

temperature change at 2½ minutes = ...7.15......... °C

[4]

(iii) **Experiment 2**: $Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$

- Use a measuring cylinder to transfer 25 cm^3 of the acid, **FA 6**, into the plastic cup supported in a 250 cm^3 beaker. The acid is in excess.
- Weigh the container with **FA 5** and record the balance reading.
- Place the thermometer in the acid and record its initial temperature.
- Carefully tip all the **FA 5**, in small portions, into the acid and stir to dissolve.
- Record the highest temperature reached.
- Reweigh the container with any residual **FA 5** and record the balance reading and the mass of **FA 5** used.

Results

Record **all** weighings and temperature readings in the space below.

mass of container + **FA 5** / g	**5.535**
mass of container + residual **FA 5** / g	**3.521**
mass of **FA 5** used / g	**2.014**
initial temperature of **FA 5** / °C	**30.0**
highest temperature / °C	**35.7**
temperature rise / °C	**5.7**

[3]

(b) **(i)** Using your answer to **2(a)(ii)**, calculate the heat energy absorbed when **FA 4** was added to the acid in **Experiment 1**.
[Assume that 4.3 J of heat energy changes the temperature of 1.0 cm^3 of solution by 1.0 °C.]

heat absorbed $= mc\,\Delta T$

$= 25 \times 4.3 \times 7.15$

$= 768.6$ J

heat energy absorbed =……768.6…… J [1]

(ii) Calculate the enthalpy change, in kJ mol^{-1}, when 1 mol of **FA 4**, $NaHCO_3$, reacts with the acid. [A_r: H, 1.0; C, 12.0; O, 16.0; Na, 23.0]

M_r of $NaHCO_3$ $= 23.0 + 1.0 + 12.0 + 3(16.0) = 84.0$

mol of $NaHCO_3 = \frac{2.487}{84.0} = 0.0296$ mol

$\therefore \Delta H_1 = +\frac{768.6}{0.0296}$ J mol^{-1}

$= +25970$ J mol^{-1}

$= +26.0$ kJ mol^{-1}

enthalpy change, ΔH_1 = ………+26.0……… kJ mol^{-1} [1]

(iii) Using your results in **2(a)(iii)**, calculate the heat energy produced when **FA 5** was added to the acid in **Experiment 2**.
[Assume that 4.3 J of heat energy changes the temperature of 1.0 cm^3 of solution by 1.0 °C.]

heat evolved = mc ΔT

= 25 × 4.3 × 5.7

= 612.8 J

heat energy produced =……**612.8**…….. J [1]

(iv) Calculate the enthalpy change, in kJ mol^{-1}, when 1 mol of **FA 5**, Na_2CO_3, reacts with the acid. [A_r: C, 12.0; O, 16.0; Na, 23.0].

M_r of Na_2CO_3 = 2(23.0) + 12.0 + 3(16.0) = 106.0

mol of Na_2CO_3 = $\frac{2.014}{106.0}$ = 0.0190 mol

$\therefore$ $\Delta H_2 = -\frac{612.8}{0.0190}$ Jmol^{-1}

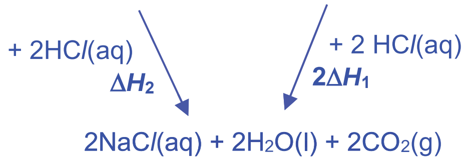
= – 32250 J mol^{-1}

= – 32.3 kJ mol^{-1}

enthalpy change, ΔH_2 = ...**–32.3**............ kJ mol^{-1} [1]

(v) Using your answers to **2(b)(ii)** and **2(b)(iv)** and the equations for **Experiment 1** and **Experiment 2**, determine the enthalpy change for the reaction:

$$Na_2CO_3(s) + H_2O(l) + CO_2(g) \rightarrow 2NaHCO_3(s)$$



By Hess' Law,

$\Delta H = \Delta H_2 - 2\Delta H_1$

= (–32.3) – 2(+26.0)

= –84.3 kJ mol^{-1}

enthalpy change, ΔH_3 = ...**–84.3**.............. kJ mol^{-1} [3]

(c) Planning

You are provided with **FA 4**, solid sodium hydrogencarbonate, $NaHCO_3$, distilled water and apparatus commonly found in the school laboratory.

Using only these materials, you are to plan an additional experiment to determine a further enthalpy change, ΔH_4, which can be put together with those from **Experiment 1** and **Experiment 2** to determine the enthalpy change for the reaction:

$$Na_2CO_3(s) + H_2O(l) + CO_2(g) \rightarrow 2NaHCO_3(aq) \qquad \Delta H_5$$

In your plan, you should include details of:

- the quantity of reactants and apparatus that you would use,
- the procedure you would follow,
- the measurements you would take, and
- an outline of how you would use your results to determine ΔH_5.

DO NOT CARRY OUT YOUR PLAN.

Plan

- **Weigh a sample (say, 2.50 g of FA 4), adds to known volume of water (say, 25 cm^3) and measure change in temperature (record initial temperature of water (T_i) and lowest temperature (T_f) reached on adding FA 4 to water).**

Treatment of results

Let mass of FA 4 added be m_1 g

temperature change, $\Delta T = (T_f) - (T_i) = x$ °C

heat energy absorbed = $mc\Delta T = (25)(4.3)(x)$ J = $108x$ J

mol of $NaHCO_3$ = $\frac{m_1}{84.0}$ mol

$$\Delta H_4 = \frac{\text{energy absorbed}}{\text{mol of NaHCO}_3} = +\frac{108x}{m_1/84.0}\ \text{J mol}^{-1} = +9072\frac{x}{m_1}\ \text{J mol}^{-1} = +9.07\frac{x}{m_1}\ \text{kJ mol}^{-1}$$

From (b)(iv), $Na_2CO_3(s) + H_2O(l) + CO_2(g) \rightarrow 2NaHCO_3(s) \qquad \Delta H_3 = -84.3\ \text{kJ mol}^{-1}$

$NaHCO_3(s) \rightarrow NaHCO_3(aq) \qquad \Delta H_4 = +9.07\frac{x}{m_1}\ \text{kJ mol}^{-1}$

$Na_2CO_3(s) + H_2O(l) + CO_2(g) \rightarrow 2NaHCO_3(aq) \qquad \Delta H_5$

$$\therefore \quad \Delta H_5 = \Delta H_3 + 2\Delta H_4$$

$$= -83.4 + 2(+9.07\frac{x}{m_1}) = (-83.4 + 18.1\frac{x}{m_1})\ \text{kJ mol}^{-1}$$

[5]

[Total: 24]

3 Qualitative Analysis

In this question, you will carry out tests, make observations and come to conclusions about the compounds.

If the evolution of a gas is observed at any stage, the gas should be tested and identified. Details of the test carried out, the observations from the test and the identity of the gas should be given with the observations.

If it appears that no reaction has taken place, this should be clearly recorded

(a) **FA 7** is an organic solid. Carry out the tests described in Table 3.1 and use the observations to identify two functional groups present in **FA 7**.

Table 3.1

tests	*observations*
Add 10 cm^3 of ethanol to your **FA 7** in a boiling tube. Stopper the boiling tube and shake to dissolve the solid. Then add 10 cm^3 of deionised water. Shake again to ensure complete mixing. Divide the solution into four clean test-tubes and use a fresh tube for each of the following tests:	
(i) add a piece of magnesium ribbon to the solution	**brisk effervescence;** **gas gives a "pop" sound with a lighted splint.** **$H_2(g)$ evolved.** ***Need to include identity of gas***
(ii) add solid sodium carbonate to the solution	**effervescence;** **gas gives a white ppt with limewater.** **$CO_2(g)$ evolved.** ***Need to include identity of gas***
(iii) add a few drops of aqueous iron(III) chloride to the solution	**violet (or purple) coloration**
(iv) add 2 cm depth of bromine water. (Take care: bromine water is corrosive.)	**orange $Br_2(aq)$ decolourised;** **white ppt.** ***accept reddish-brown $Br_2(aq)$***

[4]

(v) Complete Table 3.2, using the observations in Table 3.1 to identify the two functional groups present in **FA 7**. In each case, give evidence to support your conclusion.

Table 3.2

functional group	*evidence*
phenol	**- violet coloration with aq. $FeCl_3$** **- white ppt with aq. bromine water** ***correct functional group & with underlined evidence***
carboxylic acid ***'carboxyl group' not acceptable***	**- CO_2(g) with solid sodium carbonate** **- H_2(g) with magnesium ribbon** ***correct functional group & with underlined evidence***

[2]

(b) **Plan**

You are provided with four solutions, labelled **FA 8**, **FA 9**, **FA 10** and **FA 11**.

Each solution contains one of the following compounds.

- lead nitrate, $Pb(NO_3)_2$
- sodium chloride, NaC*l*
- sodium hydroxide, NaOH
- zinc sulfate, $ZnSO_4$

The order in the list of solutions does **not** correspond to the **FA** numbers.

(i) Using the *Qualitative Analysis Notes* on page 14, complete Table 3.3 to show the expected observations when pairs of the solutions are mixed. Solutions should be added a little at a time, with shaking, until no further change is observed.

Expected observations for $Pb(NO_3)_2$ have already been recorded in Table 3.3.

Table 3.3

	NaC*l*	**NaOH**	**$ZnSO_4$**
$Pb(NO_3)_2$	white ppt.	white ppt. soluble in excess NaOH	white ppt.
NaC*l*		**no ppt.**	**no ppt.**
NaOH			**white ppt.** **soluble in excess NaOH**

complete table (with correct observations)

Explain how you could use the expected observations in Table 3.3 to identify **each** of the solutions.

- **$Pb(NO_3)_2$ - gives white ppt with the other 3 solutions**
- **NaC*l* - gives white ppt with only 1 other solution**
- **NaOH - gives white ppt with 2 other solutions (ppt soluble in both cases)**
- **$ZnSO_4$ - gives white ppt with 2 other solutions (ppt soluble in only one)**

[5]

(ii) Carry out the experiment using **FA 8**, **FA 9**, **FA 10** and **FA 11** and record your results in a suitable table.

	FA 8 (excess)	**FA9 (excess)**	**FA 10 (excess)**	**FA 11 (excess)**
FA 8		no ppt	no ppt.	white ppt.
FA 9	no ppt.		white ppt. soluble in excess **FA 10**	white ppt.
FA10	no ppt.	white ppt.		white ppt.
FA 11	white ppt.	white ppt.	white ppt. soluble in excess **FA 10**	

[3]

(iii) Identify the substance present in each of the solutions.

FA 8 **NaC*l***

FA 9 **$ZnSO_4$**

FA 10 **NaOH**

FA 11 **$Pb(NO_3)_2$**

[1]

[Total: 15]

Qualitative Analysis Notes

[*ppt. = precipitate*]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

ion	***reaction***
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^{-}(aq)	gives white ppt. with Ag^{+}(aq) (soluble in NH_3(aq))
bromide, Br^{-}(aq)	gives pale cream ppt. with Ag^{+}(aq) (partially soluble in NH_3(aq))
iodide, I^{-}(aq)	gives yellow ppt. with Ag^{+}(aq) (insoluble in NH_3(aq))
nitrate, NO_3^{-}(aq)	NH_3 liberated on heating with OH^{-}(aq) and Al foil
nitrite, NO_2^{-}(aq)	NH_3 liberated on heating with OH^{-}(aq) and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-}(aq)	SO_2 liberated with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	***test and test result***
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	***colour of element***	***colour in aqueous solution***	***colour in hexane***
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

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