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) ⇌ 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) → 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]

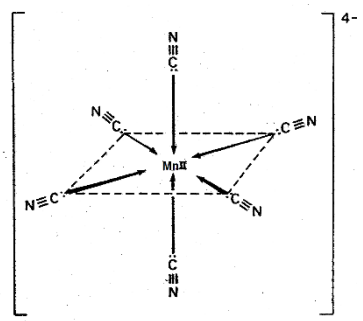
(c) Manganese is also a transition element and shows great tendency to form stable coloured complexes with ligands.

(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, $[Mn(CN)_6]^{4-}$.



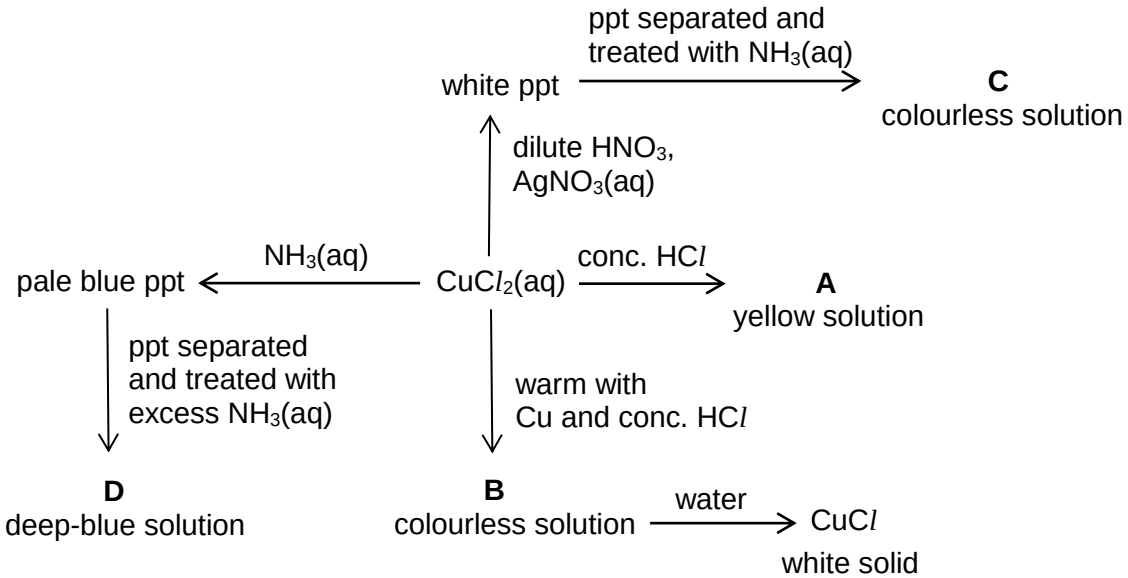
[2]

(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

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

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

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

(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]

[Turn over

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

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

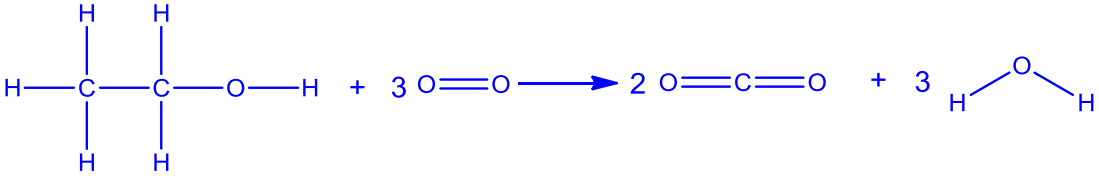
(d) Ethanol can be burned in excess oxygen as fuel. Complete combustion of ethanol releases 1367 kJ mol^{-1} of heat energy.

(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]

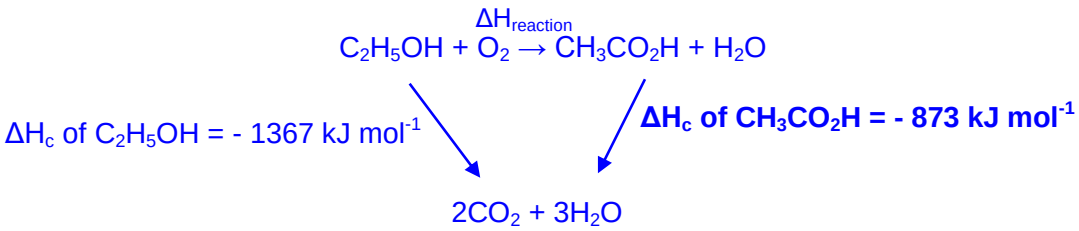
(iii) Suggest a reason for the discrepancy between this value and that quoted in **(d)**.

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

OR

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



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

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

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

$x = 68.4\%$

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.

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

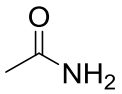
P is the observed pressure exerted by the gas.
V is the volume of the container in which the gas is contained.
The constants a and b have positive values and are characteristic of a gas.

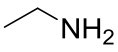
Suggest why the term $\frac{an^2}{V^2}$ is **added** to P and the term nb is **subtracted** from V respectively.

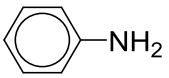
$P + \frac{an^2}{V^2}$: **Real gas particles have significant forces of attraction, the pressure exerted by a real gas is smaller than expected for an ideal gas. Thus, a term is added to P.** [1]

$V - nb$: **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 from V.** [1]

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


ethanamide


ethylamine


phenylamine

Order of basicity:

ethanamide < phenylamine < ethylamine

Explain your answer.

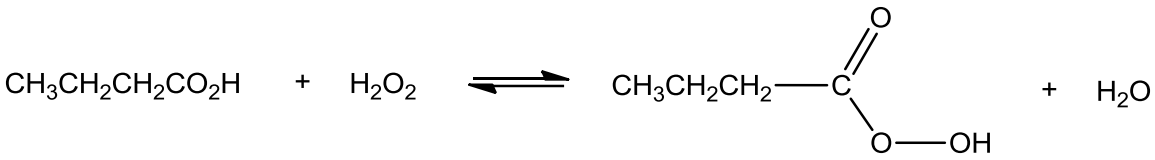
Ethanamide is an amide and the lone pair of electrons on N is delocalised into the π bond of C=O, thus it is not available to accept H^+, making ethanamide neutral and less basic than phenylamine and ethylamine. Ethylamine is more basic than phenylamine as it has an electron-donating ethyl group. Thus 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. 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^+. [3]

[Total: 9]

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

[Turn over



butanoic acid

butaneperoxoic acid
$C_4H_8O_3$

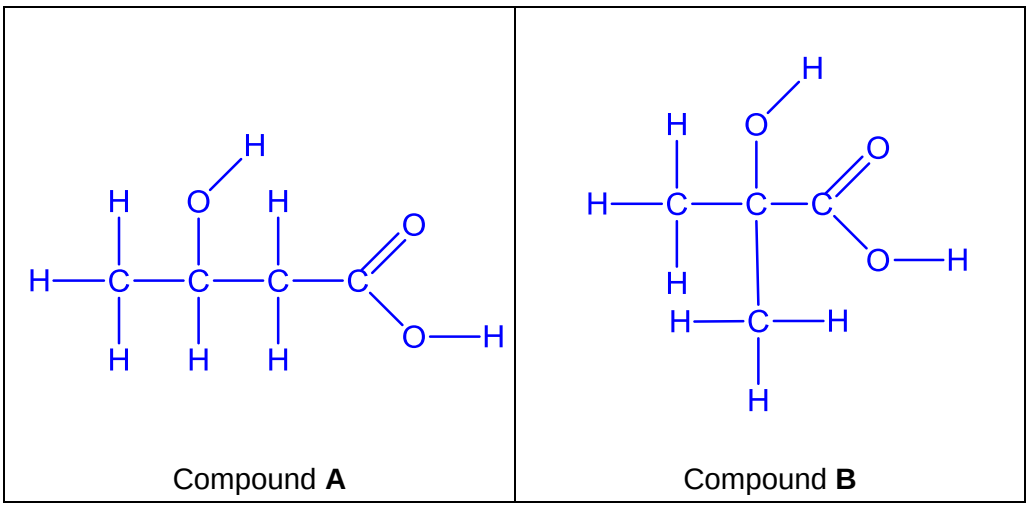
(i) Identify the type of hybridisation involved for the C atom of O=C-O in butaneperoxoic acid and hence state its bond angle.

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**.



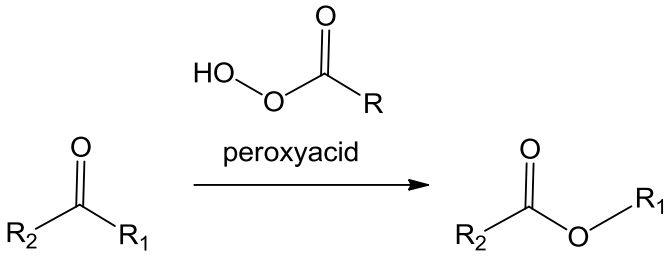
Compound **A**

Compound **B**

[2]

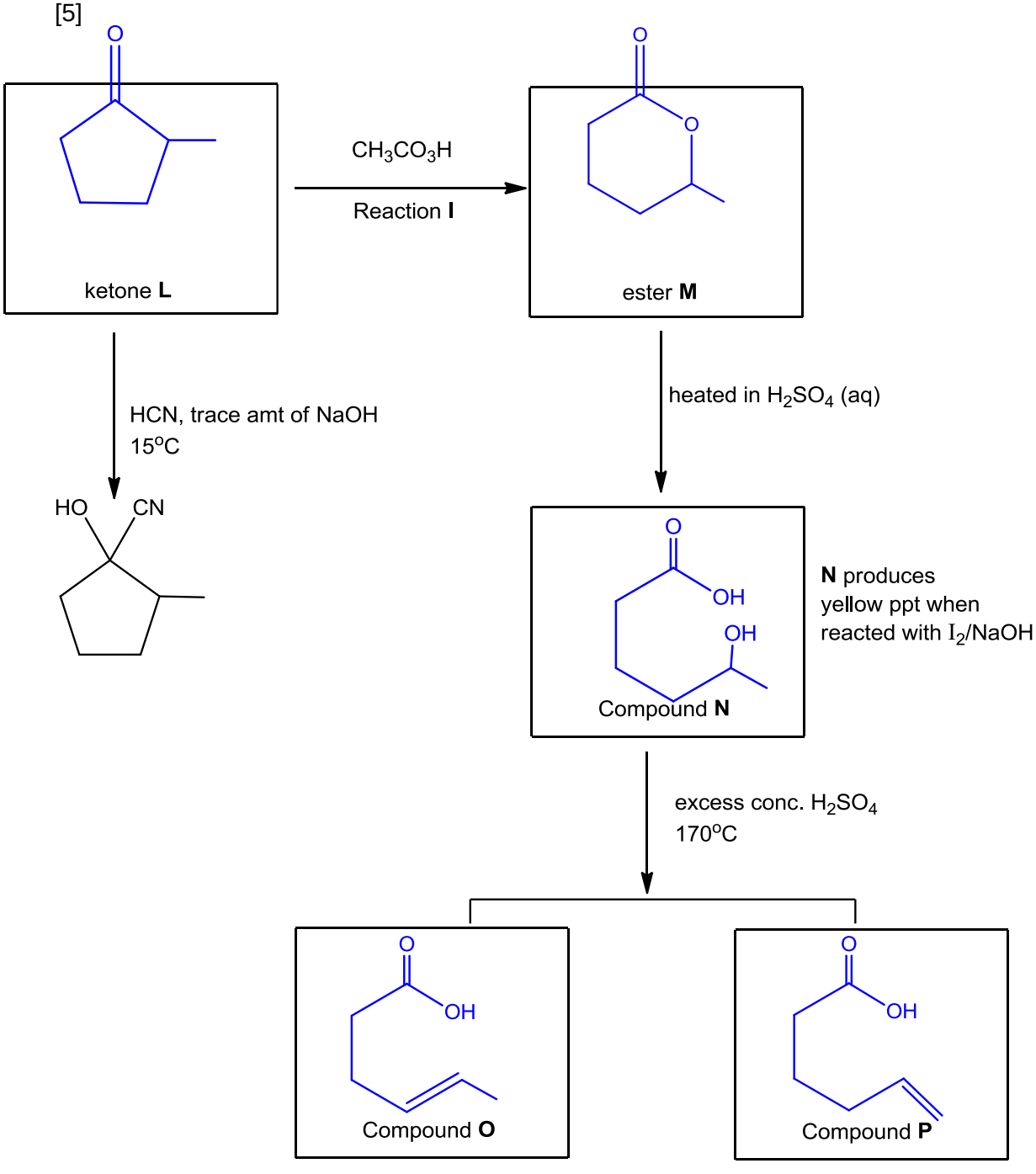
Type of isomerism between **A** and **B** ……**Chain isomerism**…… [1]

(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]



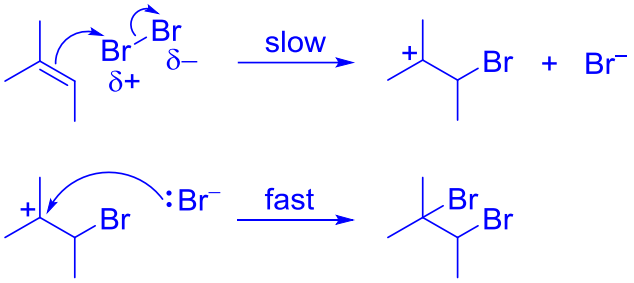
[Turn over

[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.

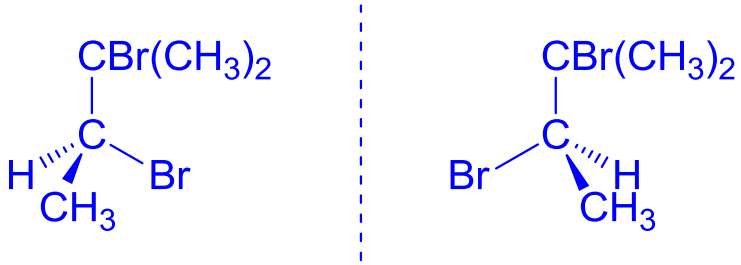
Electrophilic addition



[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]

[Turn over