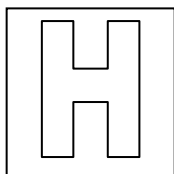


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PIONEER JUNIOR COLLEGE

2015 JC2 PRELIMINARY EXAMINATION
HIGHER 1



CHEMISTRY Paper 2

8872/02

15 September 2015

Candidates answer Section A on the Question Paper

Additional Materials: Data Booklet
 Writing Paper

2 hours

READ THESE INSTRUCTIONS FIRST

Write your name, index no and CT group on all the work you hand in.

Write in dark blue or black pen.

You may use a pencil for any diagrams, graphs or rough working.

Section A

Answer **all** questions.

Section B

Answer any **two** questions on separate writing paper. Begin each question in a fresh sheet of writing paper.

At the end of the examination, fasten all your work securely together.

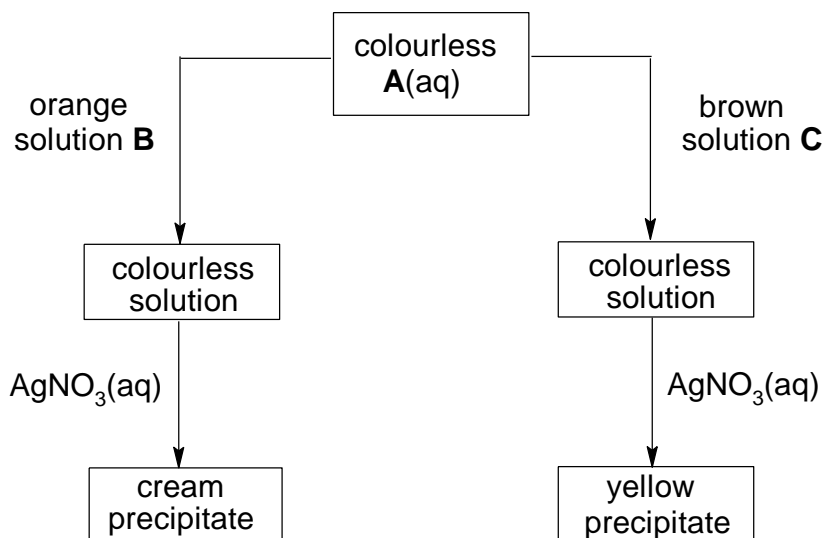
The number of marks is given in brackets [] at the end of each question or part question.

FOR EXAMINER'S USE			
Section A		Section B	
1	/ 10	5	/ 20
2	/ 9	6	/ 20
3	/ 9	7	/ 20
4	/ 12	Penalty	s.f. / units
		TOTAL	/ 80

Section A (40 marks)

Answer all questions in the spaces provided.

- 1 The diagram below shows the reactions of an aqueous salt, **A**.



A has the following composition by mass:

K, 41.1%; S, 33.7%; O, 25.2%.

The relative formula mass, M_r , of **A** is 190.4. One formula unit of **A** contains only one type of anion.

- (a) Determine the formula of the salt **A**.

Let the mass of salt **A** be 100g.

	K	S	O
Mass / g	41.1	33.7	25.2
Amount / mol	1.0512	1.0498	1.575
Ratio	1.0013	1.000	1.500
Simplest Ratio	2	2	3

Empirical formula of salt is $K_2S_2O_3$.

Let formula of salt be $(K_2S_2O_3)_n$.

$$[2(39.1) + 2(32.1) + 3(16.0)]n = 190.4$$

$$n = 1$$

Formula of salt is $K_2S_2O_3$.

[2]

- (b) Suggest the identities of the cream precipitate and the yellow precipitate.

Cream precipitate: AgBr

Yellow precipitate: AgI

[1]

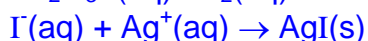
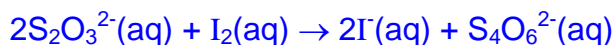
- (c) Suggest the identities of **B** and **C**.

B: Br_2

C: I_2

[1]

- (d) With reference to the *Data Booklet*, show, by means of **two** ionic equations, how the yellow precipitate is formed from **C**.



[2]

- (e) For the reaction of **A** and **B**, a titration was carried out to determine if the sulfur-containing product is $\text{S}_4\text{O}_6^{2-}$ or SO_4^{2-} .

It was found that 25.0 cm^3 of $0.200 \text{ mol dm}^{-3}$ of **B** required 10.0 cm^3 of $0.125 \text{ mol dm}^{-3}$ of **A** for complete reaction.

Use the data to determine the final oxidation state of sulfur in the product. Hence, write a balanced equation for the reaction of **A** and **B**.



Each S atom will have a gain in O.S. by +4.

Final oxidation state of S = +2 + 4 = +6



[3]

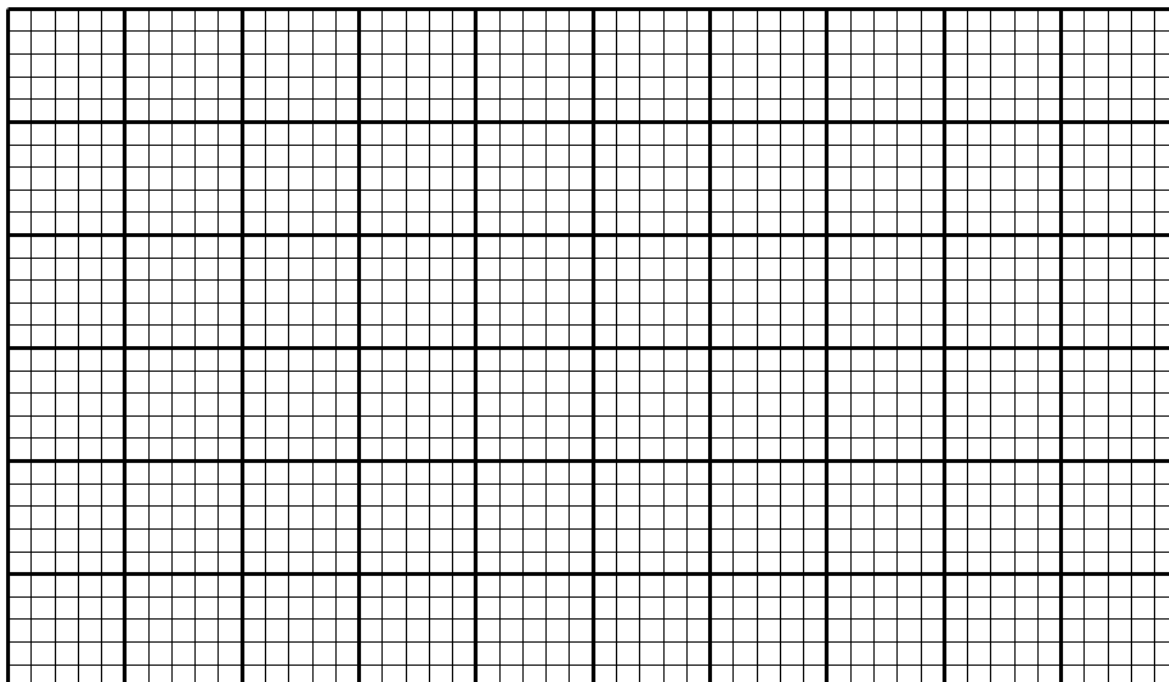
[Total: 9]

- 2 For a reaction $X \rightarrow Y$, the following experimental results were obtained.

Time / s	0	20	40	60	80	100	120	140	∞
$[Y] / \text{mol dm}^{-3}$	0	0.12	0.20	0.26	0.30	0.33	0.35	0.37	0.40

When the reaction is complete, the concentration of Y is 0.40 mol dm^{-3} .

- (a) Plot the graph of $[Y]$ against time on the grid below to find the half-life of the reaction. Hence, determine the order of reaction with respect to X .



Half-life of the reaction = 40 s

Since the two half-lives are constant, hence the order of reaction with respect to X is one.

[4]

- (b) Determine the initial rate of the reaction.

From the graph,
gradient at $t = 0$ is the initial rate of reaction = $0.20 / 32 = \underline{0.00625 \text{ mol dm}^{-3} \text{ s}^{-1}}$

[1]

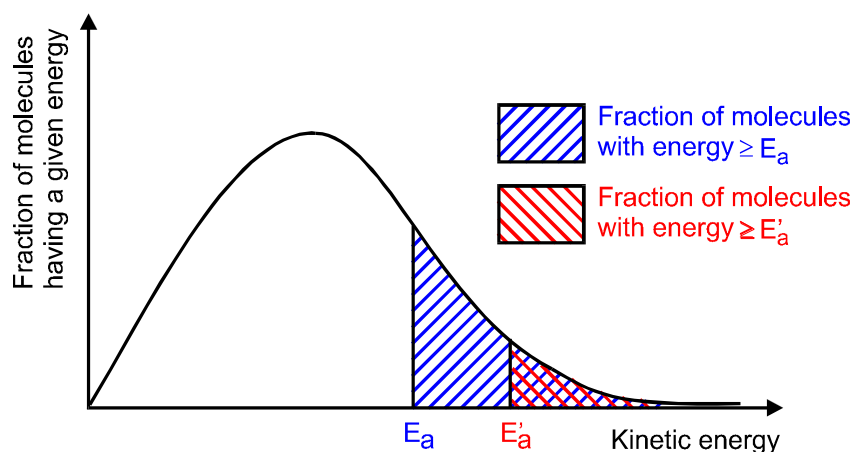
- (c) Hence, calculate the rate constant, stating its units, given that the initial concentration of X is 0.40 mol dm^{-3} .

$$0.00625 = k(0.40)$$

$$k = \underline{0.0156 \text{ s}^{-1}}$$

[1]

- (d) With the aid of a sketch of the Boltzmann Distribution, explain why an addition of catalyst increases the rate of reaction.



A catalyst

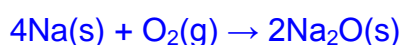
- provides an alternative reaction pathway with lower activation energy
 - increases the number of reacting particles with energy $\geq E_a$
 - increases the number of effective collisions per unit time
- hence increase the rate of reaction

[3]

[Total: 9]

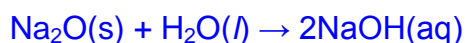
- 3 (a) Describe what you would see when sodium burns in oxygen and write the balanced equation, with state symbols, for the reaction described.

Sodium burns very vigorously in O_2 with a yellow flame, leaving behind a white residue of Na_2O .



[2]

- (b) Describe what you would see when the residue from (a) is dissolved in water containing Universal Indicator solution. Write balanced equation, with state symbols, for the reaction described.



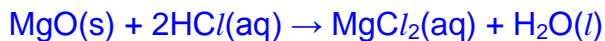
The white solid dissolves.

Universal Indicator changes from green to purple / violet.

[2]

- (c) Each of the following oxides can react with sodium hydroxide and/or hydrochloric acid. For **each** oxide, write a balanced equation for its reaction with either hydrochloric acid or sodium hydroxide.

- magnesium oxide



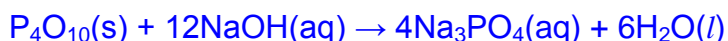
- aluminium oxide



Or



- phosphorus(V) oxide



[3]

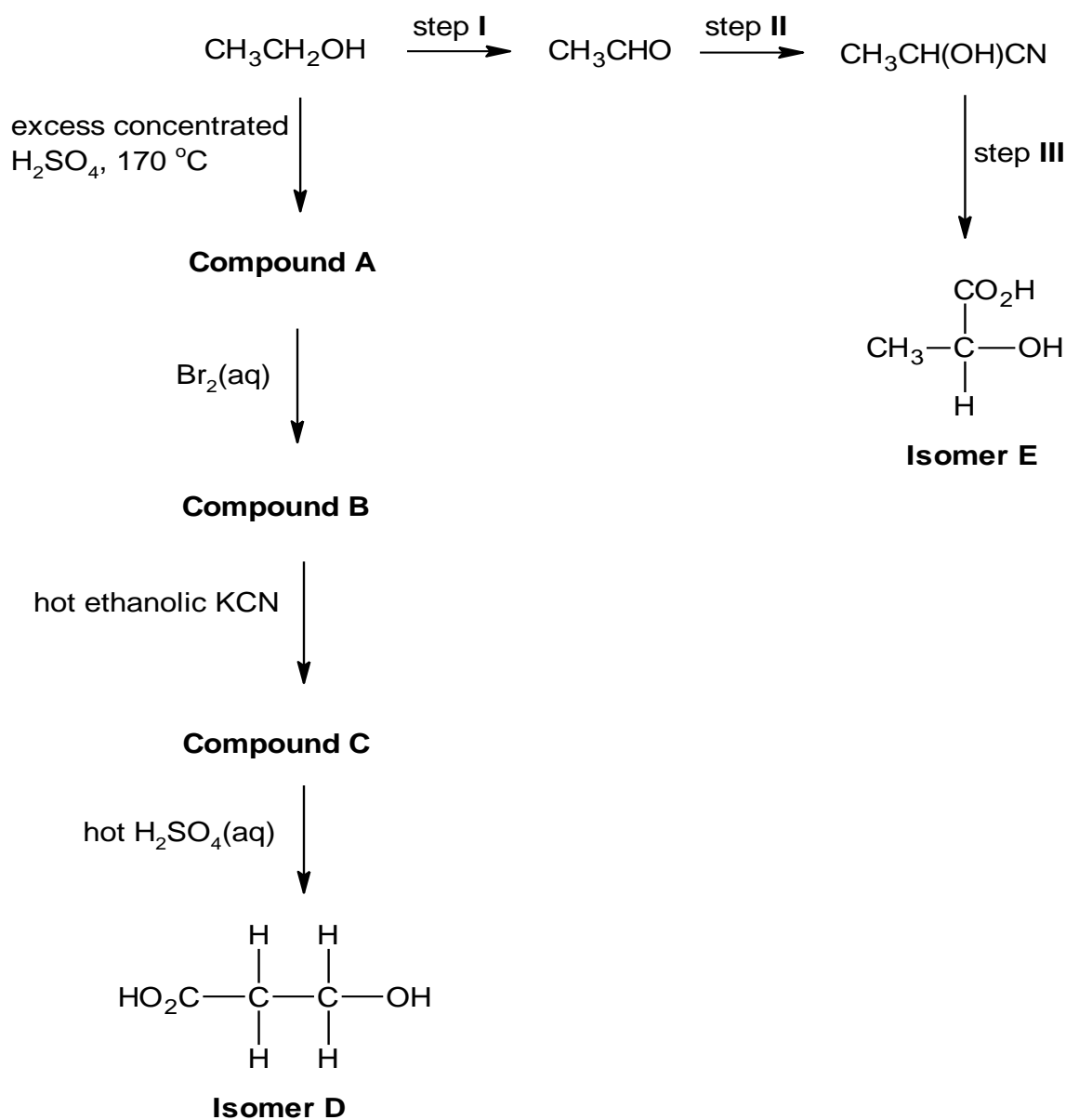
- (d) Explain, in terms of structure and bonding, why aluminium oxide melts at 2070 °C while aluminium chloride sublimes at 178 °C.

Al_2O_3 has a giant ionic lattice structure whereas AlCl_3 has a simple covalent structure. The strong electrostatic forces of attraction / ionic bonds between Al^{3+} & O^{2-} ions require a large amount of energy to be weakened. The weak van der Waals' (instantaneous dipole) forces between molecules of AlCl_3 require only a small amount of energy to overcome. Hence, Al_2O_3 has a much higher melting point than AlCl_3 .

[3]

[Total: 10]

4 (a) Consider the following reaction scheme, starting from ethanol.



(i) Suggest reagents and conditions for steps I, II and III.

step I: $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$, distill

step II: HCN , trace NaCN , $10 - 20^\circ\text{C}$

step III: $\text{H}_2\text{SO}_4(\text{aq})$, heat

(ii) Draw the structures of compounds **A**, **B** and **C** in the boxes below.

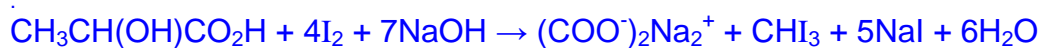
Compound A	Compound B
$ \begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{H} \end{array} $	$ \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{Br} \quad \text{OH} \end{array} $
Compound C	
$ \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{CN} \quad \text{OH} \end{array} $	

[6]

(b) (i) The two isomers **D** and **E** are subjected to a chemical test which is able to distinguish them. Give the test reagent and condition and write the observations for each of the isomers.

Isomer	D	E
Test reagent and condition	$\text{I}_2(\text{aq})$, $\text{NaOH}(\text{aq})$, warm	
Observations	No yellow ppt	<u>Yellow ppt of CHI_3 formed.</u>

(ii) Write a balanced equation for the reaction between your suggested test reagent and the isomer that gives a positive result.



- (iii) State the type of isomerism exhibited by isomers **D** and **E**.

Structural (positional) isomerism

- (iv) How do you expect the acidity of isomer **D** to compare with that of isomer **E**? Explain your answer.

Isomer **E** is more acidic as the electron withdrawing -OH group is closer to the -CO_2^- on $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2^-$ than $\text{CH}_2(\text{OH})\text{CH}_2\text{CO}_2^-$ hence there is a greater extent of dispersion of negative charge. $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2^-$ is more stable.

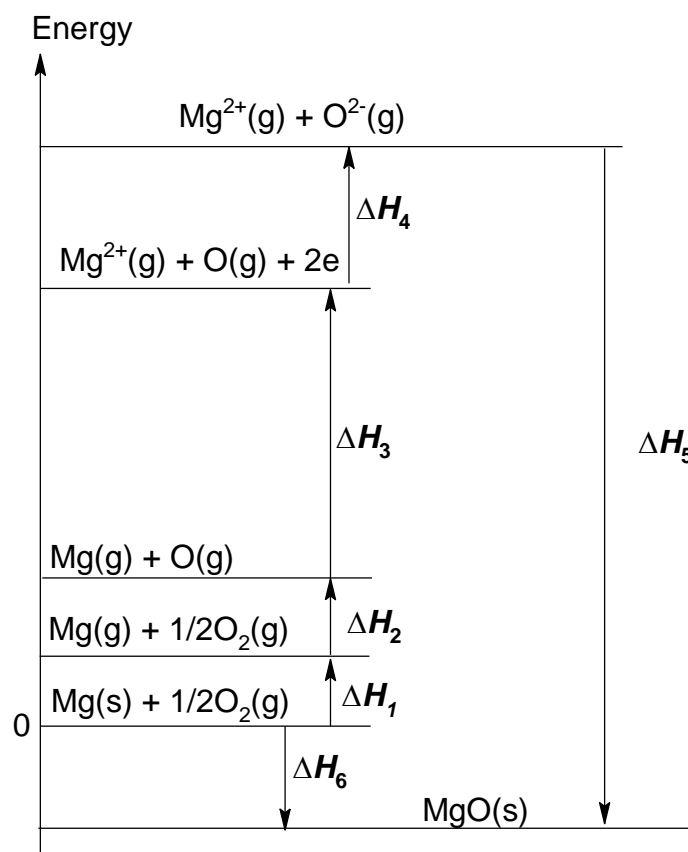
[6]

[Total: 12]

Section B

Answer **two** questions from this section on separate answer paper.

- 5 (a) The formation of magnesium oxide from its elements may be represented by a Born-Haber energy cycle shown below.



- (i) Name the enthalpy changes represented as ΔH_3 , ΔH_5 and ΔH_6 .

ΔH_3 : sum of 1st and 2nd IE of Mg

ΔH_5 : lattice energy of MgO

ΔH_6 : enthalpy change of formation of MgO

- (ii) Using relevant information from the *Data Booklet* and the following information, calculate the lattice energy of magnesium oxide.

$\text{Mg(s)} \rightarrow \text{Mg(g)}$	$\Delta H_1 = +150 \text{ kJmol}^{-1}$
$\text{O(g)} + 2\text{e}^- \rightarrow \text{O}^{2-}(\text{g})$	$\Delta H_4 = +606 \text{ kJmol}^{-1}$
$\text{Mg(s)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{MgO(s)}$	$\Delta H_6 = -602 \text{ kJmol}^{-1}$

Lattice energy of MgO (ΔH_5)

$$= -(+606) - (736 + 1450) - \frac{1}{2}(496) - (+150) + (-602)$$

$$= -3792 \text{ kJ mol}^{-1}$$

- (iii) Suggest, with reasons, how the magnitude of lattice energy of $\text{MgF}_2(\text{s})$ might compare with that of $\text{MgO}(\text{s})$.

$$\Delta H_{\text{lattice}} \propto \left| \frac{q_+ q_-}{r_+ + r_-} \right|$$

Although the ionic radius of F^- is smaller than that of O^{2-} , O^{2-} has a higher charge. As charge is a more significant factor affecting the lattice energy, the magnitude of lattice energy of MgO is greater than that of MgF_2 .

[7]

- (b) Research shows that apple juice is a good alternative to soda and other soft drinks, especially because it contains vitamin C and healthy polyphenol antioxidants that are essential for overall health.

Apple juice, which contains a monobasic acid **HA**, has a pH of 3.5 and it can be titrated with standard alkali. A 25.0 cm^3 sample of apple juice was exactly neutralised by 27.50 cm^3 of 0.10 mol dm^{-3} sodium hydroxide using phenolphthalein as an indicator.

- (i) Calculate the concentration of hydrogen ions, in mol dm^{-3} , in apple juice.

$$[\text{H}^+] = 10^{-3.5} = 3.16 \times 10^{-4} \text{ mol dm}^{-3}$$

- (ii) Calculate the concentration of **HA**, in mol dm^{-3} , in the juice.

$$\text{No. of moles of NaOH required} = 27.50/1000 \times 0.10 = 2.75 \times 10^{-3} \text{ mol}$$

Since acid is monobasic,

$$1 \text{ acid} \equiv 1 \text{ NaOH}$$

$$\text{No. of moles of HA} = 2.75 \times 10^{-3} \text{ mol}$$

$$[\text{HA}] = 2.75 \times 10^{-3} / (25.0/1000) = 0.110 \text{ mol dm}^{-3}$$

- (iii) Based on your answer in (b)(i) and (b)(ii), comment on the acid strength of **HA** present in the juice.

$[\text{HA}] \gg [\text{H}^+]$, showing that the acid can only dissociate partially in water to form A^- and H_3O^+ ions. Hence, **HA** found in apple juice is a weak acid. A large proportion of undissociated **HA** molecules are still present.

- (iv) Write an expression for the acid dissociation constant, K_a , for the acid **HA**.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad \text{or} \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

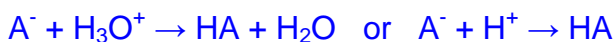
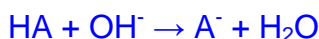
- (v) Using your answers in (b)(i) and (b)(ii), calculate a numerical value of the acid dissociation constant, K_a .

$$K_a = \frac{(3.16 \times 10^{-4})^2}{0.110} = 9.08 \times 10^{-7} \text{ mol dm}^{-3}$$

or

$$K_a = \frac{(3.16 \times 10^{-4})^2}{(0.110 - 3.16 \times 10^{-4})} = 9.10 \times 10^{-7} \text{ mol dm}^{-3}$$

- (vi) With the aid of two equations, explain how an aqueous solution of the acid (HA) and its sodium salt ($\text{Na}^+ \text{A}^-$) acts as a buffer on addition of small amount of acid and alkali.



- (vii) Suggest a reason why phenolphthalein is a suitable indicator for this titration.

Phenolphthalein has a sharp / distinct color change from colourless to pale pink.

Or

The equivalence point of the titration of pH > 7 coincides with the pH working range of phenolphthalein of 8 to 10.

[8]

- (c) Methyl butanoate is a colourless liquid with a fruity apple smell. It can undergo hydrolysis in the presence of an acid or alkali.

- (i) Write equations showing how methyl butanoate undergoes hydrolysis using
- HCl(aq)
 - NaOH(aq)

With HCl(aq)



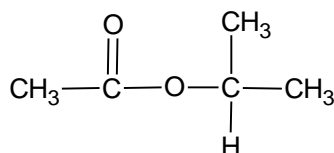
With NaOH(aq)



- (ii) Compound **P** is isomeric with methyl butanoate. Upon hydrolysis, **P** gives ethanoic acid and alcohol **Q**. **Q** undergoes tri-iodomethane (iodoform) reaction.

Give the name of alcohol **Q** and draw the structure of **P**.

Alcohol **Q** is propan-2-ol.

**P**

- (iii) Compound **R** is also isomeric with methyl butanoate. Effervescence is observed when $\text{Na}_2\text{CO}_3(\text{aq})$ is added to **R**.

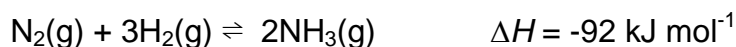
Suggest a structure for **R**.

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ / $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CO}_2\text{H}$ / $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CO}_2\text{H}$ / $(\text{CH}_3)_3\text{CCO}_2\text{H}$

[5]

[Total: 20]

- 6 (a) The Haber process is the nitrogen fixation reaction of hydrogen gas which is used industrially to produce ammonia. The reaction takes place over finely divided iron catalyst.



100 moles of nitrogen and 300 moles of hydrogen gas are heated at 470°C in a 100 dm^3 reaction vessel until equilibrium is established. The equilibrium mixture contains 80 moles of ammonia.

- (i) Write the expression for K_c .

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

- (ii) Calculate a value for K_c , giving its units.

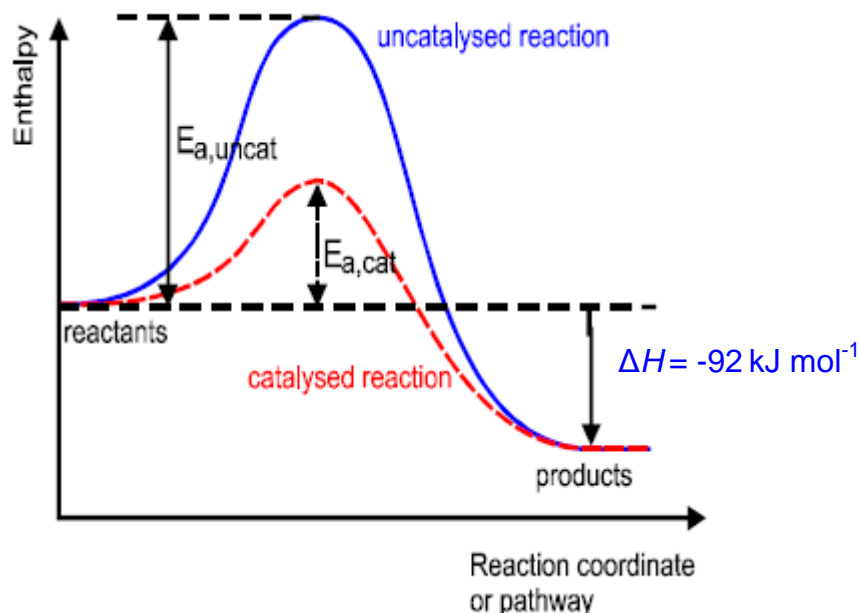
	$\text{N}_2(\text{g})$	+	$3\text{H}_2(\text{g})$	\rightleftharpoons	$2\text{NH}_3(\text{g})$
Initial amt / mol	100		300		0
Eqm amt / mol	60		180		80
Eqm [] / mol dm^{-3}	0.6		1.8		0.8

$$K_c = \frac{(0.8)^2}{(0.6)(1.8)^3} = 0.182 \text{ mol}^{-2} \text{ dm}^6$$

- (iii) State and explain how a decrease in temperature affects the yield of NH_3 .

By Le Chatelier's principle, decrease in temperature favours an exothermic reaction. Position of equilibrium shifts to the right, increasing the yield of NH_3 .

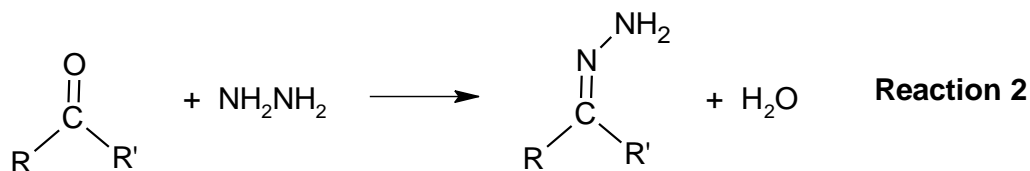
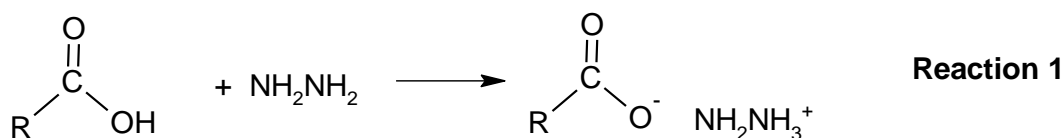
- (iv) Draw a fully labelled reaction pathway diagram for the catalysed reaction. On the same diagram, show how the reaction pathway diagram would differ if the catalyst was not used.



[7]

- (b) Hydrazine, N_2H_4 , has an ammonia-like odour and is derived from the same industrial chemical processes that manufacture ammonia.

Hydrazine can react with carboxylic acids and carbonyl compounds as shown in the following two reactions respectively.



where R and R' are alkyl groups.

- (i) State the types of reaction involved in **reactions 1** and **2**.

Reaction 1: acid-base

Reaction 2: condensation

- (ii) Compound **X**, $\text{C}_3\text{H}_6\text{O}_2$ reacts with both sodium and Tollens' reagent. On treatment with hot acidified potassium dichromate(VI), **X** forms **Y**, $\text{C}_3\text{H}_4\text{O}_3$.

Deduce the structures of **X** and **Y**, giving your reasoning.

Compound **X** undergoes redox reaction with sodium, so it contains an alcohol or carboxylic acid group.

X undergoes oxidation with Tollens' reagent, so it contains an aldehyde.

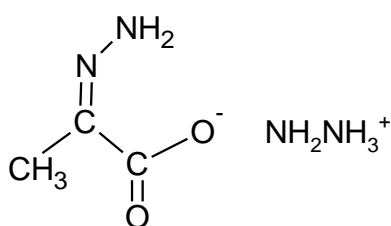
On oxidation, **X** forms **Y** with the loss of 2 H atoms and a gain of 1 O atom. **Y** contains a ketone and a carboxylic acid group.

X: $\text{CH}_3\text{CH}(\text{OH})\text{CHO}$

Y: $\text{CH}_3\text{COCO}_2\text{H}$

- (iii) Treatment of **Y** with hydrazine forms a compound **Z**, $\text{C}_3\text{H}_{10}\text{O}_2\text{N}_4$.

Using the information provided above, suggest a structure of **Z**.



Z

[7]

- (c) Hydrogen peroxide, which is isoelectronic with hydrazine, is a common cleansing agent.

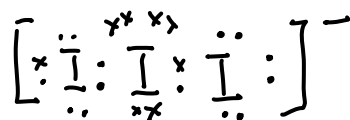
An acidified solution of hydrogen peroxide reacts with excess potassium iodide to form potassium triiodide, KI_3 as shown in the equation below.



- (i) State the bond angle in the H_2O_2 molecule and explain how this angle arises.

H-O-O bond angle is 104.5° . The 4 electron pairs around O atom try to arrange themselves as far apart as possible in a tetrahedral arrangement to minimise repulsion. However, lone pair-lone pair repulsion is greater than lone pair-bond pair repulsion which is greater than bond pair-bond pair repulsion. Thus, the bond angle is smaller than 109.5° .

- (ii) Draw the dot-and-cross diagram of the triiodide ion, I_3^- and state its shape.



Linear

- (iii) Potassium triiodide dissolves readily in water. Account for its high solubility, in terms of its interaction, with water molecules.

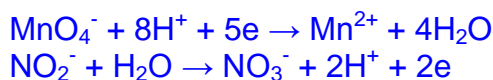
During solvation, polar water molecules surround the ions by forming ion-dipole interactions. This releases sufficient energy to overcome the ionic bonds and break down the ionic lattice structure. Thus, the solid dissolves.

[6]

[Total: 20]

- 7 (a) An unknown mass of calcium nitrite, $\text{Ca}(\text{NO}_2)_2$, was dissolved in water to form a 250 cm^3 solution. In the presence of an acid, 25.0 cm^3 of the solution required 40.00 cm^3 of $0.0200 \text{ mol dm}^{-3}$ potassium manganate(VII) to oxidise the nitrite ion, NO_2^- , to nitrate ion, NO_3^- .

- (i) Construct an equation for the reaction between acidified MnO_4^- ions and NO_2^- ions.



- (ii) State the changes in oxidation states that occur for manganese and nitrogen in the reaction.

Oxidation state of manganese decreases from +7 to +2.
Oxidation state of nitrogen increases from +3 to +5.

- (iii) Calculate the number of moles of calcium nitrite in present in 25.0 cm^3 of the solution.

$$\begin{aligned} \text{Amount of } \text{MnO}_4^- \text{ reacted} &= (40.00/1000)(0.0200) \\ &= 8.00 \times 10^{-4} \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Amount of } \text{NO}_2^- \text{ present in } 25.0 \text{ cm}^3 &= (5/2)(8.00 \times 10^{-4}) \\ &= 2.00 \times 10^{-3} \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{Amount of } \text{Ca}(\text{NO}_2)_2 \text{ present in } 25.0 \text{ cm}^3 &= (1/2)(2.00 \times 10^{-3}) \\ &= 1.00 \times 10^{-3} \text{ mol} \end{aligned}$$

- (iv) Hence, calculate the mass of calcium nitrite dissolved to form the 250 cm³ solution.

Amount of NO₂⁻ present in 250 cm³ solution = 2.00×10^{-2} mol

Amount of Ca(NO₂)₂ dissolved = $\frac{1}{2}(2.00 \times 10^{-2})$
= 1.00×10^{-2} mol

Mass of Ca(NO₂)₂ dissolved = $1.00 \times 10^{-2} \times 132.1$
= 1.32 g

[7]

- (b) (i) State and explain how the atomic radius varies across the third period of the Periodic Table from sodium to argon.

Atomic radius decreases across the period. Going across the period, nuclear charge increases. The shielding effect remains approximately constant. The valence electrons are held more tightly.

- (ii) By writing the full electronic configuration of a Mg²⁺ ion and a P³⁻ ion, state and explain how the ionic radius of a Mg²⁺ ion compares with that of a P³⁻ ion.

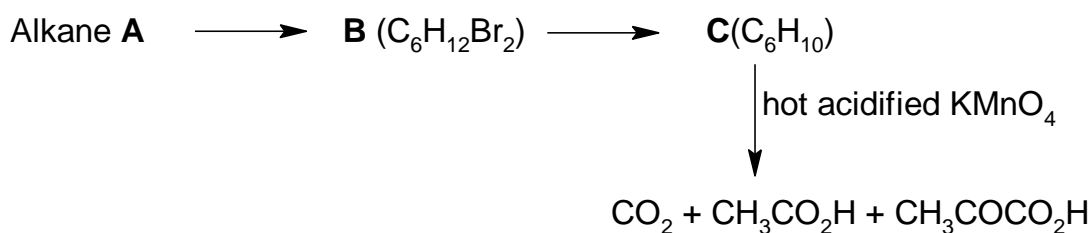
[6]

Mg²⁺: 1s² 2s² 2p⁶

P³⁻: 1s² 2s² 2p⁶ 3s² 3p⁶

P³⁻ has an additional shell of electrons. Therefore, P³⁻ has a larger ionic radius than Mg²⁺.

- (c) Consider the following reaction scheme, starting from alkane **A**.



- (i) Suggest reagents and conditions for the conversion of **A** to **B**.

Br₂, uv light

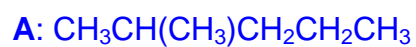
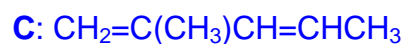
- (ii) State the type of reaction undergone when **B** is converted to **C**.

Elimination

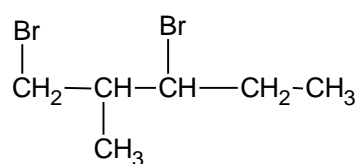
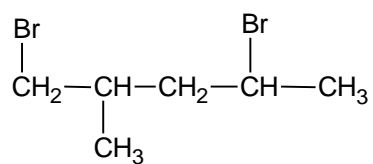
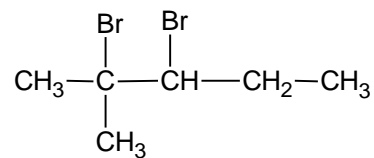
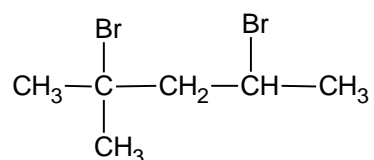
- (iii) Suggest reagents and conditions for the conversion of **B** to **C**.

NaOH in ethanol, heat

- (iv) Suggest a structure for compound **C**, and hence deduce the structure of compound **A**.



- (v) There are four possible isomers of $\text{C}_6\text{H}_{12}\text{Br}_2$ that could be converted to **C**. Draw the structures of **two** of them.



[7]

[Total: 20]

End of Paper