Class Adm No

Candidate Name:________________________________

H

millennia institute

2015 Preliminary Examination II

Pre-university 3

H2 CHEMISTRY **9647 / 03**

Paper 3 Free Response **22nd Sept 2015**

2 hours

Additional Materials: Data Booklet
Writing Paper
Cover Page
Graph Paper

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.
A Data Booklet is provided.
You are reminded of the need for good English and clear presentation in your answers.

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

Begin each question on a fresh sheet of paper.

1 The formation of a protective shield of ozone in the stratosphere shields life on Earth. However, the amount of ozone in the stratosphere decreases due to the release of chlorofluorocarbons (CFCs) from aerosol propellants and refrigerants. The mechanism that leads to ozone destruction is thought to involve three steps.

I. There is an initial homolytic breaking of a CFC molecule to give the chlorine radical.

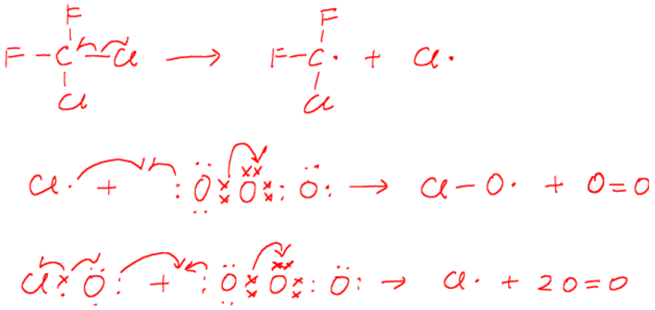
II. This is followed by the chain reaction between chlorine radical and O_3 to give C*l*O• and a gas.

III. The third step involves the reaction between C*l*O• and O_3 to give C*l*• and a gas.

Due to ozone destruction, CFCs have now been replaced by alkanes in many applications.

(a) Dichlorodifluoromethane is one of the CFCs present in refrigerants.

(i) Use the information given above to draw out the full mechanism that leads to ozone destruction. You are advised to use structural formulae for all species, so that it is clear which bonds are broken and which are formed. Indicate any unpaired electrons by a dot (•). [3]



(ii) State the type of reaction that is occurring. [1]

Free radical substitution

(iii) Write the overall equation for steps II and III to show the depletion of ozone. [1]

$2O_3 \rightarrow 3O_2$

(iv) Explain how one chlorine radical can lead to the destruction of a large number of ozone molecules. [1]

Each step in the reaction produces a new highly reactive free radical which can continue in a chain reaction.

(v) Suggest one potential hazard of using alkanes instead of CFCs. [1]

Alkanes are flammable.

(b) Draw a ‘dot-and-cross’ diagram to show the bonding in O_3 molecule and use VSEPR theory to predict the shape and bond angle. [3]

Shape: bent

Bond angle: <120°

(c) In an experiment to determine the enthalpy change of pentane, ΔH_c, a quantity of the fuel was burned underneath a copper can containing 200 g of water. It was found that the temperature of the water rose by 37 °C after 0.7 g of pentane had been burned.

(i) Calculate the ΔH_c of pentane from the data given. Ignore the heat capacity of the copper can, and use the value of 4.18 J g^{-1} K^{-1} for the specific heat capacity of water. [3]

Amount of pentane = 0.7 / (5(12.0) + 12) = 0.009722 mol

Q = 200 (4.18) (37)

= 30932 J

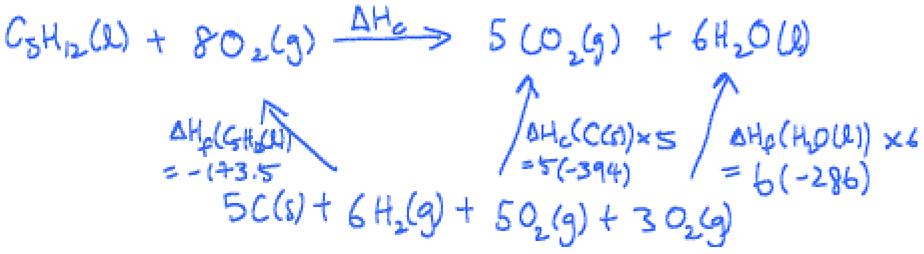
ΔH_c = - [(30932 / 0.009722)]

= -3180 kJ mol^{-1}

(ii) Use the following data to construct an energy cycle to calculate a value for the ΔH_c of pentane.

Enthalpy change of combustion of C(s)	-394 kJ mol^{-1}
Enthalpy change of formation of $H_2O(l)$	-286 kJ mol^{-1}
Enthalpy change of formation of $C_5H_{12}(l)$	-173.5 kJ mol^{-1}

[3]



ΔH_c (C_5H_{12}(l)) = -(-173.5) + 5(-394) + 6(-286)

= -3510 kJ mol^{-1}

(iii) Compare the values you calculated in **c(i)** and **(ii)** and suggest a reason for the discrepancy. [1]

Heat may be lost to the surroundings during the calorimetric experiment; thus the experimental value is less exothermic than the theoretical value.

(iv) Use the following data to calculate the entropy change of the system when pentane undergoes combustion.

Compound	**Entropy / J mol^{-1} K^{-1}**
$C_5H_{12}(l)$	263.5
$O_2(g)$	205.0
$H_2O(l)$	69.9
$CO_2(g)$	213.6

Hence, suggest how the spontaneity of the reaction changes with increasing temperature.

[3]

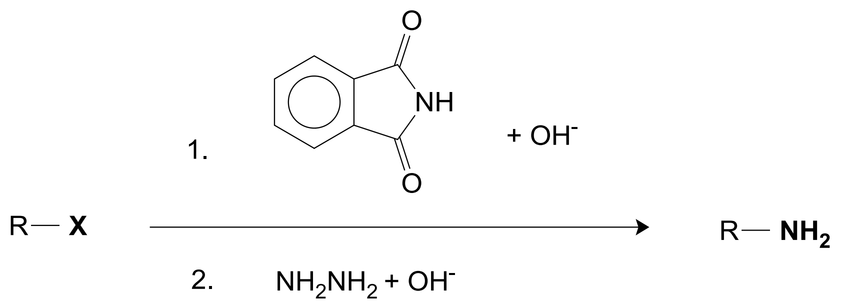
$\Delta S = [5(213.6) + 6(69.9)] - [263.5 + 8(205)]$

$= -416$ J mol^{-1} K^{-1}

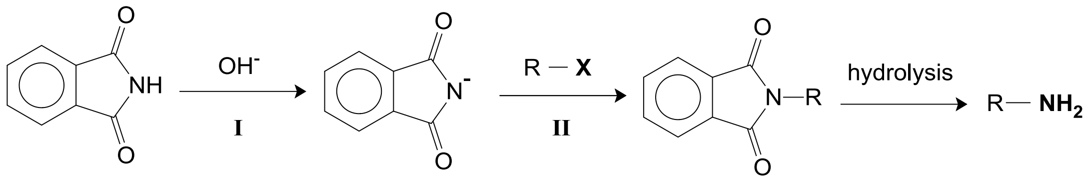
As $\underline{\Delta G = \Delta H - T\Delta S}$,
When T increases, $\underline{\Delta G \text{ becomes less negative}}$ (because both ΔH and ΔS is negative)
$\Rightarrow$ reaction becomes <u>less spontaneous</u>.

[Total: 20]

2 (a) In 1887, the German chemist Siegmund Gabriel discovered the Gabriel synthesis, which transforms primary alkyl halides to primary amines as shown below.



The reaction is thought to proceed through the following stages.



(i) State the type of reaction that takes place in stages **I** and **II**. [2]

Stage **I**: acid base reaction OR neutralisation

Stage **II**: nucleophilic substitution

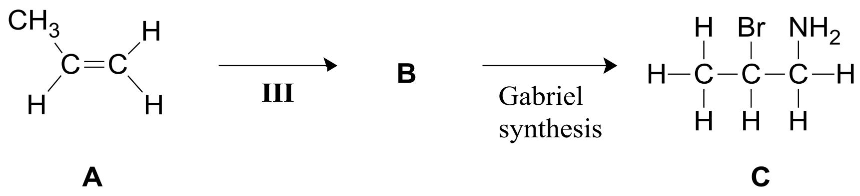
(ii) Explain why aryl amines cannot be prepared using this method. [1]

This is because the *p* orbitals of the halogen atom overlap with the π electron cloud of the benzene ring, strengthening the C-X bond, making the C-X bond in aryl halide too strong to be broken.

(iii) Both chloroethane and bromoethane can undergo Gabriel synthesis to form the respective primary amines. Describe and explain how the reactivities of the two reactions differ. [2]

Reactivity increases from C_2H_5Cl to C_2H_5Br as the C-X bond strength decreases down the group. The C-Br bond is weaker than C-Cl bond and thus, easier to break.

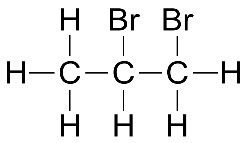
(b) The Gabriel synthesis can be used in the following synthesis.



(i) State the reagents and conditions for step **III**. [1]

$Br_2(l)$ in CCl_4, r.t.

(ii) Identify the structure of compound **B**. [1]



$$\begin{array}{ccccccc} & H & & Br & & Br & \\ & | & & | & & | & \\ H- & C & - & C & - & C & -H \\ & | & & | & & | & \\ & H & & H & & H & \end{array}$$

(iii) Suggest a simple test-tube reaction by which compounds **A** and **C** can be distinguished from each other. The reagents and conditions must be different from those used in step **III**. You should state all reagents and conditions for each test, and describe the expected observations. [3]

To a test tube containing the unknowns, add in Br_2(aq)

Compound A: orange solution decolourises to a colourless solution

Compound C: orange colour remains.

OR

To a test tube containing the unknowns, add in $KMnO_4$, H_2SO_4(aq), heat.

Compound A: purple colour decolourises to a colourless solution

Compound C: purple colour remains.

OR

To a test tube containing the unknowns, add in $KMnO_4$, NaOH(aq), cold.

Compound A: purple colour decolourises to give a brown precipitate

Compound C: purple colour remains.

(c) When a sample of an oxide of phosphorus, P_xO_y, was vapourised in a suitable apparatus at 178 °C and 36 kPa, the density of the gas was found to be 2.13 g dm^{-3}.

(i) Calculate the molar mass of the gas and hence suggest the identity of P_xO_y. [3]

$36 \times 1000 \times M = 2.13 \times 10^3 \times 8.31 \times (178 + 273)$

Molar mass of gas = 221.7 g mol^{-1}

Hence x = 4, y = 6

Identity: P_4O_6

(ii) Explain why the molar mass obtained in **(c)(i)** is different from the theoretical value. [1]

There is significant van der Waals forces of attraction between the P_4O_6 molecules.

(iii) Using your answer from **(c)(i)**, write an equation for the reaction between water and P_xO_y. Suggest the approximate pH of the resulting solution formed and describe the colour observed when Universal Indicator was added. [3]

$P_4O_6(s) + 6H_2O(l) \rightarrow 4H_3PO_3(aq)$

pH = 2-3

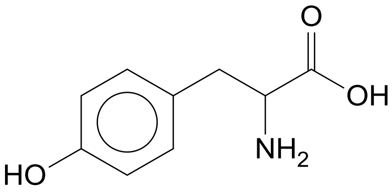
Universal Indicator: red or orange

(iv) At room temperature and pressure, P_xO_y exists as liquid but SiO_2 exists as solid. Explain. [3]

SiO_2 has a giant molecular structure with strong covalent bonds between atoms while P_xO_y has a simple molecular structure with weak van der Waals' forces of attraction between molecules. More energy is needed to break the strong covalent bonds; in SiO_2, thus SiO_2 exists as solid.

[Total: 20]

3 Tyrosine is a non-essential amino acid which acts as a building block for several important brain chemicals known as neurotransmitters including epinephrine, norepinephrine, and dopamine. It is involved in the structure of almost every protein in the body.



Tyrosine

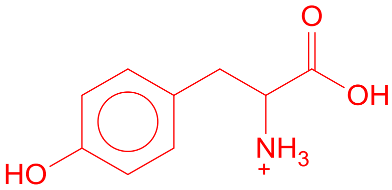
The three pK_a values associated with Tyrosine are 2.2, 9.1 and 10.1.

(a) What is meant by the term *non-essential amino acid*? [1]

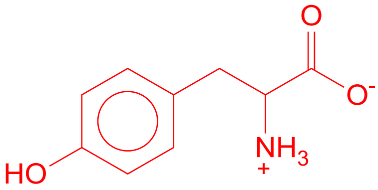
Amino acid that can be synthesised by the body in sufficient quantities.

(b) Use the pK_a values given to draw the structures of the major species present in solutions of Tyrosine at the following pH values.

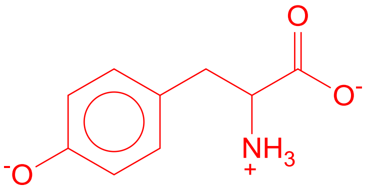
(i) pH 1.2



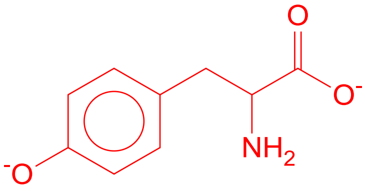
(ii) pH 5.7



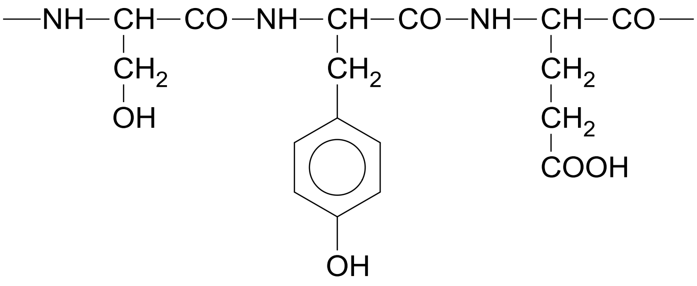
(iii) pH 9.5



(iv) pH 11.5 [4]



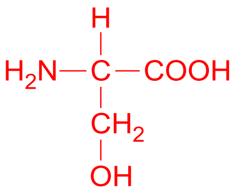
(c) The following structure represents part of the formula of a protein molecule containing Tyrosine.



(i) What reagents and conditions could you use to hydrolyse this protein into its amino acids? [1]

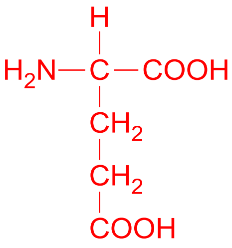
6 mol dm^{-3} HCl, prolong heating

(ii) Draw the structures of the two amino acid residues (other than Tyrosine) that would be produced by hydrolysing this segment of the protein. [2]



$H_2N-C(H)(CH_2OH)-COOH$

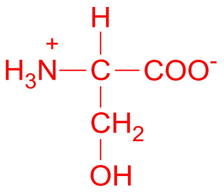
;



$H_2N-C(H)(CH_2CH_2COOH)-COOH$

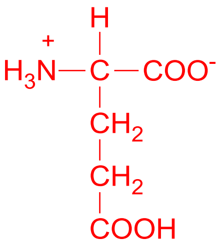
;

(iii) Amino acids exist as zwitterions in aqueous solution. Draw the structural formula of the zwitterion formed from one of the two amino acids in **(c)(ii)**, and write equations to show how it can act as a buffer. [3]



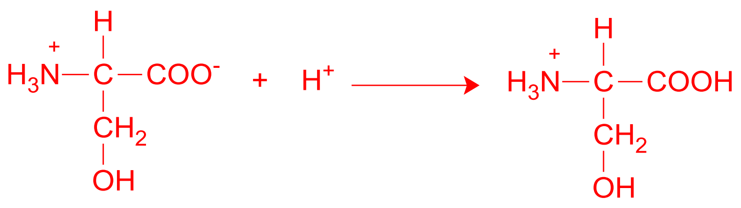
$H_3N^+-C(H)(CH_2OH)-COO^-$

or



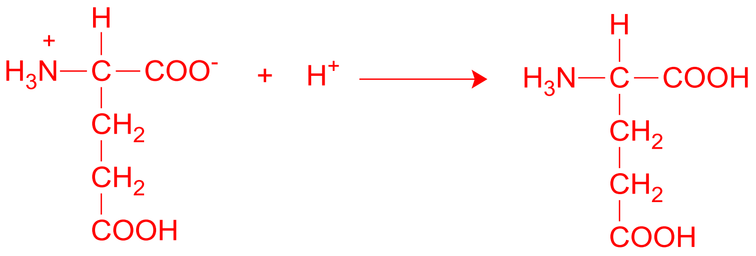
$H_3N^+-C(H)(CH_2CH_2COOH)-COO^-$

;



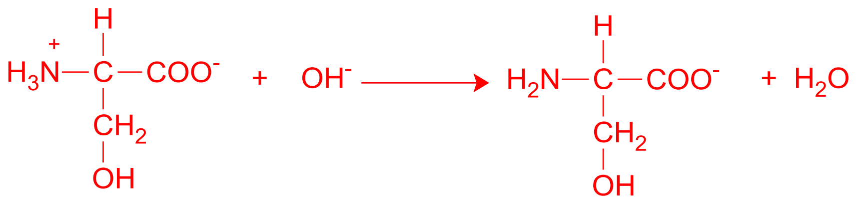
$$H_3\overset{+}{N}-\underset{\substack{|\\CH_2\\|\\OH}}{\overset{\substack{H\\|}}{C}}-COO^- + H^+ \longrightarrow H_3\overset{+}{N}-\underset{\substack{|\\CH_2\\|\\OH}}{\overset{\substack{H\\|}}{C}}-COOH$$

or



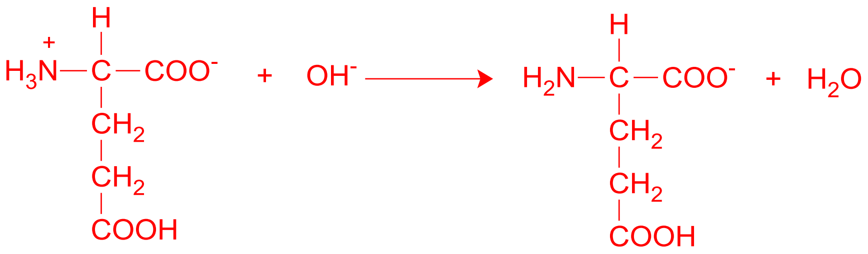
$$H_3\overset{+}{N}-\underset{\substack{|\\CH_2\\|\\CH_2\\|\\COOH}}{\overset{\substack{H\\|}}{C}}-COO^- + H^+ \longrightarrow H_3N-\underset{\substack{|\\CH_2\\|\\CH_2\\|\\COOH}}{\overset{\substack{H\\|}}{C}}-COOH$$

;



$$H_3\overset{+}{N}-\underset{\substack{|\\CH_2\\|\\OH}}{\overset{\substack{H\\|}}{C}}-COO^- + OH^- \longrightarrow H_2N-\underset{\substack{|\\CH_2\\|\\OH}}{\overset{\substack{H\\|}}{C}}-COO^- + H_2O$$

or



$$H_3\overset{+}{N}-\underset{\substack{|\\CH_2\\|\\CH_2\\|\\COOH}}{\overset{\substack{H\\|}}{C}}-COO^- + OH^- \longrightarrow H_2N-\underset{\substack{|\\CH_2\\|\\CH_2\\|\\COOH}}{\overset{\substack{H\\|}}{C}}-COO^- + H_2O$$

;

(iv) Show, with a diagram, how the side-chains on amino acids in **(c)(ii)** could be involved in the maintenance of the tertiary structure of the protein, stating the type of interactions involved. [1]

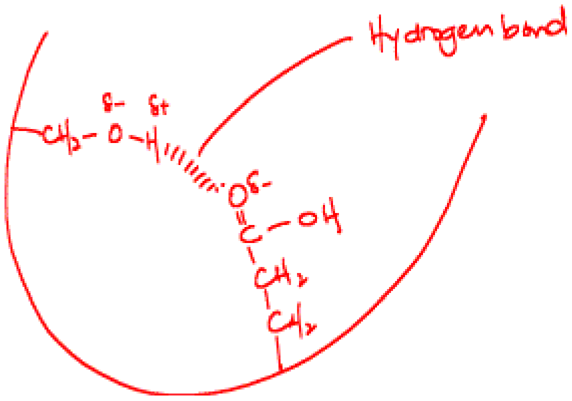
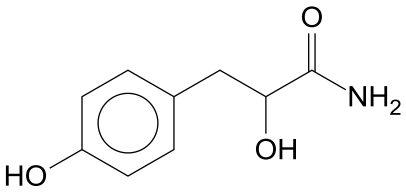


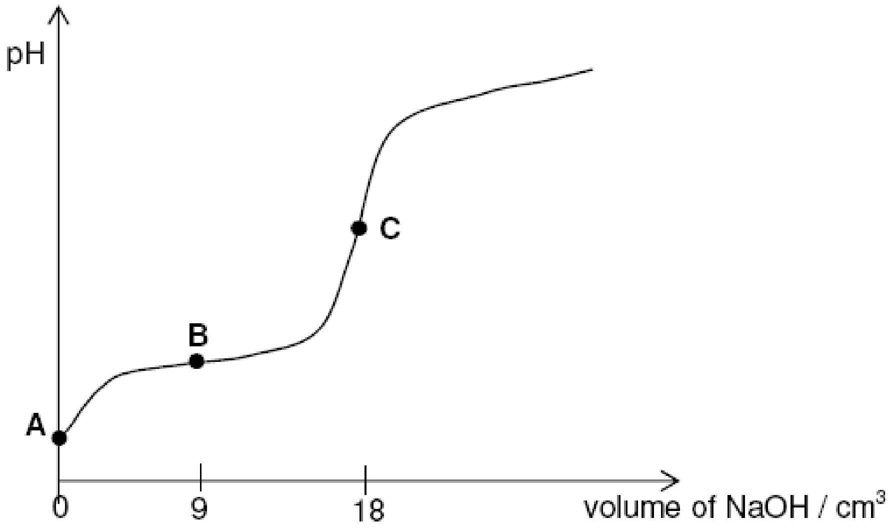
diagram plus stating hydrogen bond

(d) Compound **P**, an isomer of Tyrosine, is a monobasic acid.

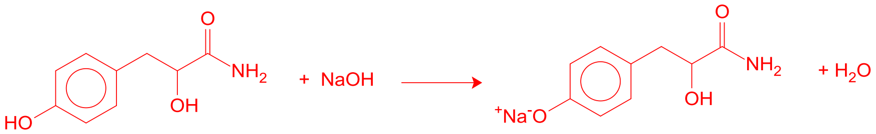


compound **P**

When *V* cm^3 of 0.100 mol dm^{-3} of solution of compound **P** was titrated against 0.200 mol dm^{-3} sodium hydroxide solution, the following titration curve was obtained.



(i) Write a balanced equation for the reaction between **P** and NaOH, showing the structures of all organic compounds. [1]



(ii) Determine the volume of the sample of **P** used in the titration, *V*. [1]

amount of P = amount of NaOH
V(0.1) = 18(0.2)
V = 36.0 cm^3

(iii) Given that the pH at point **A** is 3.22, calculate the K_a of **P**. [1]

$[H^+] = 10^{-3.22} = 6.026 \times 10^{-4}$ mol dm^{-3}

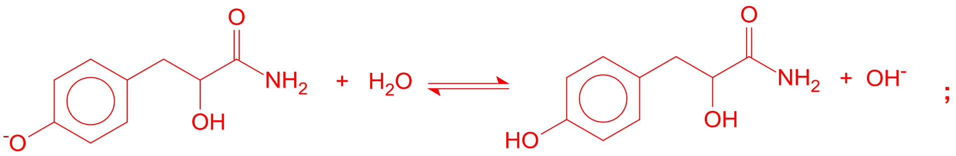
$K_a = \frac{(6.026\times10^{-4})^2}{0.1 - 6.026\times10^{-4}} = 3.65 \times 10^{-6}$ mol dm^{-3}

(iv) Determine the pH of the solution at point **B**. [1]

At point B, P is half neutralised, [salt] = [acid]
pH = pK_a = 5.44

(v) Predict if the pH at point **C** is greater or smaller than 7, and write an equation to support this, showing the structural formulae of all organic compounds. [2]

pH > 7



(e) In an experiment, equal volumes of 0.0120 mol dm^{-3} of aqueous NaOH and 0.0350 mol dm^{-3} of dilute $Mg(NO_3)_2$ were mixed. Predict, with reason, if precipitation would occur.

[K_{sp} of $Mg(OH)_2 = 1.80 \times 10^{-11}$ mol^3 dm^{-9}] [2]

$[OH^-] = 0.00600$ mol dm^{-3}
$[Mg^{2+}] = 0.0175$ mol dm^{-3}
$Q_{sp} = (0.0175)(0.00600)^2 = 6.30 \times 10^{-7}$ $mol^3\,dm^{-9}$
Since $Q_{sp} > K_{sp}$, precipitation will occur.

[Total: 20]

4 **(a)** Describe and explain how the thermal stability of the hydrogen halides varies down Group VII. [3]

Down Group VII,

size of atom increases in the order Cl < Br < I or

Bond length of H-X increases in the order HCl < HBr < HI

Bond strength of H-X decreases in the order HCl > HBr > HI

Thermal stability decreases in the order HCl > HBr > HI

(b) When gaseous HBr is bubbled into a solution **X**, a cream precipitate is formed. The resultant mixture is filtered and excess reagent **Y** is added to the cream precipitate. The cream precipitate dissolves.

Suggest the identities of solution **X** and reagent **Y**. [2]

X – $AgNO_3$

Y – concentrated NH_3

(c) An electrolytic cell was set up using two inert electrodes. The electrolyte was a solution made up of equal volumes of dilute HBr and dilute NaC*l*.

A current of 1.6 A was passed through the cell for 30 minutes.

(i) Write equations for the reaction taking place at the anode and cathode respectively. [2]

Cathode: $2H^+ + 2e \rightarrow H_2$
Anode: $2Br^- \rightarrow Br_2 + 2e$

(ii) Calculate the total volume of the gas produced from the electrolysis at room temperature and pressure, assuming there is no reaction between the products. [3]

Q = It = nF
amount of e = (1.6 × 30 × 60)/96500 = 0.02984 mol
amount of gases = 0.02984 mol/2
vol of gases = 0.01492 × 24 = 0.358 dm^3

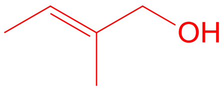
(d) Compound **U**, $C_5H_{10}O$, reacts with gaseous HBr to give **V**, $C_5H_{10}Br_2$. **U** also decolourises hot acidified sodium manganate(VII), giving two compounds, **W**, $C_2H_4O_2$, and **X**, $C_3H_4O_3$.

Both **W** and **X** reacts with solid calcium carbonate to give effervescence. When warm aqueous alkaline iodine is added to **W** and **X** separately, only **X** gives a yellow precipitate.

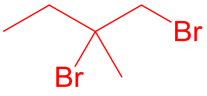
X reacts with $NaBH_4$ in methanol to give **Y**, $C_3H_6O_3$. When **Y** is refluxed with concentrated sulfuric acid, a sweet-smelling neutral compound **Z**, $C_6H_8O_4$ is formed.

Deduce the structures of **U** – **Z**, explaining the chemistry of the reactions. [10]

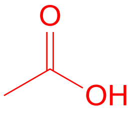
Information	**Deductions**
Compound **U**, $C_5H_{10}O$, reacts with gaseous HBr to give **V**, $C_5H_{10}Br_2$.	Electrophilic addition and nucleophilic substitution **U** contains alkene and alcohol
U also decolourises hot acidified sodium manganate(VII), giving two compounds, **W**, $C_2H_4O_2$, and **X**, $C_3H_4O_3$.	Oxidation **U** is an alkene
Both **W** and **X** reacts with solid calcium carbonate to give effervescence.	**W** and **X** have carboxylic acid
When warm aqueous alkaline iodine is added to **W** and **X** separately, only **X** gives a yellow precipitate.	Only **X** has CH_3CO-
X reacts with $NaBH_4$ in methanol to give **Y**, $C_3H_6O_3$.	Reduction **Y** contains secondary alcohol and carboxylic acid
When **Y** is refluxed with concentrated sulfuric acid, a sweet-smelling neutral compound **Z**, $C_6H_8O_4$ is formed.	**Z** is an ester



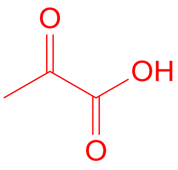
U



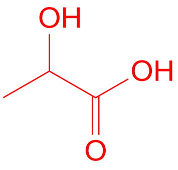
V



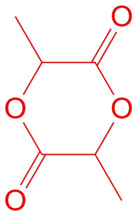
W



X



Y



Z

[Total: 20]

5 **(a)** Propanone, CH_3COCH_3, reacts with aqueous iodine in the presence of acid as follows:

$$CH_3COCH_3(aq) + I_2(aq) \xrightarrow{H^+(aq)} CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

In an experiment, 5.0 cm^3 of 2.0 mol dm^{-3} propanone, 10.0 cm^3 of 2.0 mol dm^{-3} hydrochloric acid and 10.0 cm^3 of 0.100 mol dm^{-3} iodine were mixed. The solution was made up to 100.0 cm^3 with deionised water.

10.0 cm^3 samples of the mixture were withdrawn with a pipette at 5 minute intervals and quenched immediately. The resulting solutions were then titrated with aqueous sodium thiosulfate. Care was taken to ensure that the experiment was carried out at constant temperature and pressure of 298K and 1 atm.

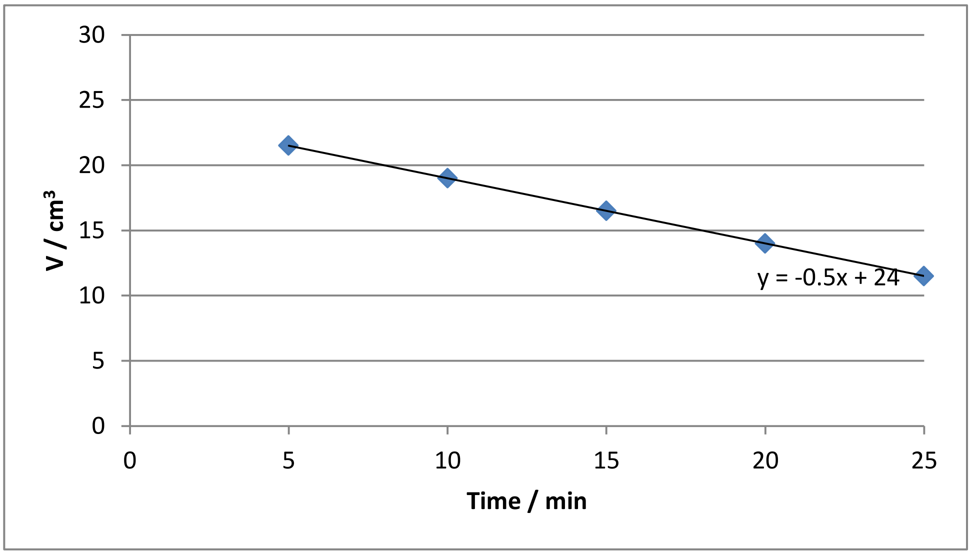
The results obtained are shown below.

Time / min	5	10	15	20	25
Volume of thiosulfate used, V / cm^3	21.50	19.00	16.50	14.00	11.50

(i) Suggest how the 10.0 cm^3 samples can be quenched. [1]

By reacting the samples with excess sodium carbonate or sodium hydrogen carbonate.

(ii) Plot a graph of V against time and determine the order of reaction with respect to iodine. Explain your answer. [3]



Reason: volume of $S_2O_3^{2-}$ used is proprotional to $[I_2]$, constant gradient implies rate is constant when concentration changes

zero order with respect to iodine

(iii) Using the graph you have plotted in **(a)(ii)** and the equation below,

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

calculate the concentration of aqueous sodium thiosulfate used in the titration. [3]

amount of iodine in 10.0 cm³ original soln = 0.100 × 10.0 /1000 = 0.001 mol

$[I_2]$ in the 100 cm³ bulk solution = 0.001 / 0.1 = 0.01 mol dm⁻³

amount of I_2 in the pipetted solution at the start = 0.01 × 10/1000 = 0.0001 mol

From the y-intercept, volume of thiosulfate required to react with 10.0 cm³ original solution = 24.00 cm³

amount of thiosulfate = 2 × amount of I_2

$24.00 \times [S_2O_3^{2-}] / 1000 = 2 \times 0.0001$

$[S_2O_3^{2-}] = 0.00833 \text{ mol dm}^{-3}$

(iv) The experiment was repeated at 308 K and 1 atm using the same set of reagents. Sketch the graph you would obtain on the same graph paper as in **(a)(ii)**. Label this graph as **(iv)**. Briefly explain your answer. [2]

Straight line graph with the same y-intercept and approximately double the gradient.

Reason: When temperature increases by 10 K, rate of reaction doubles hence gradient is doubled.

(b) Propanone can be converted into propane-1,2-diol in 3 steps. State the reagents and conditions for each step, and draw the structures of the intermediates. [5]

$$\begin{tikzcd}
CH_3COCH_3 \arrow[r, "LiAlH_4", "\text{dry ether}"'] & CH_3CH(OH)CH_3 \arrow[r, "\text{excess conc } H_2SO_4", "180^\circ C"'] & CH_2{=}CHCH_3 \arrow[d, "\text{cold } KMnO_4,\ NaOH(aq)"] \\
 & & CH_2(OH)CH(OH)CH_3
\end{tikzcd}$$

(c) Many transition metals and their compounds are useful catalysts. An aqueous solution of Co^{2+} is able to catalyse the reaction between iodide and peroxodisulfate, $S_2O_8^{2-}$, whereas Ca^{2+} cannot.

(i) Explain why Co^{2+} is a suitable catalyst but not Ca^{2+}? [1]

Co has variable oxidation states but Ca does not.

(ii) With reference to the *Data Booklet*, explain, with the aid of equations, how Co^{2+} is able to catalyse the reaction. [3]

Step 1:

$S_2O_8^{2-} + 2e \rightleftharpoons 2SO_4^{2-}$

$\underline{Co^{2+} \rightleftharpoons Co^{3+} + e}$

$S_2O_8^{2-} + 2Co^{2+} \rightarrow 2SO_4^{2-} + 2Co^{3+}$

$E^\circ_{cell} = +2.01 - (+1.82) = +0.19V$

Step 2:

$2I^- \rightleftharpoons I_2 + 2e$

$\underline{Co^{3+} + e \rightleftharpoons Co^{2+}}$

$2I^- + 2Co^{3+} \rightarrow I_2 + 2Co^{2+}$

$E^\circ_{cell} = +1.82 - (+0.54) = +1.28V$

(iii) Explain why an aqueous solution of Co^{2+} is coloured. [2]

The partially filled d-orbitals of Co^{2+} is split into two groups with a small energy gap when water ligand approaches the central metal ion.

Energy from the visible light region of the electromagnetic spectrum is absorbed to promote an electron from the lower energy d-orbital to the higher orbital d orbital. Light not absorbed will be seen as the colour of the complex.

[Total: 20]