Class Adm No

Candidate Name:________________________________

H

millennia institute

2015 Preliminary Examination II

Pre-university 3

H2 CHEMISTRY **9647 / 03**

Paper 3 Free Response **22^{nd} 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.

This question paper consists of **11** printed pages and **1** blank page.

Answer any **four** questions.

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 $ClO\bullet$ and a gas.
III. The third step involves the reaction between $ClO\bullet$ and O_3 to give $Cl\bullet$ 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Due to ozone destruction, CFCs have now been replaced by alkanes in many applications.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]

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

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

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

(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]

(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]

(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]

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

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

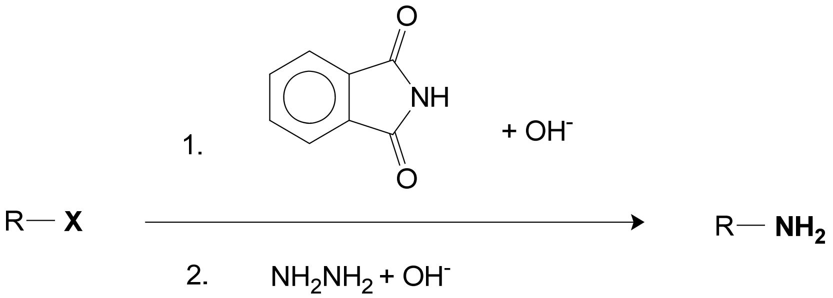
Compound	**Entropy / J mol^{-1} K^{-1}**
$C_5H_{12}(l)$	263.5
$O_2(g)$	205.0
$H_2O(l)$	69.9
$CO_2(g)$	213.6

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

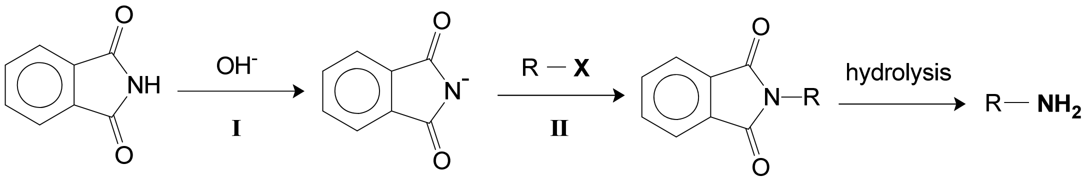
[3]

[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.

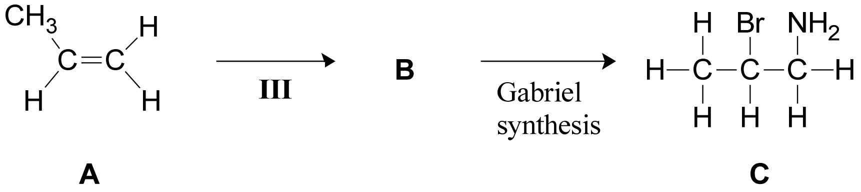


(i) State the type of reaction that takes place in stages **I** and **II**. [2]

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

(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]

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



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

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

(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]

(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]

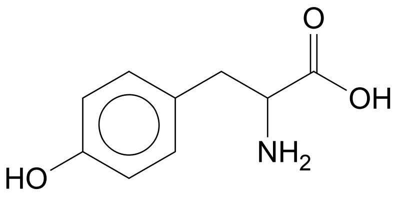
(ii) Explain why the molar mass obtained in **(c)(i)** is different from the theoretical value. [1]

(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]

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

[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]

(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.

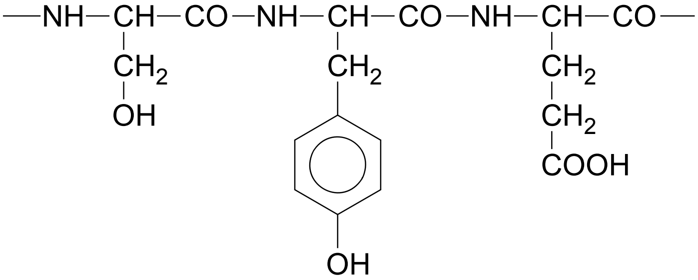
(i) pH 1.2

(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.



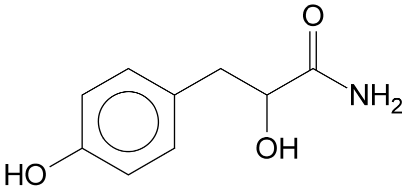
(i) What reagents and conditions could you use to hydrolyse this protein into its amino acids? [1]

(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]

(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]

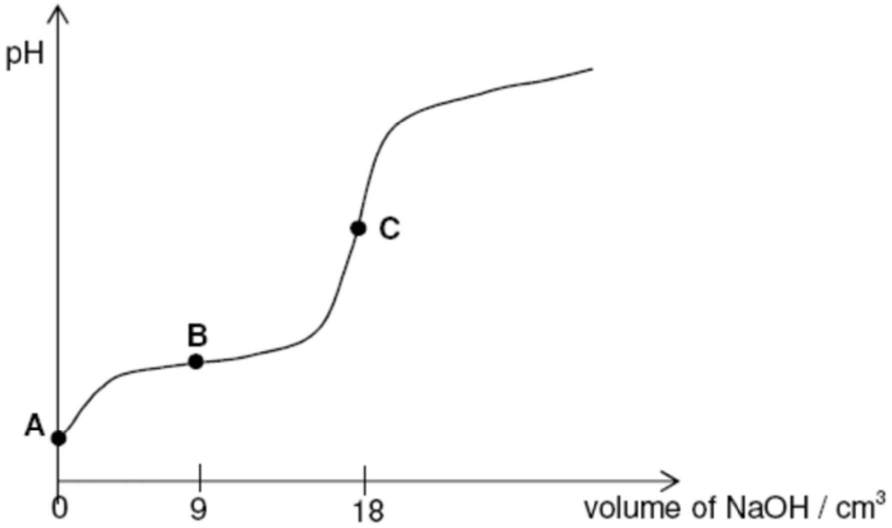
(iv) Show, with a diagram, how the side-chains on amino acids in **(c)(ii)** could be involved in the maintenance of the tertiary structure of the protein, stating the type of interactions involved. [1]

(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]

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

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

(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]

(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 $Mg(OH)_2$ = 1.80×10^{-11} mol^3 dm^{-9}] [2]

[Total: 20]

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

(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]

(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 Na*Cl*.
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]

(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]

(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]

[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]

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

(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]

(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]

(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]

(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]

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

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

[Total: 20]

END OF PAPER

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