Class Adm No

Candidate Name: _____

H

millennia institute

2017 Preliminary Examination II
Pre-university 3

H2 CHEMISTRY 9647/02

Paper 2 Structured Questions **12th Sept 2017**

2 hours

Candidates answer on the Question paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission number 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.

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.

Question	1	2	3	4	5	Total
Marks	/12	/14	/15	/11	/20	/72

1 Planning (P)

Hydrogen peroxide undergoes a redox reaction with acidified $KMnO_4$ as follows:

$$2MnO_4^-(aq) + 5H_2O_2(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5O_2(aq) + 8H_2O(l)$$

By itself, hydrogen peroxide decomposes slowly in accordance to the following equation:

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

It is found that the decomposition reaction is first order with respect to H_2O_2. The reaction can be accelerated by using solid manganese(IV) oxide as the catalyst.

(a) Write the rate equation for the decomposition of hydrogen peroxide.

…… [1]

Rate = k[H_2O_2]

(b) Using the information given, you are required to write a plan to determine the rate constant for the decomposition of hydrogen peroxide using the continuous titration method.

You may also assume that you are provided with:

- 250 cm^3 of 0.0100 mol dm^{-3} acidified $KMnO_4$;
- 250 cm^3 of 0.0250 mol dm^{-3} H_2O_2 solution;
- Solid manganese(IV) oxide;
- 25.0 cm^3 pipette;
- Stopwatch;
- the apparatus normally found in a school or college laboratory.

Your plan should include:

- practical details of how you would
  - determine if dilution of the reaction mixture is needed for titration against H_2O_2;
  - ensure the reaction is complete;
  - carry out the titration;
- a sketch of the graph you would expect to obtain;
- brief, but specific, details of how the results would then be used to obtain
  - the initial rate of reaction of decomposition in mol dm^{-3} $min^{-1,}$
  - the rate constant for the reaction

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…….. [11]

[Total: 12 marks]

$2MnO_4^-(aq) + 5H_2O_2(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5O_2(aq) + 8H_2O(l)$

Assuming that 25 cm^3 of 0.0250 mol dm^{-3} of H_2O_2 is used,

Amount of H_2O_2 present = 25/1000 x 0.025 = 0.000625 mol

Amount of MnO_4^- needed = 2/5 x 0.000625 = 0.00025 mol

Vol. of $KMnO_4$ needed = 0.00025/0.01 = 0.025 dm^3 ;

Since two volumes used are within the capacity of the apparatus used, no dilution of the solutions needed;

Procedure:

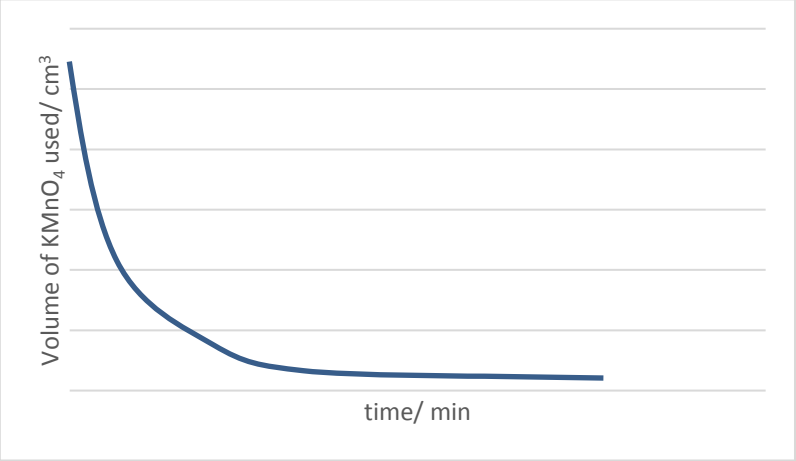
1. From the 250 cm^3 of 0.0250 mol dm^{-3} H_2O_2 solution, pipette 25.0 cm^3 into another conical flask.
2. Fill up the 50.00 cm^3 burette with the standard acidified $KMnO_4$ solution.
3. Take the initial burette reading.
4. Titrate the solution with acidified $KMnO_4$. Swirl continuously during the addition of the titrant.
5. Toward the end-point, add the $KMnO_4$ solution dropwise and swirl. Stop the addition of the titrant when one drop of titrant causes the solution in the conical flask to change from colourless to pale pink.
6. Record the final burette reading. Calculate the volume of acidified $KMnO_4$ solution needed to react with the hydrogen peroxide solution. (This titre volume would give us the concentration of the H_2O_2 solution at that instant of decomposition).

7. Add some solid manganese(IV) oxide into the 500 cm^3 conical flask containing the H_2O_2 solution. Start the stopwatch. Swirl gently.
8. At every 1 min (student can put a range from 30 s to 10 min) interval, pipette 25.0 cm^3 aliquots of the solution containing 20 cm^3 of cold water.
9. Repeat steps 2 to 7 at 1st, 2nd, 3rd, 4th and 5th min.

Table of results

Time/min	**0**	**1**	**2**	**3**	**4**	**5**
Initial burette reading/ cm^3						
Final burette reading/ cm^3						
Titre volume/ cm^3						

Sketch of graph



Since the gradient of the graph at t = 0 is ***x*** cm^3 min^{-1},

Initial rate of reaction = (***x***/1000 x 0.01 x 5/2) ÷ 25/1000 mol dm^{-3} min^{-1}

Since rate = k [H_2O_2],

k = [(***x***/1000 x 0.01 x 5/2) ÷ 25/1000] / 0.025

2 Hydrogen iodide can undergo decomposition to give a mixture of hydrogen gas and iodine gas.

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g) \qquad \Delta H = +12.0 \text{ kJ mol}^{-1}$$

(a) State Le Chatelier's Principle.

……

…… [1]

Le Chatelier's Principle states that when a system in equilibrium is disturbed, the position of the equilibrium will shift in a direction that tends to reduce that change so as to re-establish the equilibrium.

(b) Predict and explain the effect of the following changes on the position of the above equilibrium, if any.

(i) Increasing the temperature

……

……

…… [2]

When temperature of the system is increased, by Le Chatelier's Principle, the equilibrium position shifts to the right towards the endothermic reaction to remove the excess heat

(ii) Reducing the pressure

……

……

…… [1]

When pressure is reduced, by Le Chatelier's Principle, the equilibrium position does not shift as the number of gaseous particles on both the reactants and products are the same.

(iii) Addition of catalyst

……

……

…… [1]

Catalyst catalyses both forward and backward reactions to the same extent in a reversible reaction, hence there is no shift in equilibrium position.

(c) When 1.4 mol of hydrogen iodide is heated in a closed vessel at 550 K, the total pressure at equilibrium was 6 atm.

Given that the mole ratio of hydrogen iodide to iodine gas at equilibrium is 9:4, calculate the equilibrium constant, K_p, at 550 K.

[3]

$P_{H2} = P_{I2} = (4/17) \times 6 = 1.41$ atm ;

$P_{HI} = (9/17) \times 6 = 3.18$ atm ;

$K_p = (1.411)^2 / (3.176)^2 = 0.198$;

(d) Hydrogen chloride and hydrogen bromide also undergoes a similar decomposition to give hydrogen gas and its respective halogens.

Describe the trend in the volatility and colours of the halogens.

……

……

……

……[3]

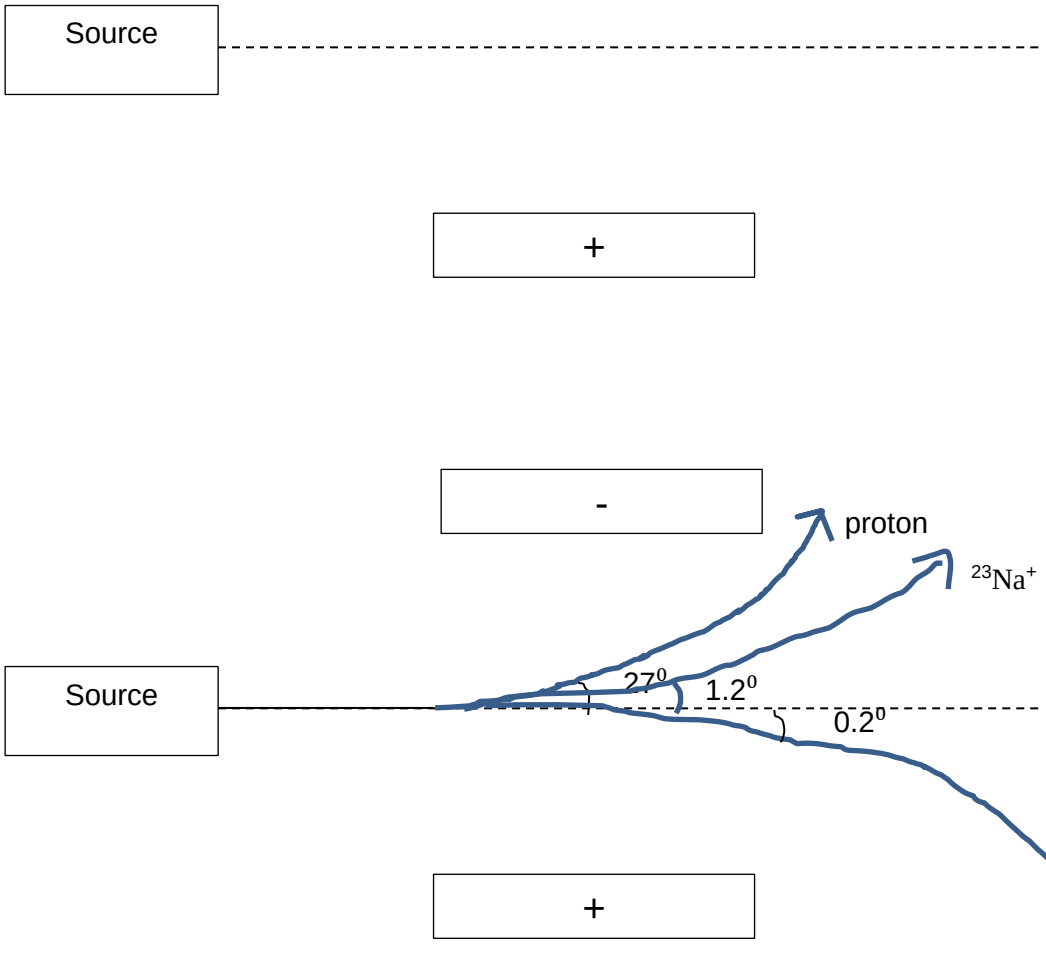
Volatility decreases down the group for halogens; colour intensity increases down the group;

Chlorine: yellowish-green gas

Bromine: reddish-brown liquid

(e) It was observed that a beam of protons gives an angle of 27° in the following electric field.

Indicate on the diagram below how a beam of protons, $^{127}I^-$ and $^{23}Na^+$ ions, travelling at the same speed, behave in the same electric field. Calculate the respective angles of deflection.



[3]

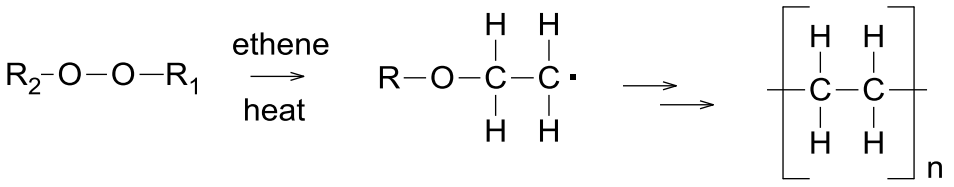
Angle of deflection for H^+ = 1/1 x 27° = 27°

Angle of deflection for Na^+ = 1/23 x 27° = 1.2°

Angle of deflection for I^- = 1/127 x 27° = 0.2°

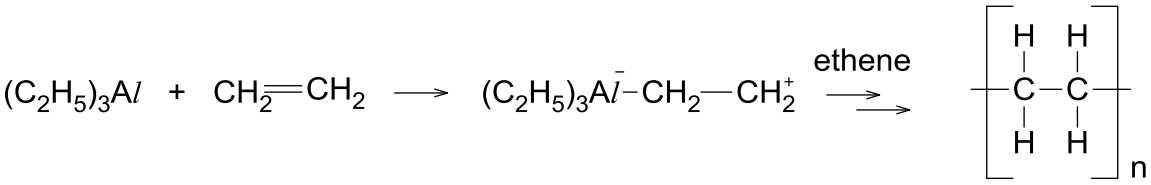
[Total: 14]

3 In 1933, chemists in Britain discovered that when ethene was subjected to high pressures in the presence of a trace amount of oxygen or organic peroxide, it produced low-density poly(ethene) (LDPE). The radical mechanism using organic peroxides is shown below.



LDPE

Using triethylaluminium, also known as Ziegler-Natta catalyst, developed by Karl Ziegler and Giulio Natta in 1953, ethene can be polymerised at much lower pressures to produce high-density poly(ethene) (HDPE). In the first step, triethylaluminium can accept the pair of π electrons of ethene to form a carbocation which is very similar to that found in the usual electrophilic addition reactions. This carbocation then undergoes an addition reaction with another ethene molecule. Eventually, long chains of ethene units form.



HDPE

The major differences between the structures of LDPE and HDPE are that:

- the average chain length of LDPE is much shorter than that of HDPE
- the chains of LDPE are branched, while the chains of HDPE are unbranched.

The table below compares the physical properties of LDPE and HDPE.

Property	**Polymer**	
	LDPE	**HDPE**
Density	Low	High
Melting Point	Approximately 130 ^{o}C	Approximately 160 ^{o}C
Tensile strength	Low	High
Flexibility	Very flexible	Much more rigid

(a) **(i)** Using structure and bonding, explain the difference in melting point between LDPE and HDPE.

……

……

……

…… [2]

Both have simple molecular structures with weak td-id forces of attraction between molecules. HDPE have are straight chain molecules which have **larger** surface area of contact between adjacent molecules than the branched-chain LDPE which is more spherical and packed less closely together. Hence, more energy is needed to break the more extensive td-id forces between HDPE, resulting in higher melting point.

Or

Both have simple molecular structures with weak td-id forces of attraction between molecules. HDPE has a longer chain length as compared to LDPE, thus resulting in a larger electron cloud size. Hence, more energy is needed to break the more extensive td-id forces between HDPE, resulting in higher melting point.

(ii) Suggest why LDPE has a lower density than HDPE.

……

……

……

…… [1]

Since HDPE chains are unbranched, they have a more regular arrangement, thus giving a more compact arrangement.

(b) **(i)** Write an equation to represent the first step in the radical mechanism.

…… [1]

(ii) With reference to the mechanism given, explain why the production of LDPE only starts upon heating.

……

…… [1]

Heat is needed to cause homolytic fission of the O-O bond of organic peroxide to produce the alkoxy radicals that will react with the ethene molecules.

(iii) Suggest why the chains of LDPE are branched.

……

…… [1]

During propagation step, due to the high reactivity of organic free radicals, the primary radical can abstract the hydrogen from the carbon atom in the middle of the chain.

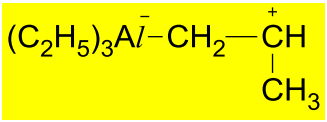
(c) **(i)** State the role of triethylaluminium in the reaction using Ziegler-Natta catalysts.

…… [1]

Triethylaluminium acts as an electrophile.

(ii) Similar to ethene, propene can be polymerised using the Ziegler-Natta catalysts. Show the structure of the carbocation intermediate formed in the first step.

[1]



(d) **Use the table of characteristics values for the infra-red absorption in the Data Booklet to answer this question.**

Infra-red absorptions can be used to identify functional groups in organic compounds. For example, ethanol shows absorptions at 1000-1300 cm^{-1} and 3230-3550 cm^{-1}.

Use the table to identify the infra-red absorption range that will be shown by

(i) Ethene but not by poly(ethene)

…… cm^{-1}

1610-1680 cm^{-1}

(ii) Propyl ethanoate but not by propene

…… cm^{-1}

1000-1300 and 1680-1750 cm^{-1}

[3]

(e) The four methods used to dispose polymers are incineration, recycling, depolymerisation and bacterial fermentation.

(i) Combustion of the polymers during incineration can lead to the formation of pollutants such as carbon monoxide which is toxic to humans, if the conditions are not carefully controlled.

In terms of the bonding involved, explain how carbon monoxide prevents oxygen from being transported around the body.

……

……

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…… [2]

Oxygen molecule is reversibly bonded to the haem group.

$\Rightarrow$ the Fe^{2+}-O_2 bond is weak allowing oxygen to be easily given up to the cells.

In the presence of CO, which is a stronger ligand than O_2, ligand exchange takes place and CO is strongly and irreversibly adsorbed at this site, destroying haemoglobin's oxygen carrying capacity.

(ii) State two advantages of recycling.

……

…… [2]

Recycling saves energy; recycling conserves the resources needed to process the new polymers; recycling produces less pollution to the air, land and water.

[Total: 15]

4 Iron is a transition element in Period 4 of the Periodic Table.

(a) Explain what is meant by a transition element.

…… [1]

A transition element is a **d-block element** which forms **at least one simple ion**, in compounds, with a **partially filled d-subshell**.

(b) Most iron oxide samples have a mole ratio of iron to oxygen in a range between 0.84 : 1 to 0.96 : 1. Suggest why these samples have variable compositions.

……....

…… [1]

Since iron can exist in both +2 and +3 oxidation states, some of the iron (II) ions in iron (II) oxide is oxidised to iron(III) ions.

(c) The reaction between peroxodisulfate ions, $S_2O_8^{2-}$ and iodide ions is very slow at room conditions, while addition of iron(III) ions can speed up the reaction rate.

(i) Suggest why the reaction between $S_2O_8^{2-}$ and iodide ions is very slow.

……

…… [1]

The reaction involves collision of ions of the same charge, $S_2O_8^{2-}$ and I^-, hence the number of effective collisions are small due to electronic repulsion.

(ii) Construct ionic equations to outline the catalytic role of iron(III) ions in the reaction.

……

…… [2]

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

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

(iii) State another iron species that can also act as a catalyst for the reaction.

…… [1]

Fe^{2+} ion

(d) When thiocyanate ligand, SCN^-, is added to the yellow solution of $FeCl_3$, a deep red solution **H** is obtained.

(i) Suggest the formula of the complex responsible for the deep red solution **H**.

…… [1]

$[Fe(SCN)(H_2O)_5]^{2+}$

(ii) State the type of reaction when $FeCl_3$ forms **H**.

…… [1]

Ligand exchange reaction

(iii) Explain why aqueous Fe^{3+} solutions are coloured.

……

……

……

…… [3]

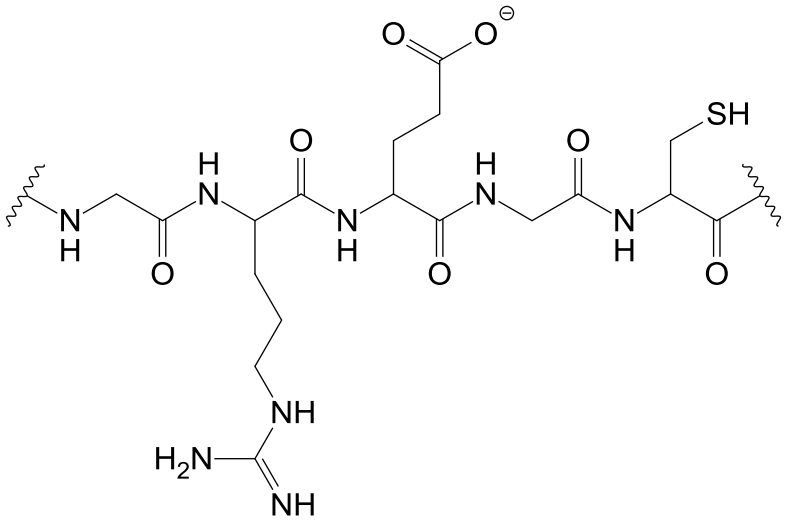
For $Fe^{3+}(aq)$, in the presence of ligands, partially-filled 3d orbitals in vanadium ions are split into two levels (i.e. become non–degenerate) with an energy gap, ΔE, falling within the energy range of the visible spectrum of light.

When light falls on the complex, a particular wavelength of light corresponding to ΔE is absorbed and this causes the electrons from the lower energy d orbitals to be promoted to a vacant higher energy level d orbital; a process known as the d–d electron transition. The colour observed is the complement of the colour absorbed.

[Total: 11]

5 The pancreas produces the protein insulin that regulates the metabolism of carbohydrates, fats and proteins.

The structure of a portion of the insulin molecule is shown below. This portion contains a number of amino acids.



(a) Describe the tertiary structure of insulin.

……

……

…… [2]

Tertiary structure refers to the overall 3D conformation of the protein involving folding or coiling of the chains via side-chain (R groups) interactions. Side-chain interactions which hold the tertiary structure in its shape are ionic bonds, disulfide, hydrogen bonding or van der Waals interactions;

(b) **(i)** What is meant by the term *denaturation*?

……

…… [1]

Denaturation of proteins involves the disruption of the secondary, tertiary and quarternary structures as these are held together by relatively weak attractions, forming random coil of polypeptide chain.

(ii) Suggest a brief outline of one method by which insulin may be denatured.

……

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…… [2]

Addition of H^+ or OH^- protonates or deprotonates the ionic R groups and hence disrupts the polar side chain interactions such as ionic bonds and hydrogen bonds holding the tertiary and quaternary structure of the protein. OR

When heat is applied, weak bonds, such as Van der Waals' forces and hydrogen bonds, holding together the quaternary, tertiary and secondary structures of the protein can be broken.

The increase in temperature increases the vibration of molecules, and the molecules can vibrate so strongly that the intermolecular interactions of the α–amino acid residues are destroyed causing denaturation. OR

Mechanical actions such as beating, whipping, shaking and kneading can also disrupt the intramolecular interactions within the protein molecules, destabilising the protein structure leading to the loss of the tertiary and secondary structures and hence denaturation. OR

The addition of heavy metal ions such as Ag^+, Hg^+, and As^+ which can combine permanently and preferentially with the sulfur atoms in -SH groups, destroying the disulfide (S-S) covalent bonds and thus changing the structure.

Heavy metals form salts or complex ions, hence breaking the ionic interactions

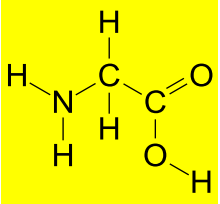
(iii) State the reagent and conditions required for complete hydrolysis of protein in the laboratory.

…… [1]

Heat under reflux with 6 mol dm^{-3} HCl for 6 hours

(iv) One of these amino acid residues are present more than once in the above portion of the insulin molecule. Draw a displayed formula for this amino acid residue.

[1]



(v) Explain, with the aid of equations, how the zwitterionic form of the amino acid in **(b)(iv)** act as a buffer.

…… [2]

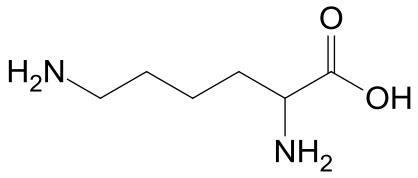
When little amount of acid is added,

$^{+}H_3NCH_2COO^{-} + H^{+} \rightarrow {}^{+}H_3NCH_2COOH$

When little amount of base is added,

$^{+}H_3NCH_2COO^{-} + OH^{-} \rightarrow H_2NCH_2COO^{-} + H_2O$

(c) Lysine is a α-amino acid that is used in the biosynthesis of proteins.



(i) Explain what is meant by the term pK_a as applied to a weak acid H*A*.

……

…… [1]

$pK_a = -\log K_a$

(ii) State the functional groups present in lysine.

…… [1]

Primary amine and carboxylic acid

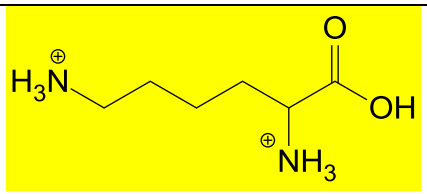
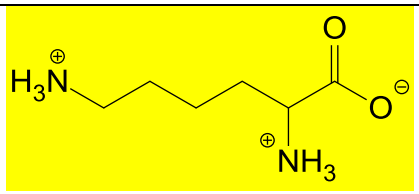
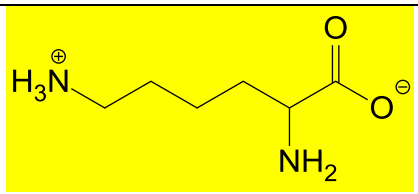
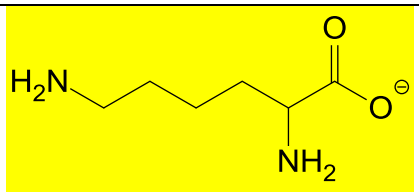
(iii) There are three pK_a values associated with lysine: 2.1, 8.9 and 10.5.

Make use of these pK_a values to suggest the major species present in the solutions of the amino acid with the following pH values.

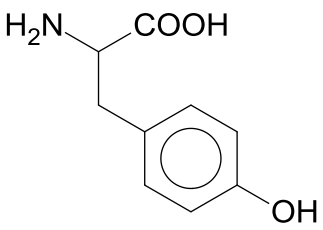
pH 1	**pH 4**

pH 9	pH 12

[4]

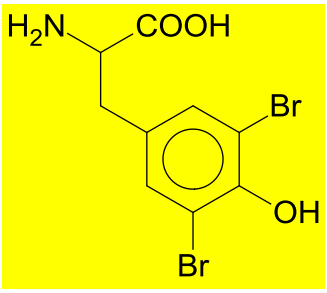
pH 1	pH 4
	
pH 9	**pH 12**
	

(d) Tyrosine is another amino acid present in insulin.



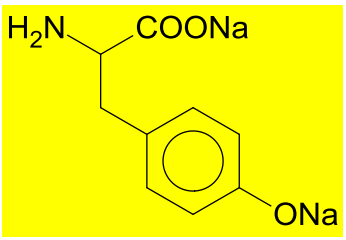
Draw the organic products when tyrosine undergoes reaction with

(i) $Br_2(aq)$



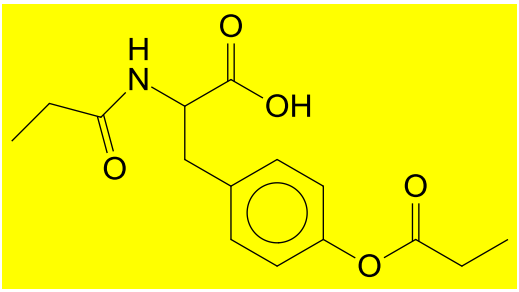
[1]

(ii) NaOH(aq)



[1]

(iii) excess CH_3CH_2COCl



[1]

(e) State the type of reactions for reaction with

$Br_2(aq)$ ……

NaOH(aq) …… [2]

Reaction with $Br_2(aq)$**:** electrophilic substitution

Reaction with NaOH(aq)**:** acid-base reaction

[Total: 20]

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