

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE
NAME

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CLASS

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INDEX
NO.

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TUTOR

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CHEMISTRY

9647/02

Paper 2 Structured

22 September 2014

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 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 **all** questions in the spaces provided.
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		
1	P	/12
2	/26	
3	/18	
4	/ 6	
5	/10	
		/60

This document consists of **18** printed pages and **0** blank page.

Answer **all** questions in the spaces provided.

1 Planning (P)

HA is a solid monoprotic acid. It is a weak organic acid with pK_a value of 4.15. Its solubility in water is only about 3.44 g dm^{-3} under normal laboratory temperature. Its sodium salt, NaA ($M_r = 144.0$), is soluble in water.

FA 1 is a fine powder of HA with NaA as an impurity.

FA 2 is $0.975 \text{ mol dm}^{-3}$ aqueous sodium hydroxide.

The reaction between HA and NaOH(aq) is exothermic. A preliminary experiment was conducted using 2.50 g of **FA 1** and 40 cm^3 of **FA 2**. The sample of **FA 1** dissolved completely to give a temperature rise of 6.3°C . The experiment was repeated two more times with different masses of **FA 1**. **FA 1** dissolved completely when 5.00 g were used but only partially when 5.50 g were used.

To determine the percentage by mass of HA in **FA 1**, $m \text{ g}$ of **FA 1** can be reacted with $V \text{ cm}^3$ of **FA 2** to obtain the temperature rise, ΔT . By repeating the experiments for different sets of m and V values, a suitable graph can be plotted to determine the set of m and V values required for complete neutralisation (the end-point).

- (a) If a series of five experiments is to be carried out, suggest suitable masses and volumes so that ΔT is **at least** 10°C for each experiment. Show relevant calculations.

Experiment	I	II	III	IV	V
Mass of FA 1 , m / g					
Volume of FA 2 , V / cm^3					

[3]

- (b) Using the information given above, you are required to write a plan to determine the temperature rise for Experiment I.

You may assume that you are provided with:

- **FA 1**;
- **FA 2**;
- polystyrene cup;
- the apparatus and chemicals normally found in a school or college laboratory.

In your plan, you should give essential details and include a labeled diagram of the experimental set-up.

Diagram of experimental set-up:

Plan for Experiment I:

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.....

[5]

[2]

- (d) **FA 3** is another solid sample of HA and NaA with a different percentage composition from **FA 1**.

The following data at the end-point were obtained from a series of eight experiments using **FA 3** and **FA 2**.

Mass of **FA 3** = 4.04 g

Volume of **FA 2** = 30 cm³

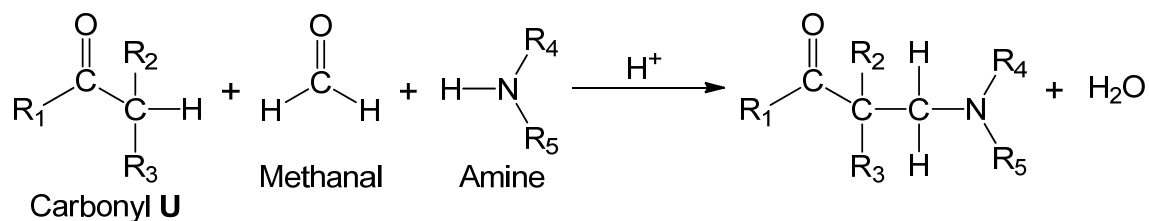
$\Delta T = 13.1\text{ }^{\circ}\text{C}$

Calculate the percentage by mass of HA in **FA 3**.

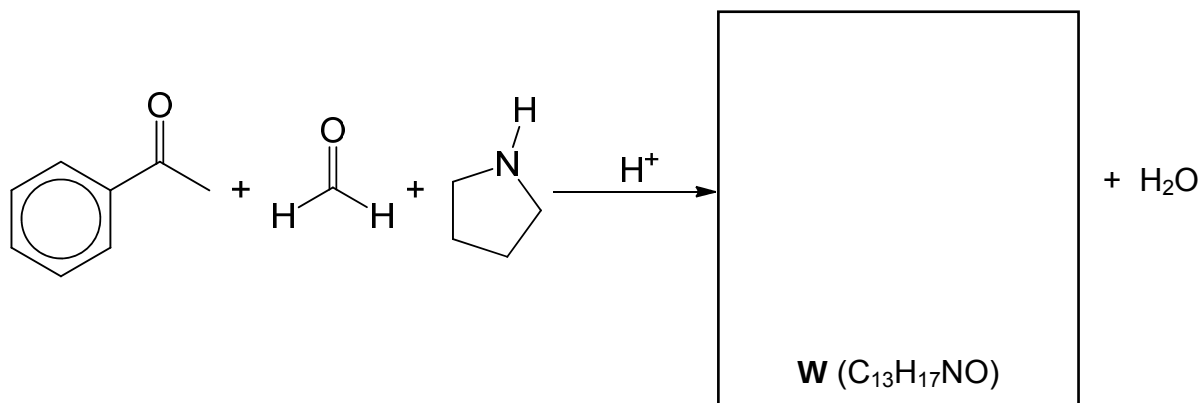
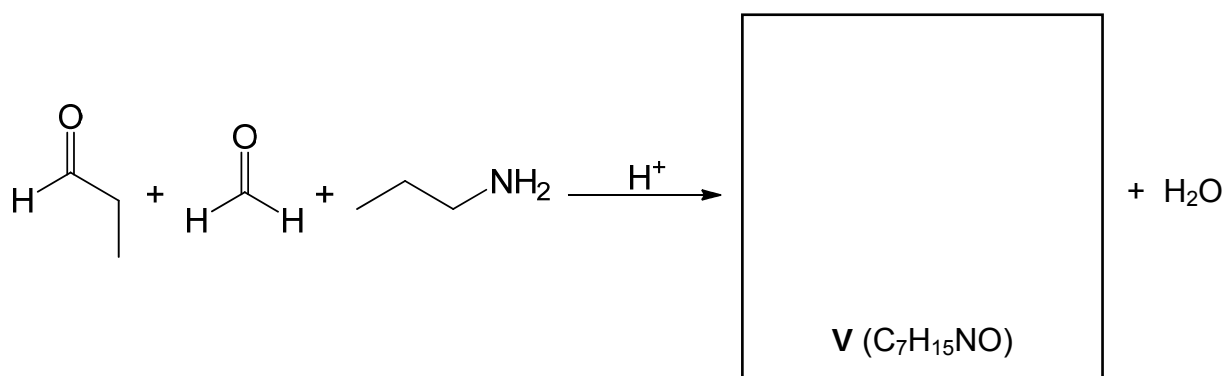
%HA =[2]

[Total: 12]

- 2 Mannich reaction is an organic reaction which consists of an amino alkylation of the hydrogen atom adjacent to a carbonyl functional group, by methanal and a primary amine, secondary amine or ammonia, in the presence of acid.

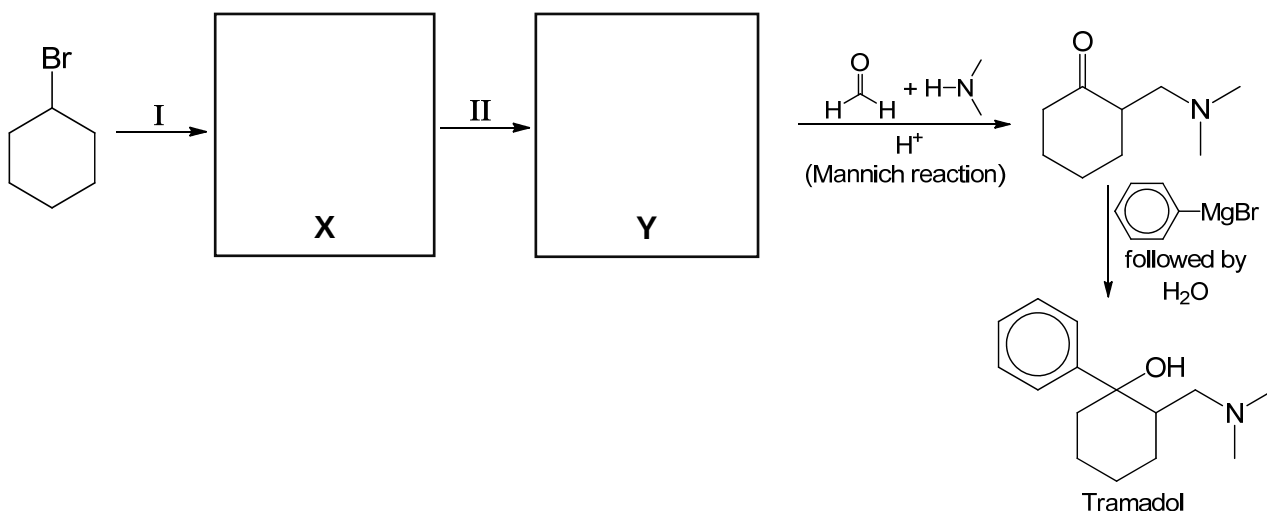


- (a) Predict the structures of **V** and **W** for each of the following Mannich reactions.



[2]

- (b) Tramadol is a narcotic-like pain reliever. It could be synthesised from bromocyclohexane via a four step synthetic route. The third step of the reaction scheme involves a Mannich reaction.



(i) Draw the structures of **X** and **Y** in the space above.

(ii) Suggest the reagents and conditions for **I** and **II**.

I

II

[4]

- (c) When aqueous silver nitrate is added to a solution containing sodium chloride, a white precipitate is formed. When excess aqueous ammonia is added to the resulting solution, the white precipitate dissolves to give solution **Z**.

(i) Suggest the identity of the white precipitate and complex ion found in solution **Z**.

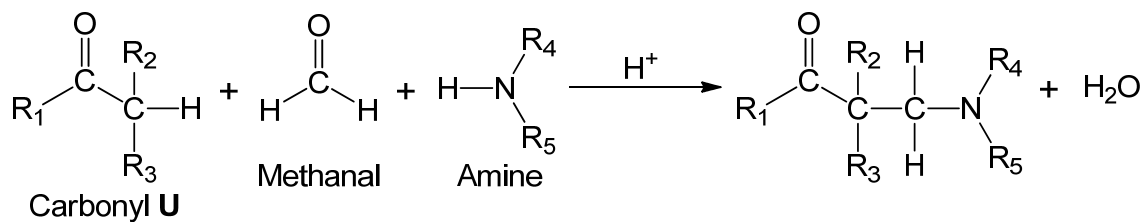
white precipitate

complex ion

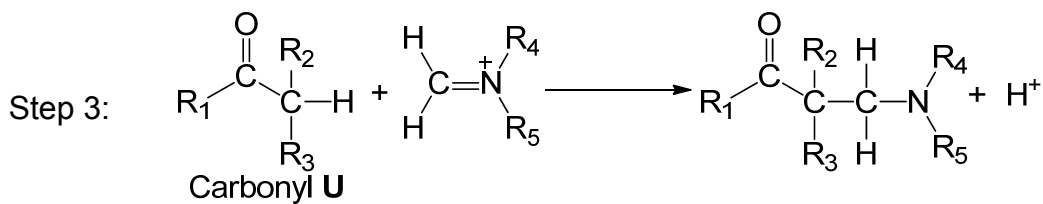
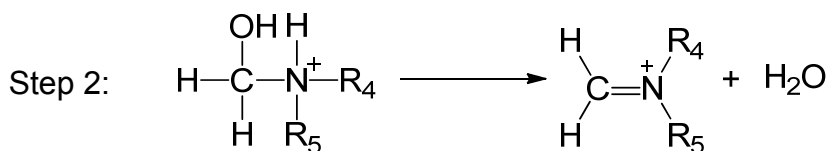
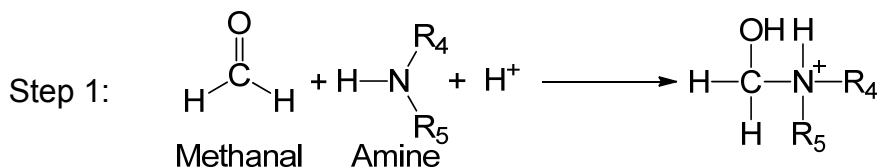
(ii) Solution **Z** is added separately to compounds **V** and **W** from (a) and warmed. State the observation and write equations for any reactions that occur.

[5]

This equation for Mannich reaction is repeated from *page 6*.



The proposed mechanism for Mannich reaction:



(d) Suggest the types of reaction that occurred in steps 1 and 2.

Step 1.....

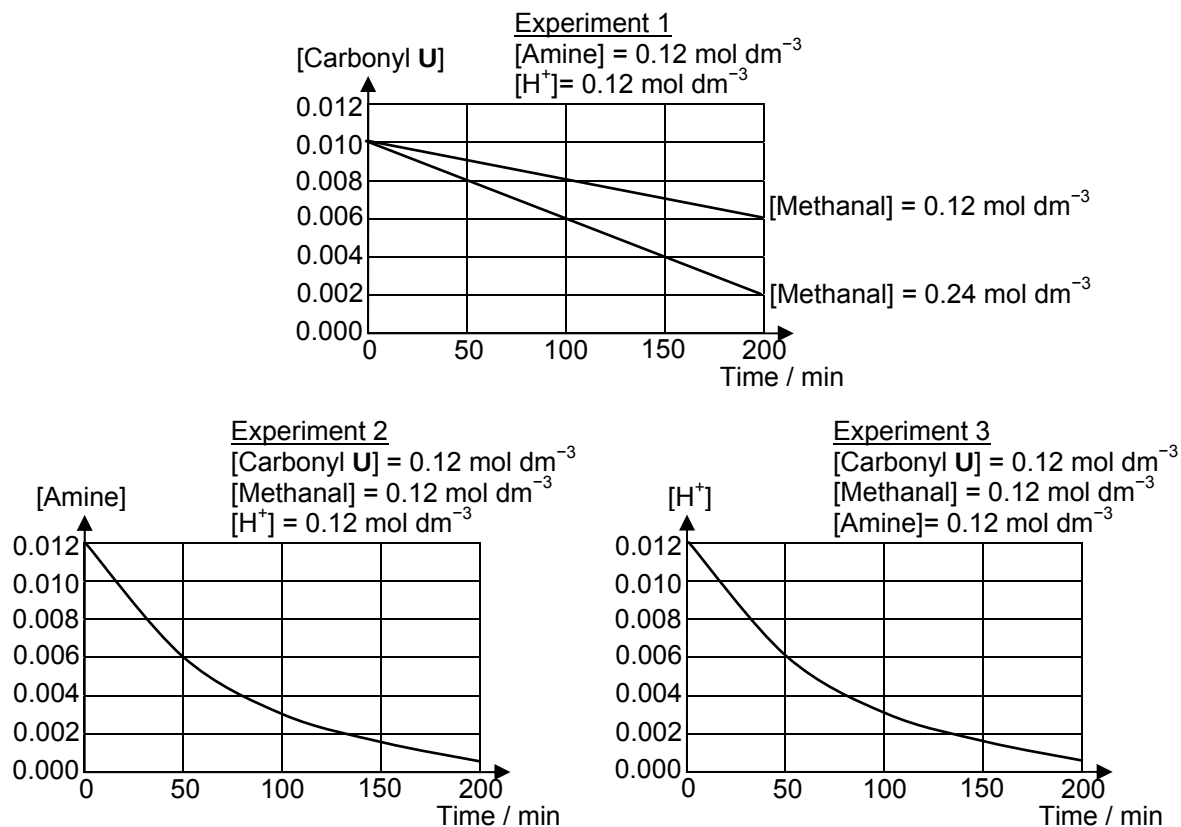
Step 2.....

[2]

- (e) The rate equation for the Mannich reaction can be expressed as

$$\text{rate} = k [\text{Carbonyl U}]^p [\text{Methanal}]^q [\text{Amine}]^r [\text{H}^+]^s$$

A chemist carried out a series of experiments to investigate the order of reaction with respect to each of the reactants.



- (i) Determine the values of p , q , r and s . (You may make use of the space provided on the next page.)

- (ii) State and explain which step of the mechanism is the rate-determining step.

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- (iii) Suggest why such a reaction is unusual.

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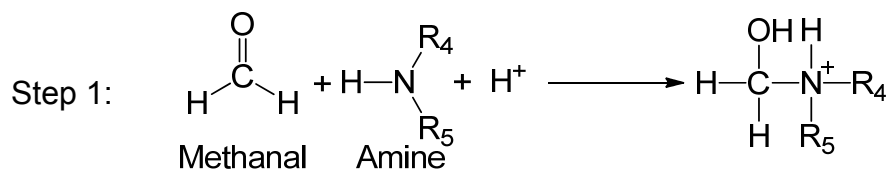
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- (iv) Using data from experiment 2, calculate the rate constant k , stating its units.

rate constant k =

[9]

- (f) The chemist decides to further investigate step 1 of the mechanism by replacing methanal with other carbonyl compounds, and using different amines. The concentrations of all the reactants are kept constant for all experiments.



experiment	carbonyl compound	amine	initial rate / $\times 10^{-4} \text{ mol dm}^{-3} \text{ min}^{-1}$
4	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}-\text{N} \\ \\ \text{CH}_3 \end{array}$	0.55
5	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C}-\text{C}-\text{H} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}-\text{N} \\ \\ \text{CH}_3 \end{array}$	1.02
6	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C}-\text{H} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}-\text{N} \\ \\ \text{CH}_3 \end{array}$	1.98
7	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C}-\text{H} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}-\text{N} \\ \\ \text{H} \end{array}$	1.01
8	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C}-\text{H} \end{array}$	NH_3	0.33

Suggest an explanation of the trend in the initial rate for

- (i) Experiments 4, 5 and 6

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.....

- (ii) Experiments 6, 7 and 8

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.....

[4]

[Total: 26]

- Solution J $\xrightarrow[\text{NaOH(aq)}]{\text{I}}$ alkaline pungent gas and yellow solution
- $\downarrow \text{II SO}_2$
- green solution $\xrightarrow[\text{NaOH(aq)}]{\text{III}}$ green ppt $\xrightarrow[\text{NaOH(aq) in excess}]{\text{IV}}$ dark green solution

-
-

H2 Chemistry 9647/02 NYJC J2/14 PX

On heating a sample of **J**, a violent reaction takes place with the evolution of steam and a diatomic gas **M** ($M_r = 28.0$). The residue from the reaction is a green powder that does not dissolve in water but dissolves in sulfuric acid to give a green solution. The addition of aqueous sodium hydroxide to this green solution gives the precipitate that had been produced in reaction **III**.

- (b) Suggest the identity of gas **M** hence write a balanced equation for the action of heat on **J**.

M

..... [2]

- (c) Draw a labelled diagram to show how you could measure the standard electrode potential of the $\text{Cr}^{3+}(\text{aq})/\text{Cr}^{2+}(\text{aq})$ system.

[3]

- (d) Chrome plating is a technique of electroplating a thin layer of chromium onto a metal or plastic object. The electrolyte is a solution of $\text{CrCl}_3(\text{aq})$. In a given electroplating experiment, a current of 4.0 A was passed through the circuit. How long would it take to plate a 20 cm^2 area of an object with 0.10 mm thickness?
[Density of chromium = 7.15 g cm^{-3}]

[2]

$$\begin{array}{ll} \text{Mn}^{3+} + e \rightleftharpoons \text{Mn}^{2+} & E^\bullet = +1.49 \text{ V} \\ \text{Fe}^{3+} + e \rightleftharpoons \text{Fe}^{2+} & E^\bullet = +0.77 \text{ V} \end{array}$$

The electrode potentials show that Mn(III) is a stronger oxidising agent than Fe(III). Using electronic configurations, suggest a possible reason for this observation.

[2]

[Total:18]

4(a) When chlorine is bubbled through potassium iodide, a brown solution is formed. On shaking the mixture in tetrachloromethane, a purple layer is observed.

(i) Write an equation for the reaction between chlorine and potassium iodide.

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(ii) What is the ion responsible for the brown solution?

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(iii) Explain why the purple layer is observed.

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[3]

(b) In an experiment, H_2S was reacted with 12.00 cm^3 of 0.30 mol dm^{-3} of an unknown bromate ion, BrO_x^- in acidic medium to form sulfur of mass 0.289 g as well as bromine solution.

Deduce the oxidation state of Br in BrO_x^- , and hence the value of x .

[3]

[Total: 6]

5(a) Insulin is a peptide hormone that is essential in regulating carbohydrates and fat metabolism in the body. It is composed of two peptide chains (e.g. chain A and chain B). Both the chains are joined together by two disulfide linkages, and another disulfide linkage is formed within chain A. In most species, the insulin is composed of 51 amino acids, where chain A consists of 21 amino acids while chain B consists of 30 amino acids.

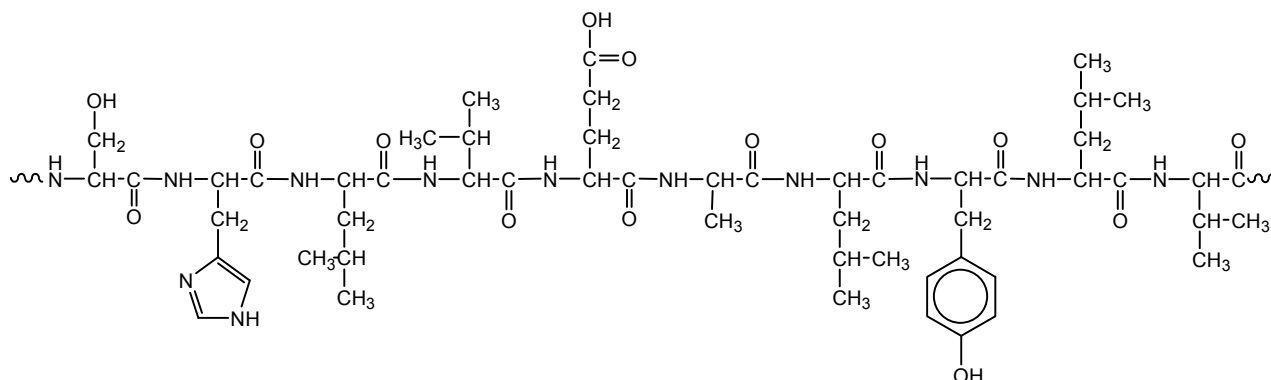
- (i)** Which amino acid forms the disulfide linkages? Illustrate this process by means of an equation.

.....

- (ii)** Suggest a method by which the disulfide linkage can be broken and how it brings about denaturation.

.....

The structure of a portion of chain B is shown below.



- (iii)** How many different amino acid residues are present in this portion of chain B?

.....

- (iv)** Using the above portion of chain B, draw the structures of the R groups that give rise to ionic bonds.

- (b) A nonapeptide **P** was analysed and it contained the following amino acids:

<i>amino acid</i>	<i>abbreviation</i>	<i>formula of R-group</i>	<i>number of residues</i>
Aspartic acid	Asp	$-\text{CH}_2\text{CO}_2\text{H}$	3
Lysine	Lys	$-(\text{CH}_2)_4\text{NH}_2$	2
Tyrosine	Tyr	$-\text{CH}_2-\text{C}_6\text{H}_4-\text{OH}$	3
Valine	Val	$-\text{CH}(\text{CH}_3)_2$	1

An enzyme **C** digests proteins or polypeptides at the carboxylic acid end of the amino acid tyrosine, Tyr. The following peptides were identified after digestion of **P** with **C**, and subsequent separation.

Asp –Val
Lys – Asp – Tyr
Tyr

Another enzyme **D** digests at the amino end of aspartic acid, Asp. The following peptides were identified after digestion of the same polypeptide **P** with **D**, and subsequent separation.

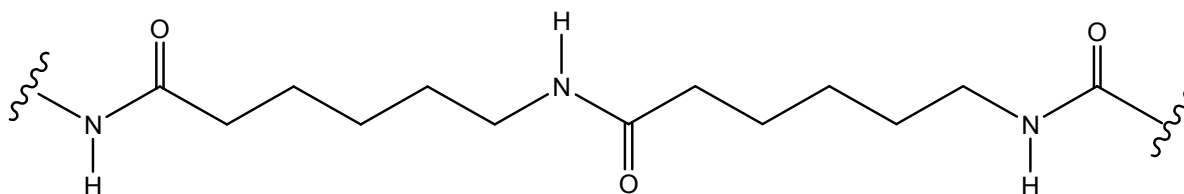
Asp-Tyr
Asp-Tyr-Lys
Asp-Val
Tyr-Lys

- (i) Use the above information to deduce the amino acid sequence of peptide **P** and explain your reasoning.

- (ii) Draw the displayed formula of the Lys-Asp-Tyr tripeptide at pH 11.

[5]

- (c) Nylon 6 is synthesised by ring opening polymerisation of caprolactam molecules. When caprolactam molecule polymerises, the ring breaks and the molecules join up in a continuous chain as shown below.



Suggest the structure of caprolactam.

[1]

[Total: 10]