VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATIONS
Higher 2

CANDIDATE NAME ……………………………………………..…………..

CT GROUP ……………………………..

CHEMISTRY

9729/02

Paper 2 Structured Questions

15 September 2023

Candidates answer on the Question Paper.

2 hours

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your index number, name and CT group in the spaces at the top of this page.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

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

For Examiner's Use	
1	**/ 7**
2	**/ 18**
3	**/ 10**
4	**/ 15**
5	**/ 15**
6	**/ 10**
Total	**/ 75**

This document consists of **24** printed pages and **2** blank pages.

1 **(a)** State three ways in which an ideal gas differs from a real gas.

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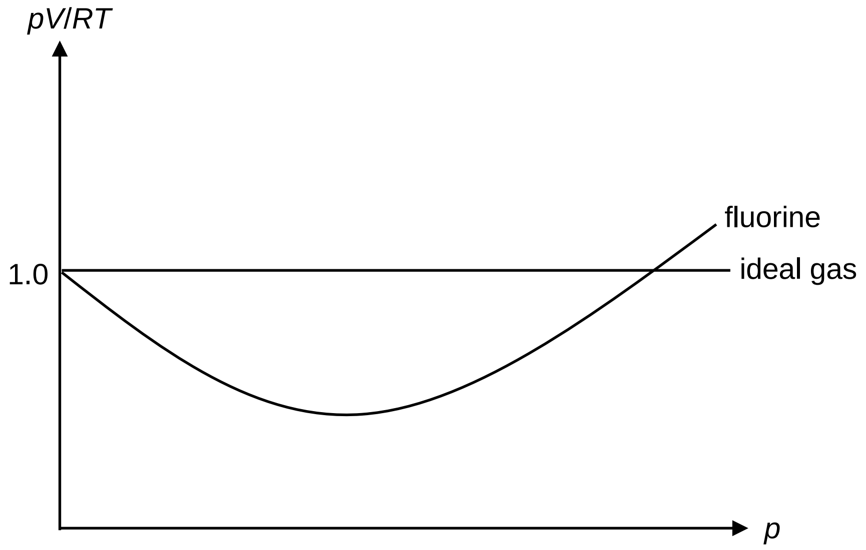
[3]

(b) **(i)** Draw a labelled diagram to show the significant force of attraction between **two** molecules of hydrogen fluoride. Include the name of the attraction in your diagram.

[2]

(ii) The value of pV/RT is plotted against p for 1 mol of an ideal gas and 1 mol of fluorine gas at 300 K, where p is the pressure and V is the volume of the gas.



On the same axes, sketch the variation of pV/RT against p for one mole of hydrogen fluoride, HF, at the same temperature of 300 K. Briefly explain your answer.

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[2]

[Total: 7]

2 **(a)** The type of bonding present in a binary compound can be predicted from the electronegativities of the elements involved. This can be shown on a van Arkel-Ketelaar triangle in **Figure 2.1**, which plots the difference in electronegativity, $\Delta\chi$, on the y-axis against the average electronegativity of the two elements, $\bar{\chi}$, on the x-axis.

In this triangle, the three corners represent the extremes of metallic, ionic, and covalent bonding, with caesium (Cs), caesium fluoride (CsF) and fluorine (F_2) at these corners.

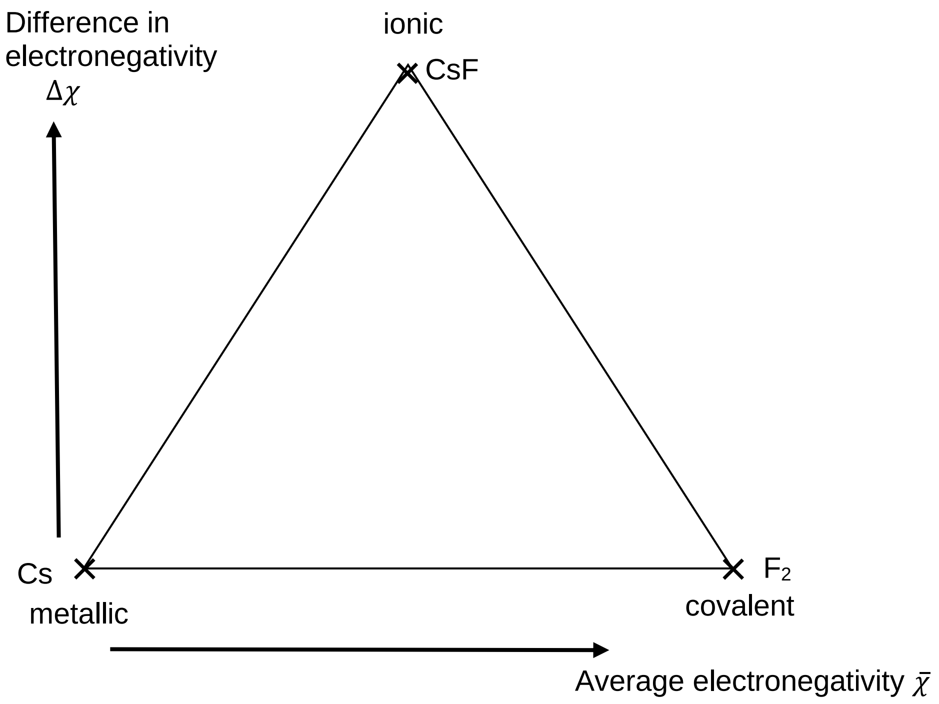

Figure 2.1

(i) Describe and explain the variation in electronegativity across the third period of the Periodic Table.

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[2]

(ii) State the type of bonding present in sodium fluoride (NaF), silicon tetrafluoride (SiF_4) and the magnesium-aluminium alloy (Mg-A*l*).

Type of bonding in NaF: ……………………………………

Type of bonding in SiF_4: ……………………………………

Type of bonding in Mg-A*l*: ………………………………….

[2]

(iii) Mark the approximate positions of NaF and SiF_4 on **Figure 2.1**

[2]

(b) Lattice energies can be obtained from constructing a Born-Haber cycle with the aid of experimental data. They can also be calculated theoretically from knowledge of the distances between the cations and anions in the crystal structure and the charge on each ion.

Table 2.1 shows the values of lattice energies for some compounds. These have been either determined from experimental data or theoretically calculated.

Table 2.1

compound	experimental value / kJ mol^{-1}	theoretical value / kJ mol^{-1}
NaC*l*	–781	–766
NaBr	–743	–730
NaI	–699	–685
CaC*l* (non-existent compound)	–	–687
CaCl_2	–	–
AgF	–967	–824
AgI	–889	–618

(i) Define, with the aid of an equation, the lattice energy of CaCl_2.

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[2]

(ii) The given data show the lattice energies of the sodium halides becoming less exothermic from $NaCl$ to NaI.

By quoting relevant data from the *Data Booklet*, predict and explain whether you expect the lattice energy of $CaCl_2$ to be more or less exothermic than that of $NaCl$.

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(iii) A larger difference between the experimental and theoretical values of the lattice energy is observed for AgI as compared to that for AgF.

Suggest why.

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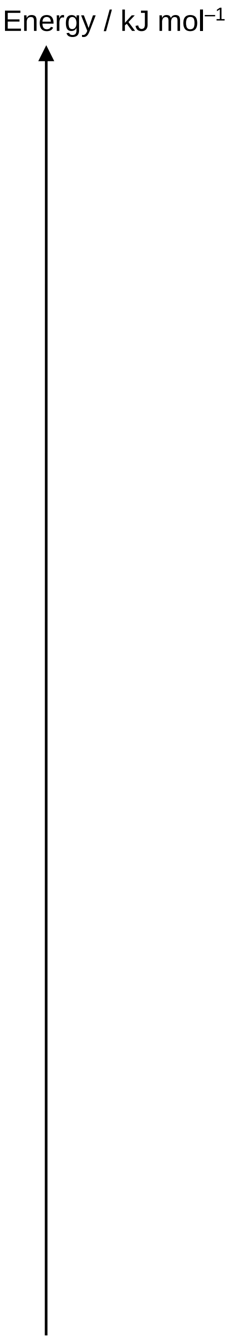
[2]

(iv) Using the data below as well as relevant data from **Table 2.1** and the *Data Booklet*, construct a Born-Haber cycle in the grid provided and calculate the enthalpy change of formation of solid calcium(I) chloride, CaC*l*(s).

enthalpy change of atomisation of calcium = +178 kJ mol^{-1}
first electron affinity of chlorine = –349 kJ mol^{-1}



[3]

(v) Calcium(I) chloride is not known to exist as it readily reacts as shown in the following equation.

$$2CaCl(s) \rightarrow Ca(s) + CaCl_2(s)$$

State, with justification, the type of reaction that has occurred.

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[1]

(c) One of the Group 2 chlorides, beryllium chloride, has many similar properties with aluminium chloride. In the vapour state at high temperatures, beryllium chloride, like aluminium chloride, exists as a dimer with the formula Be_2Cl_4. Around each beryllium atom is a trigonal planar arrangement.

(i) Explain how new bonds are formed between two molecules of beryllium chloride during the process of dimerisation.

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[1]

(ii) Draw the structure of the Be_2Cl_4 dimer.

[1]

[Total: 18]

3 Quinidine, **Q**, (M_r = 324.4) is a diacidic organic base commonly used as a drug for the control of heart rhythm disturbance. Due to the low solubility of quinidine, quinidine must be fully protonated to form $\mathbf{Q}H_2^{2+}$ before its concentration can be measured by carrying out a titration.

The pK_a values of the acidic groups in fully protonated quinidine are given below.

$$\mathbf{Q}H_2^{2+} \rightleftharpoons \mathbf{Q}H^+ + H^+ \qquad pK_{a1} = 4.00$$

$$\mathbf{Q}H^+ \rightleftharpoons \mathbf{Q} + H^+ \qquad pK_{a2} = 8.60$$

A 10.0 cm^3 sample containing 0.662 g of the fully protonated quinidine was titrated against aqueous NaOH. The first endpoint was seen after 20.00 cm^3 of aqueous NaOH was added.

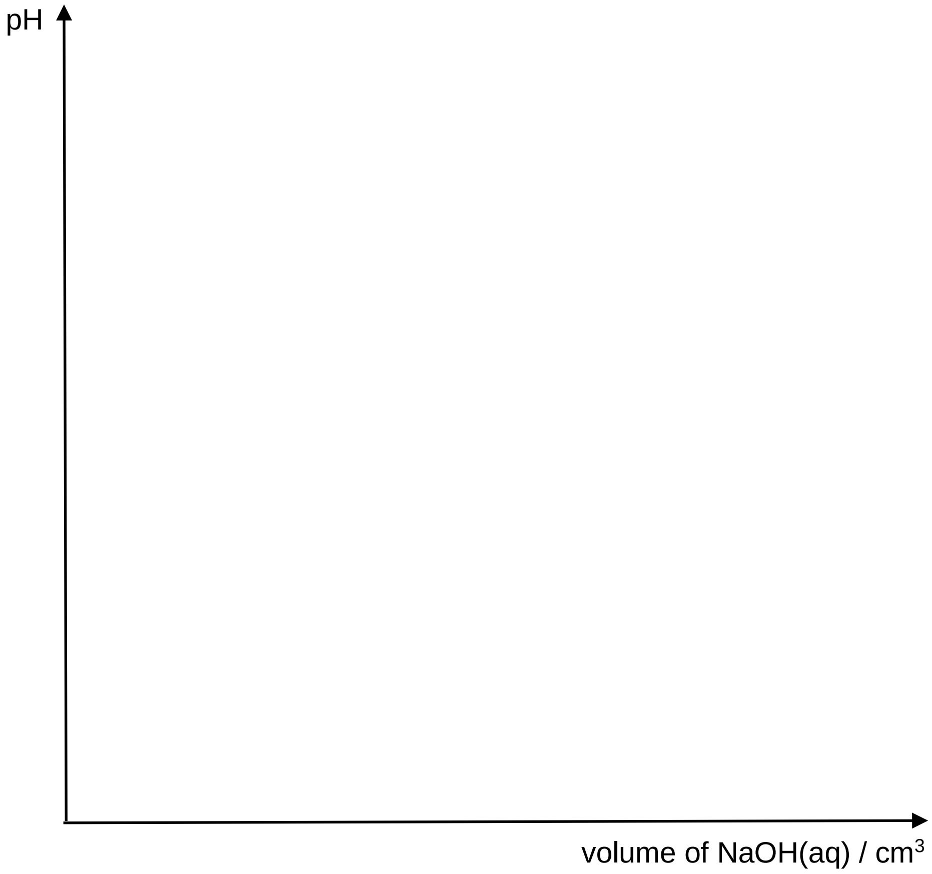
(a) Calculate the concentration of the fully protonated quinidine in the 10.0 cm^3 sample and hence determine its pH (ignore the effects of the second acid dissociation on the pH).

[2]

(b) **(i)** On the axes below, sketch a graph showing the variation of the pH of the solution as 50 cm^3 of aqueous NaOH was gradually added to the 10.0 cm^3 sample of protonated quinidine.

Indicate clearly

- the pH value obtained in **(a)**,
- the pH values where maximum buffer capacity is attained, and the corresponding volumes of aqueous NaOH added.



[3]

(ii) **Table 3.1** shows some acid–base indicators together with the pH ranges over which they change colour.

Table 3.1

name of indicator	**working pH range**
malachite green	0.2 – 1.8
methyl orange	3.1 – 4.4
bromothymol blue	6.0 – 7.6
thymolphthalein	9.3 – 10.6

Name a suitable indicator that can be used to detect the second endpoint of the titration. Explain your answer.

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[2]

(iii) Explain what is meant by the term *buffer solution*.

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[1]

(iv) When 8.00 cm^3 of the above aqueous NaOH is added to another 10.0 cm^3 sample of the above protonated quinidine solution, the resulting mixture is capable of acting as a buffer.

Explain, with the aid of two equations, the buffering action of the resulting mixture.

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[2]

[Total: 10]

4 **(a)** At 800 K, nitrogen monoxide reacts with hydrogen according to the equation.

$$2H_2(g) + 2NO(g) \rightarrow 2H_2O(l) + N_2(g)$$

Table 4.1 shows how the initial rate of this reaction depends on the initial partial pressures of the reactants.

Table 4.1

experiment	p_{H_2} / atm	p_{NO} / atm	initial rate / atm s^{-1}
1	0.64	1.60	1.50×10^{-7}
2	0.64	0.80	3.75×10^{-8}
3	0.32	1.60	7.50×10^{-8}

(i) Determine the order of reaction with respect to H_2 and NO.

Hence state, in terms of partial pressures, the rate equation for the reaction.

[3]

(ii) Using the rate equation, calculate a value for the rate constant. Include units in your answer.

[2]

(b) **(i)** Another experiment was carried out by reacting H_2 and NO at 800 K. The initial partial pressures of H_2 and NO were 0.099 atm and 2.10 atm respectively.

Calculate the time elapsed to reduce the partial pressure of H_2 to half of its initial value.

[2]

(ii) Suggest how the time calculated in **(b)(i)** would change when the initial partial pressure of H_2 is doubled. Explain your answer.

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[1]

(c) The following mechanism has been put forward for this reaction.

Step 1 (fast) $2NO \rightleftharpoons N_2O_2$

Step 2 (slow) $H_2 + N_2O_2 \rightarrow H_2O + N_2O$

Step 3 (fast) $H_2 + N_2O \rightarrow N_2 + H_2O$

Suggest, with reasoning, whether the mechanism fits the observed kinetics data.

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(d) The basicities of ammonia, ethylamine and phenylamine are different. **Table 4.2** shows the K_b values of these three compounds.

Table 4.2

Compound	**K_b / mol dm^{-3}**
NH_3	1.74×10^{-5}
$CH_3CH_2NH_2$	6.40×10^{-4}
$C_6H_5NH_2$	4.30×10^{-10}

(i) Explain the relative basicities of these three compounds in terms of their structures.

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(ii) Suggest the structure formulae of the products of the following reactions.

$C_2H_5NH_2$ + $(CH_3)_2CHCOCl$

$C_6H_5NH_2$ + $Br_2(aq)$

[2]

[Total: 15]

5 **(a)** A compound **S** with the molecular formula $C_7H_{15}Cl$ has one chiral carbon. An optically pure sample containing only one enantiomer of **S** was heated with excess aqueous KOH for a prolonged duration so that all the **S** initially present was completely reacted.

Upon analysis, it was found that the resulting solution does **not** rotate plane-polarised light.

(i) Based on the given information, **S** has two possible structures. Draw these two structures.

[2]

(ii) Using any one structure that you have drawn in **(a)(i)**, outline the mechanism that has occurred in the reaction. Your answer should show clearly relevant lone pairs, dipole and curly arrows to indicate the movement of electron pairs.

[2]

(iii) With reference to the mechanism that you have described in **(a)(ii)**, explain why the resulting solution obtained after the reaction does not rotate plane-polarised light.

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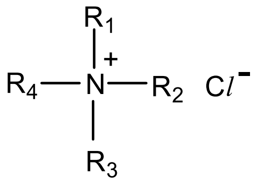
[2]

(b) Organohalogen-compounds such as **S** are important in the production of quaternary ammonium compounds, QACs. The general structure of a QAC formed from a chloroalkane is shown below:



$$R_4-\overset{\overset{R_1}{|}}{\underset{\underset{R_3}{|}}{N^+}}-R_2\ \ Cl^-$$

R_1, R_2, R_3 and R_4 represent alkyl groups which may be the same or different from one another.

An attempt to prepare QACs was made by reacting dimethylamine, $(CH_3)_2NH$, with a 1:1 molar mixture of 1–chloropropane and 1–chlorobutane. The conditions used are such that all the $(CH_3)_2NH$ is converted to a QAC.

(i) Three possible QACs, **A**, **B** and **C**, can be formed. Draw their skeletal formulae in the space below.

	Skeletal formula
A	
B	
C	

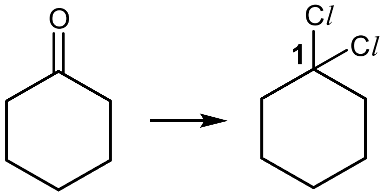
[3]

(ii) Assuming that 1-chloropropane and 1-chlorobutane react with $(CH_3)_2NH$ at the same rate, predict the ratio in which the three QACs will be formed.

Show your working and refer clearly to the structures by using the letters provided in **(b)(i)**.

[2]

(c) PCl_5 reacts with ketones in a 1 : 1 molar ratio to give gem-dichlorides. A gem-dichloride contains two chlorine atoms bonded to the same carbon atom. For example, cyclohexanone reacts with PCl_5 to give 1, 1–dichlorocyclohexane:



The carbon bonded to the two chlorine atoms is labelled **1**.

(i) Suggest the phosphorus-containing by-product of this reaction.

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[1]

(ii) When 1, 1–dichlorocyclohexane is heated with an excess of ethanolic KOH, a product **T**, C_6H_9Cl, is obtained and no further loss of chlorine occurs. **T** decolourises bromine water.

Draw the structure of **T**.

[1]

(iii) By considering how the type of hybridisation and the C–C–C bond angle around the carbon labelled **1** would change, suggest why the loss of both chlorine atoms does not occur.

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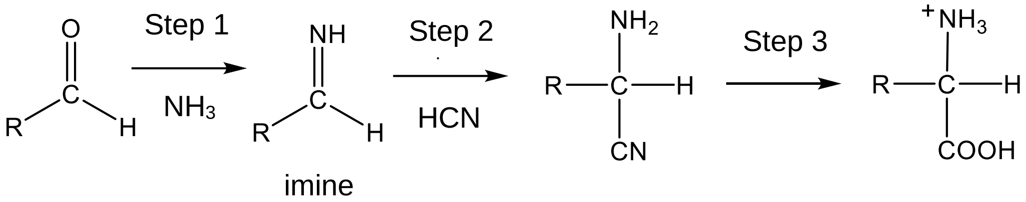
[2]

[Total 15]

6 **(a)** The first known synthesis of an amino acid occurred in 1850 in the laboratory of Adolf Strecker. It involves the formation of an imine compound which contains a carbon–nitrogen double bond:



(i) Name the type of reaction in Step 1.

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[1]

(ii) In Step 2, the reaction proceeds via a two-stage mechanism as described below:

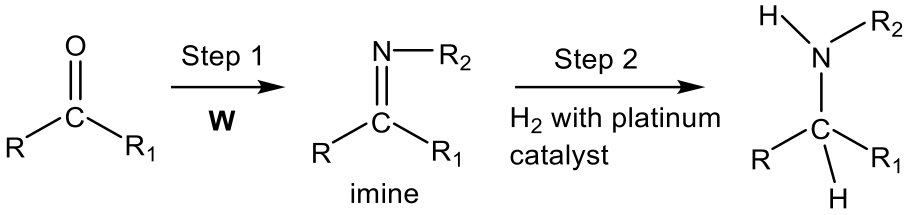
(I) protonation of the N atom in the imine by HCN to form a nucleophile and an organic intermediate.

(II) attack of the nucleophile on the organic intermediate to form the final product.

Draw the mechanism of the reaction occurring in Step 2. Your answer should show clearly relevant lone pairs and curly arrows to indicate the movement of electron pairs.

[2]

(iii) The synthesis of secondary amines from ketones also occurs via the formation of an imine compound.



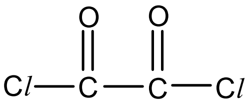
Suggest the structure of the starting ketone and the nitrogen-containing reagent, **W,** to be used for Step 1 in the preparation of $(CH_3)_2CHNHCH_2CH_3$.

structure of the starting ketone:

nitrogen-containing reagent, **W**:

[2]

(iv) Ethanedioyl dichloride has the following structure:

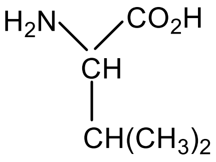


An amine **X**, $CH_3CH(NH_2)CH_2NH_2$, reacts with ethanedioyl dichloride to produce compound **Y** with the molecular formula $C_5H_8N_2O_2$.

Write an equation for the conversion of **X** to **Y**, showing clearly the structure of **Y**.

[2]

(b) Valine is an essential amino acid in humans.



valine

Table 6.1 shows some data of valine and butanedioic acid, $HO_2CCH_2CH_2CO_2H$.

Compound	M_r	**Melting point / °C**
valine	117.0	298
butanedioic acid	118.0	185

Table 6.1

Explain, with the aid of a suitable structure, why valine has a much higher melting point than butanedioic acid despite both compounds having similar M_r.

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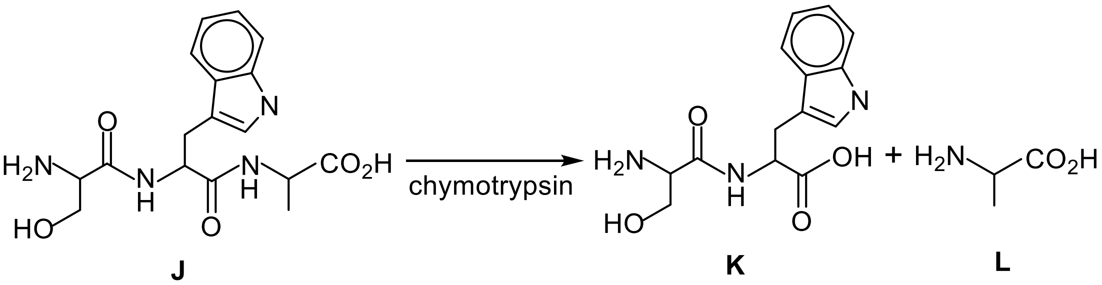
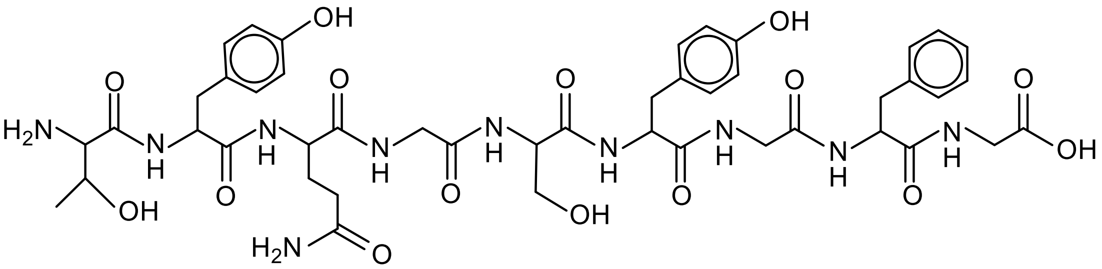
[2]

(c) Chymotrypsin is an enzyme that hydrolyses proteins into smaller peptides and amino acids. It specifically hydrolyses the peptide bond on the carboxyl side of a residue that contains an aromatic ring. For example, the tripeptide **J** produces two compounds **K** and **L** as shown.



The following shows the structure of a peptide containing a few amino acid residues:



Draw the two dipeptides formed when the above peptide is hydrolysed by chymotrypsin.

[2]

[Total: 10]