Attention!

- Write your name and student code (posted at your station) in the upper corner of all pages of the answer sheets.

- You have 5 hours to complete all of the tasks and record your results on the answer sheets. You must stop your work immediately after the stop command is given. A delay in doing this by 3 minutes will lead to cancellation of the current task and will result in zero points for the task.

- All results must be written in the appropriate areas on the answer sheets. Anything written elsewhere will not be marked. Do not write anything on the back of your answer sheets. If you need additional sheets or a replacement answer sheet, request it from the supervisor.

- When you have finished the examination, you must put all of your papers into the envelope provided, then you must seal the envelope. Only papers in the sealed envelope will be marked.

- A receipt will be issued for your sealed envelope. Do not leave the examination room until you are directed to do so.

- Use only the pen and calculator provided.

- This examination has 9 pages of problems and 18 pages of answer sheets.

- An official English language version is available only on request.

Problem 1

$ FRP SRXQG4 (molar mass 122.0 g mol^{-1}) FRQVLVWRI FDUERQK GURJHQDQGR[\JHQ

PART A
The standard enthalpy of formation of $CO_2(g)$ and $H_2O(l)$ at 25.00 ^{O}C are -393.51 and -285.83 kJ mol^{-1} respectively. The gas constant, R, is 8.314 JK^{-1}mol^{-1}.
(Atom masses : H = 1.0, C = 12.0, O = 16.0)

A sample of solid Q which weighs 0.6000 g is combusted in an excess of oxygen in a bomb calorimeter, which initially contains 710.0 g of water at 25.000 ^{O}C. After the reaction is completed, the temperature is observed to be 27.250 ^{O}C, and 1.5144 g of CO_2 (g) and 0.2656 g of $H_2O(l)$ are produced.

    1-1.   Determine the molecular formula and write a balanced equation with correct state of matters for the combustion of Q.

If the specific heat of water is 4.184 J. g^{-1} K^{-1} and the internal energy change of the reaction (ΔU^O) -3079 kJ mol^{-1}.

    1-2.   Calculate the heat capacity of the calorimeter (excluding the water).

    1-3.   Calculate the standard enthalpy of formation ($\Delta H_f^{\,o}$) of Q.

PART B
The following data refer to the distribution of Q between benzene and water at 6°C, C_B and C_w being equilibrium concentrations of the species of Q in the benzene and water layers, respectively :
Assume that there is only one species of Q in benzene independent of concentration and temperature.

Concentration (mol L^{-1})	
C_B	C_W
0.0118	0.00281
0.0478	0.00566
0.0981	0.00812
0.156	0.0102

    1-4.   Show whether Q is monomer or dimer in benzene by calculation assume that Q is a monomer in water.

The freezing point depression, for an ideal dilute solution, is given by

$$T_f^0 - T_f \quad = \quad \frac{R(T_f^0)^2.X_s}{?\,H_f}$$

where T_f is the freezing point of the solution, T_f^0 the freezing point of solvent, ΔH_f the heat of fusion of the solvent, and X_S the mole fraction of solute. The molar mass of benzene is 78.0 g mol^{-1}. At 1 atm pure benzene freezes at 5.40 $^\circ$C. The heat of fusion of benzene is 9.89 kJ mol^{-1}.

> 1-5. Calculate the freezing point (T_f) of a solution containing 0.244 g of Q in 5.85 g of benzene at 1 atm.

PART A

A diprotic acid , H_2A , undergoes the following dissociation reactions :

$$H_2A \rightleftharpoons HA^- + H^+; \qquad K_1 = 4.50 \times 10^{-7}$$

$$HA^- \rightleftharpoons A^{2-} + H^+; \qquad K_2 = 4.70 \times 10^{-11}$$
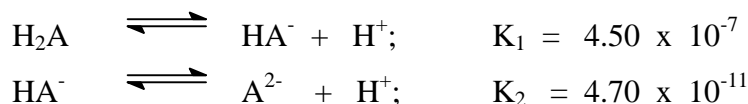
A 20.00 mL aliquot of a solution containing a mixture of Na_2A and NaHA is titrated with 0.300 M hydrochloric acid. The progress of the titration is followed with a glass electrode pH meter. Two points on the titration curve are as follows :

mL HCl added	pH
1.00	10.33
10.00	8.34

2-1.   On adding 1.00 mL of HCl, which species reacts first and what would be the product?

2-2.   What is the amount (mmol) of the product formed in (2-1)?

2-3.   Write down the main equilibrium of the product from (2-1) reacting with the solvent ?

2-4.   What are the amounts (mmol) of Na_2A and NaHA initially present?

2-5.   Calculate the total volume of HCl required to reach the second equivalence point.

PART B

Solutions I, II and III contain a pH indicator HIn ($K_{In} = 4.19 \times 10^{-4}$) and other reagents as indicated in the table. The absorbance values at 400 nm of the solutions measured in the same cuvette are also given in the table. K_a of CH_3COOH is 1.75×10^{-5}.

Table:

	Solution I	Solution II	Solution III
Total concentration of indicator HIn	1.00×10^{-5} M	1.00×10^{-5} M	1.00×10^{-5} M
Other reagents	1.00 M HCl	0.100 M NaOH	1.00 M CH_3COOH
Absorbance at 400 nm	0.000	0.300	?

2-6.   Calculate the absorbance at 400 nm of Solution III.

2-7.   Apart from H_2O, H^+ and OH^-, what are all the chemical species present in the solution resulting from mixing Solution II and Solution III at   1:1   volume ratio?

2-8.   What is the absorbance at 400 nm of the solution in (2-7)?

2-9.   What is the transmittance at 400 nm of the solution in (2-7)?

Problem 3

One of naturally occurring radioactive decay series begins with $^{232}_{90}\text{Th}$ and ends with a stable $^{208}_{82}\text{Pb}$.

3-1. How many beta (β^-) decays in this series? Show by calculation.

3-2. How much energy in MeV is released in the complete chain?

3-3. Calculate the rate of production of energy (power) in watts ($1\text{W} = \text{J s}^{-1}$) produced by 1.00 kilogram of ^{232}Th ($t_{1/2} = 1.40 \times 10^{10}$ years).

3-4. ^{228}Th is a member of the thorium series, what volume in cm^3 of helium at 0 °C and 1 atm collected when 1.00 gram of ^{228}Th ($t_{1/2} = 1.91$ years) is stored in a container for 20.0 years. The half-lives of all intermediate nuclides are short compared to the half-life of ^{228}Th.

3-5. One member of thorium series, after isolation, is found to contain 1.50×10^{10} atoms of the nuclide and decays at the rate of 3440 disintegrations per minute. What is the half-life in years?

The necessary atomic mass are

$$^4_2\text{He} \ = \ 4.00260 \text{ u}, \qquad ^{208}_{82}\text{Pb} = 207.97664 \text{ u}, \qquad ^{232}_{90}\text{Th} \ = \ 232.03805 \text{ u ; and}$$

$$1\text{u} \ = 931.5 \ \text{MeV}$$

$$1\text{MeV} = 1.602 \times 10^{-13} \text{ J}$$

$$N_A \ = \ 6.022 \times 10^{23} \text{ mol}^{-1}$$

The molar volume of an ideal gas at 0°C and 1 atm is 22.4 L.mol^{-1}.

Problem 4

Ligand **L** can form complexes with many transition metals. **L** is synthesized by heating a mixture of a bipyridine, glacial acetic acid and hydrogen peroxide to 70-80°C for 3 hrs. The final product **L**, crystallizes out as fine needles and has a molecular mass of 188. An analogous reaction with pyridine is ;
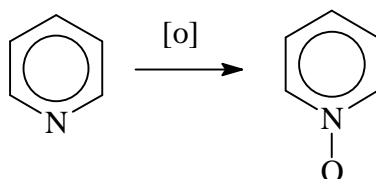
Complexes of **L** with Fe and Cr have the formulae of $FeL_m(ClO_4)_n.3H_2O$ (**A**) and $CrL_xCl_y(ClO_4)_z.H_2O$ (**B**). Their elemental analyses and physical properties are given in Tables 4a and 4b. The relationship of colour and wavelength is given in Table 4c.

Table 4a Elemental analyses.

Complex	Elemental analyses , (wt.%)
A	Fe 5.740, C 37.030, H 3.090 , Cl 10.940, N 8.640
B	Cr 8.440, C 38.930, H 2.920, Cl 17.250, N 9.080

Use the following data:

Atomic number : Cr = 24, Fe = 26

$\mu_{eff} = \sqrt{n(n+2)}$ B.M.

Table 4b Physical property

.

Complex	Magnetic moment , μ (B.M.)	Colour
A	6.13	Yellow
B	Not measured	Purple

Table 4c Relationship of wavelength to colour.

Wavelength (nm) and colour absorbed	Complementary colour
400 (violet)	Yellow Green
450 (blue)	Yellow
490 (blue green)	Orange
500 (green)	Red
570 (yellow green)	Violet
580 (yellow)	Blue
600 (orange)	Blue green
650 (red)	Green

4-1.   Write down the molecular formula of **L**.

4-2.   If **L** is a bidentate chelating ligand, draw the structure of the bipyridine used. Also draw the structure of **L** .

4-3.   Does the ligand **L** have any charge, i.e. net charge?

4-4.   Draw the structure when one molecule of **L** binds to metal ion (M).

4-5.   From the data in Table 4a, determine the empirical formula of **A**. What are the values of m and n in $FeL_m(ClO_4)_n.3H_2O$? Write the complete formula of **A** in the usual IUPAC notation. What is the ratio of cation to anion when A dissolves in water?

4-6.   What is the oxidation number of Fe in **A**? How many d-electrons are present in Fe ion in the complex? Write the high spin and the low spin configurations that may exist for this complex. Which configuration, high or low spin, is the correct one ? What is the best evidence to support your answer?

4-7.   From Table 4c, estimate λ_{max} (in unit of nm) of **A**.

4-8.   Detail analysis of **B** shows that it contains Cr^{3+} ion. Calculate the 'spin-only' magnetic moment of this compound.

4-9.   Compound **B** is a 1:1 type electrolyte. Determine the empirical formula of **B** and the values of x, y, z in $CrL_xCl_y(ClO_4)_z.H_2O$.

Problem 5

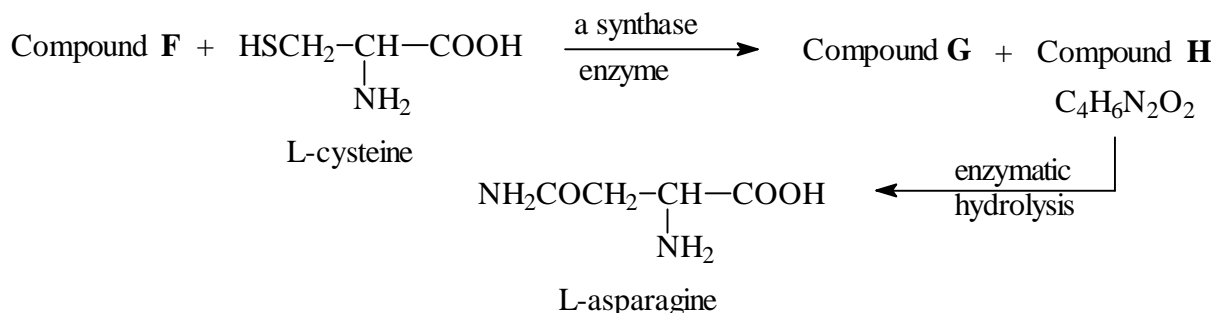Glycoside **A** ($C_{20}H_{27}NO_{11}$), found in seeds of *Rosaceae* gives a negative test with Benedicts' or Fehling's solutions. Enzymatic hydrolysis of **A** yields (-) **B**, C_8H_7NO and **C**, $C_{12}H_{22}O_{11}$, but complete acid hydrolysis gives as organic products, (+) **D**, $C_6H_{12}O_6$ and (-) **E**, $C_8H_8O_3$.

C has a *b*-glycosidic linkage and gives positive test with Benedicts' or Fehling's solution. Methylation of **C** with MeI/Ag_2O gives $C_{20}H_{38}O_{11}$, which upon acidic hydrolysis gives 2,3,4-tri-*O*-methyl-D-glucopyranose and 2,3,4,6-tetra-*O*-methyl-D-glucopyranose.
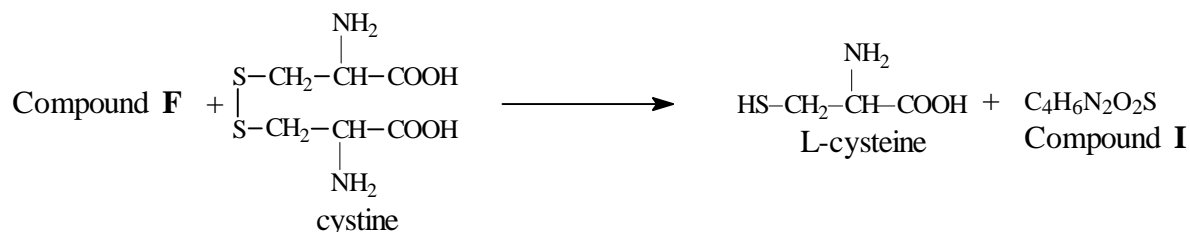
($\pm$) **B** can be prepared from benzaldehyde and $NaHSO_3$ followed by NaCN. Acidic hydrolysis of ($\pm$) **B** gives ($\pm$) **E**, $C_8H_8O_3$.

> 5-1. Write structures of **A - D** with appropriate stereochemistry in Haworth projection, except for **B**.

Glycoside **A** is found to be toxic and believed to be due to extremely toxic compound **F**, liberated under the hydrolytic conditions. Detoxification of compound **F** in plant may be accompanied by the reactions (stereochemistry not shown).

Compound **F** + HSCH$_2$−CH—COOH $\xrightarrow[\text{enzyme}]{\text{a synthase}}$ Compound **G** + Compound **H**

(under the HSCH$_2$−CH—COOH is NH$_2$; L-cysteine)

Compound **H** is $C_4H_6N_2O_2$

NH$_2$COCH$_2$−CH—COOH $\xleftarrow[\text{hydrolysis}]{\text{enzymatic}}$

(under the CH is NH$_2$)

L-asparagine

A small amount of compound **F** in human being is believed to be detoxified by a direct reaction with cystine giving L-cysteine and compound **I**, $C_4H_6N_2O_2S$ which is excreted in urine (stereochemistry not shown).
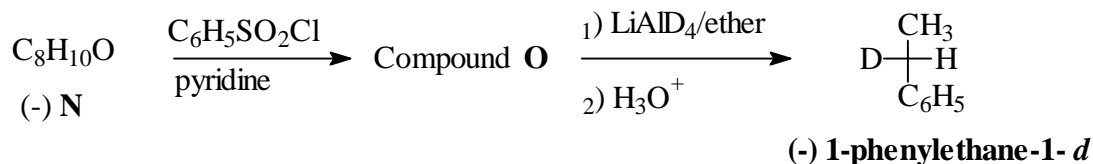
Compound **F** + cystine $\longrightarrow$ HS–CH$_2$–CH–COOH (NH$_2$) L-cysteine + $C_4H_6N_2O_2S$ Compound **I**

(cystine structure: S−CH$_2$−CH−COOH with NH$_2$ on top CH; S−CH$_2$−CH−COOH with NH$_2$ on bottom CH)

Compound **I** shows no absorption at 2150-2250 cm^{-1} in its IR spectrum but a band at 1640 cm^{-1} and the bands of carboxyl group are observed.

> 5-2. Write molecular formula for compounds **F** and **G**, and structural formula for compounds **H** and **I** and indicate stereochemistry of **H**. (Table 5.1 may be useful for structure identification.)
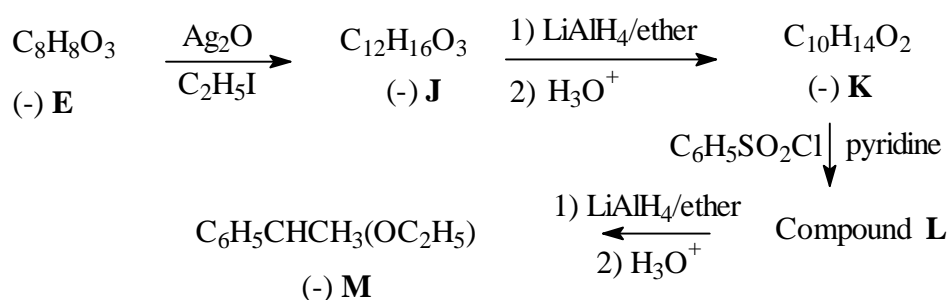
(-) **1-Phenylethane-1-*d***, $C_6H_5CHDCH_3$ can be prepared in optically active form and the magnitude of its rotation has the relatively high value, $[\alpha]_D$ is equal to -0.6.

$$C_8H_{10}O \xrightarrow[\text{pyridine}]{C_6H_5SO_2Cl} \text{Compound } \mathbf{O} \xrightarrow[\text{2) } H_3O^+]{\text{1) } LiAlD_4/\text{ether}} \begin{array}{c} CH_3 \\ D \!-\!\!\!\!|\!-\! H \\ C_6H_5 \end{array}$$

(-) **N**

(-) **1-phenylethane-1-*d***

The absolute configuration of (-) **1-phenylethane-1-*d*** is related to (-) **E** according to the following reactions.

$$C_8H_8O_3 \xrightarrow[C_2H_5I]{Ag_2O} C_{12}H_{16}O_3 \xrightarrow[\text{2) } H_3O^+]{\text{1) } LiAlH_4/\text{ether}} C_{10}H_{14}O_2$$

(-) **E**   (-) **J**   (-) **K**

$$C_6H_5SO_2Cl \downarrow \text{pyridine}$$

$$C_6H_5CHCH_3(OC_2H_5) \xleftarrow[\text{2) } H_3O^+]{\text{1) } LiAlH_4/\text{ether}} \text{Compound } \mathbf{L}$$

(-) **M**

Compound (-) **M** can also be obtained from compound **N** as follows.
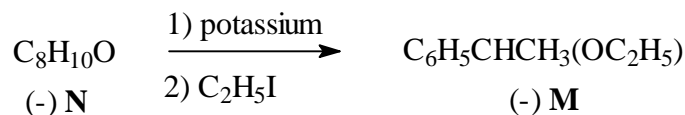
$$C_8H_{10}O \xrightarrow[\text{2) } C_2H_5I]{\text{1) potassium}} C_6H_5CHCH_3(OC_2H_5)$$

(-) **N**   (-) **M**

5-3.   Deduce the absolute configuration of (-) **E** and the structure with configuration of each intermediate (**J-O**) in the sequence with the proper R,S-assignment as indicated in the answer sheet.

5-4.   Choose the mechanism involved in the conversion of compound **O** to **1-phenylethane-*1-d***.

Table 5.1 Characteristic Infrared Absorption

Stretching Vibration	Region (cm^{-1})	Stretching Vibration	Region (cm^{-1})
C-H (alkane)	2850-2960	O-H (free alcohol)	3400-3600
C-H (alkene)	3020-3100	O-H (H-bonded alcohol)	3300-3500
C=C	1650-1670	O-H (acid)	2500-3100
C-H (alkyne)	3300	C-O	1030-1150
C≡C	2100-2260	NH, NH$_2$	3310-3550
C-H (aromatics)	3030	C-N	1030, 1230
C=C (aromatics)	1500-1600	C=N	1600-1700
C-H (aldehyde)	2700-2775, 2820-2900	C≡N	2210-2260
C=O	1670-1780		

Problem 6

Peptide **A** has a molecular weight of 1007. Complete acid hydrolysis gives the following amino acids in equimolar amounts: Asp, Cystine, Glu, Gly, Ile, Leu, Pro, and Tyr (see Table 1). Oxidation of **A** with HCO_2OH gives only **B** which carries two residues of cysteic acid (**Cya** which is a cysteine derivative with its thiol group oxidized to sulfonic acid).

    6-1.   How many sulfonic acid groups are formed from oxidation of a disulfide bond ?

Partial hydrolysis of **B** gives a number of di and tri-peptides (B1-B6). The sequence of each hydrolysis product is determined in the following ways.

The N-terminal amino acid is identified by treating the peptide with 2,4-dinitrofluorobenzene (DNFB) to give DNP-peptide. After complete acid hydrolysis of the DNP-peptide, a DNP-amino acid is obtained which can be identified readily by comparison with standard DNP-amino acids.

    6-2.   B1, on treatment with DNFB followed by acid hydrolysis gives a product, DNP-Asp. This suggests that B1 has aspartic acid at the N-terminus. Write down the ***complete*** structure of DNP-Asp at its isoelectric point (no stereochemistry required).

Next, the C-terminal amino acid is identified by heating the peptide at 100 °C with hydrazine, which cleave all the peptide bonds and convert all except C-terminal amino acids into amino acid hydrazides, leaving the C-terminal carboxyl group intact.

In this way N- and C-terminal amino acids are identified and the complete sequences of B1-B6 are as shown :

B1	Asp-Cya	B4	Ile-Glu
B2	Cya-Tyr	B5	Cya-Pro-Leu
B3	Leu-Gly	B6	Tyr-Ile-Glu

Hydrolysis of **B** with an enzyme from *Bacillus subtilis* gives B7-B9 with the following compositions:

        B7   Gly-NH$_2$ (Glycinamide)
        B8   Cya, Glu, Ile, Tyr
        B9   Asp, Cya, Leu, Pro

    6-3.   Write down the sequence of B8, if DNP-Cya is obtained on treatment of B8 with DNFB followed by complete acid hydrolysis.

    6-4.   If the N- and C-terminal amino acids of B9 are identified as Asp and Leu respectively, write down the sequence of B9.

    6-5.   Write down the complete structure of **A** using abbreviation in Table 1, indicating the position of the disulfide bond.

However, the calculated molecular weight of **A** based on the above sequence is 2 mass units higher than the experimental value. On careful observation of the mixture from complete acid hydrolysis of **A**, 3 molar equivalents of ammonia are also produced in addition to the amino acids detected initially.

6-6. Suggest the revised structure of **A** and circle the site(s) of the structure to indicate all the possible source of ammonia.

6-7. Using the information in Table 2, calculate the isoelectric point of **A**.

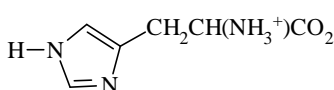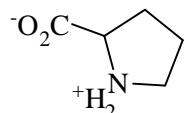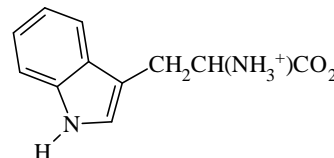**Table 2 : Formulae and Formula common amino acids at isoelectric point**
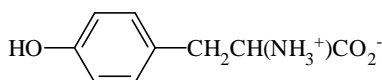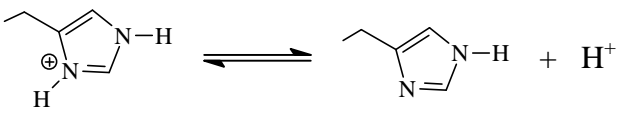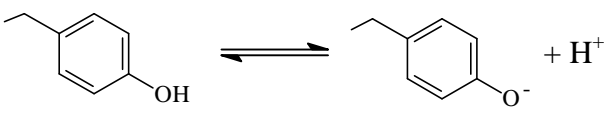
Name	Formula	Three-letter symbol
Alanine	$CH_3CH(NH_3^+)CO_2^-$	Ala
Arginine	$H_2NC(=NH)NH(CH_2)_3CH(NH_3^+)CO_2^-$	Arg
Asparagine	$H_2NCOCH_2CH(NH_3^+)CO_2^-$	Asn
Aspartic Acid	$HO_2CCH_2CH(NH_3^+)CO_2^-$	Asp
Cysteine	$HSCH_2CH(NH_3^+)CO_2^-$	Cys
Cystine	$[SCH_2CH(NH_3^+)CO_2^-]_2$	-
Glutamic Acid	$HO_2CCH_2CH_2CH(NH_3^+)CO_2^-$	Glu
Glutamine	$H_2NCOCH_2CH_2CH(NH_3^+)CO_2^-$	Gln
Glycine	$^+H_3NCH_2CO_2^-$	Gly
Histidine		His
Isoleucine	$CH_3CH_2CH(CH_3)CH(NH_3^+)CO_2^-$	Ile
Leucine	$(CH_3)_2CHCH_2CH(NH_3^+)CO_2^-$	Leu
Lysine	$H_2N(CH_2)_4CH(NH_3^+)CO_2^-$	Lys
Methionine	$CH_3SCH_2CH_2CH(NH_3^+)CO_2^-$	Met
Phenylalanine	$PhCH_2CH(NH_3^+)CO_2^-$	Phe
Proline		Pro
Serine	$HOCH_2CH(NH_3^+)CO_2^-$	Ser
Threonine	$CH_3CH(OH)CH(NH_3^+)CO_2^-$	Thr
Tryptophan		Trp
Tyrosine		Tyr
Valine	$(CH_3)_2CHCH(NH_3^+)CO_2^-$	Val

Table 2: pK$_a$ of some important groups in amino acids

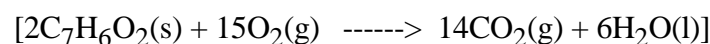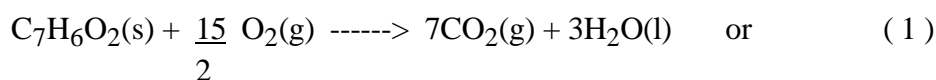| Groups	Equilibrium	pK$_a$
Terminal carboxyl	$-CO_2H \rightleftharpoons -CO_2^- + H^+$	3.1
Asp /or Glu side-chain carboxyl	$-CO_2H \rightleftharpoons -CO_2^- + H^+$	4.4
His side-chain		6.5
Terminal amino	$-NH_3^+ \rightleftharpoons -NH_2 + H^+$	8.0
Cys side-chain	$-SH \rightleftharpoons -S^- + H^+$	8.5
Tyr side-chain		10.0
Lys side-chain amino	$-NH_3^+ \rightleftharpoons -NH_2 + H^+$	10.0
Arg side-chain	$-NH(NH_2)C=NH_2^+ \rightleftharpoons -NH(NH_2)C=NH + H^+$	12.0

Problem 1 _____23 points

PART A

1-1.   Determine the molecular formula and write a balanced equation with correct state of matters for the combustion of Q.

Mole C : H : O = $\dfrac{(1.5144)(12.0/44.0)}{12.0}$: $\dfrac{(0.2656)(2.0/18.0)}{1.0}$: $\dfrac{(0.1575)}{16.0}$

$\qquad\qquad$ = 0.0344 : 0.0295 : 0.00984 = 7 : 6 : 2

The formula mass of $C_7H_6O_2$ = 122 which is the same as the molar mass given.   (2)

$C_7H_6O_2(s) + \dfrac{15}{2} O_2(g)$ ------> $7CO_2(g) + 3H_2O(l)$ or   (1)

$[2C_7H_6O_2(s) + 15O_2(g)$ ------> $14CO_2(g) + 6H_2O(l)]$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ 3 marks

2 marks for correct formula of Q.
1 mark for correct balanced equation with proper states.

1-2.   Calculate the heat capacity of the calorimeter (excluding the water).
       Calculation with proper units:

Mole Q = $\dfrac{0.6000}{122.0}$ = 4.919×10^{-3} (0.5)

$\qquad q_v = n\Delta U^o = \dfrac{0.6000}{122.0} \times (-3079)$ = -15.14 kJ   (2)

Total heat capacity = $\dfrac{-q_v}{\Delta T}$ = $\dfrac{15.14}{2.250}$ = 6.730 kJ K^{-1} (1.5)

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ = 6730 J K^{-1}

Heat capacity of water = 710.0×4.184 = 2971 J K^{-1} (1)

Heat capacity of calorimeter = 6730-2971 = 3759 J K^{-1} (1)

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ 6 marks

The heat capacity of calorimeter is | 3759 | J K^{-1}

Problem 1

1-3.   Calculate the standard enthalpy of formation (ΔH^o_f) of Q.
       <u>Calculation with proper units:</u>

$\Delta n_g = 7 - \dfrac{15}{2} = -0.5$ mol   (0.5)

$\Delta H^o = \Delta U^o + RT\,\Delta n_g$ (0.5)

$\quad = -3079 + (8.314 \times 10^{-3})(298)(-0.5)$ (1)

$\quad = -3079 - 1$

$\quad = -3080$ (0.5)

$\Delta H^o = (7\Delta H^o_f, CO_2(g) + 3\Delta H^o_f, H_2O(l)) - (\Delta H^o_f, Q)$ (1)

ΔH^o_f of Q $= 7(-393.51) + 3(-285.83) - (-3080)$ (1)

$\quad = -532$ kJ mol^{-1} (0.5)

5 marks

ΔH^o_f of Q is | -532 | kJ mol^{-1}

Problem 1

PART B

1-4. Show whether Q is monomer or dimer in benzene by calculation assume that Q is a monomer in water.
Calculation:

C_B (mol L^{-1})	0.0118	0.0478	0.0981	0.156	
C_W (mol L^{-1})	0.00281	0.00566	0.00812	0.0102	
either C_B/C_W	4.20	8.44	12.1	15.3	
or C_B/C_W^2	1.49×10^3	1.49×10^3	1.49×10^3	1.50×10^3	(2)
(or $\sqrt{C_B}/C_W$	38.6	38.6	38.6	38.7)	

From the results show that the ratio C_B/C_W varies considerably, whereas the ratio C_B/C_W^2 or $\sqrt{C_B}/C_W$ is almost constant, showing that in benzene, Q is associated into double molecule.

Q in benzene is ☐ monomer √ dimer.   (1)

                                                    3 marks

1-5. Calculate the freezing point (T_f) of a solution containing 0.244 g of Q in 5.85 g of benzene at 1 atm.
Calculation

If Q is completely dimerized in benzene, the apparent molecular mass should be 244.

Mole fraction of Q_2 = $\dfrac{0.244/244}{(\frac{0.244}{244} + \frac{5.85}{78.0})}$ = 1.32×10^{-2} (0.01316)   (3)

ΔT_f = $\dfrac{(8.314)(278.55)^2}{9.89\times10^3}$. 1.32×10^{-2} = 0.861   (2)

T_f = 5.40-0.861 = 4.54 ^{o}C   (1)

T_f of solution is ☐ 4.54 °C

                                6 marks
-1 mark for incorrect temperature.
-1 mark for incorrect heat of fusion.

Problem 2   20 points

PART A

2-1.   On adding 1.00 mL of HCl, what species reacts first and what would be the product?

Species which reacts first is A^{2-}
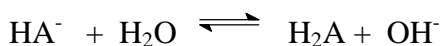   0.5 mark

The product is HA^-
                                                        0.5 mark

2-2.   What is the amount (mmol) of the product formed in (2-1)?

mmol of product   = $1.00 \times 0.300 = 0.300$
                                                        0.5 mark

2-3.   Write down the main equilibrium of the product from (2-1) reacting with the solvent?

$$HA^- + H_2O \rightleftharpoons H_2A + OH^-$$

                                                        1 mark

2-4.   What are the amounts (mmol) of Na_2A and $NaHA$ initially present?

Calculation:

At pH 8.34 which is equal to $(pK_{a1} + pK_{a2})/2$ all A^{2-} are protonated as HA^-.

Therefore no. of A^{2-} initially present in the solution = 0.300×10.00
                                                        = 3.00 mmol

At pH 10.33, the system is a buffer in which the ratio of $[A^{2-}]$ and $[HA^-]$ is equal to 1. Thus

$[HA^-]_{initial} + [HA^-]_{formed}$ = $[A^{2-}]_{initial} - [HA^-]_{formed}$

The amount of initial HA^- = $3.00 – 0.300 - 0.300$ mmol = 2.40 mmol

_____ **Problem 2**

| mmol of Na$_2$A | = | 3.00 | 2.0 marks |
| mmol of NaHA | = | 2.40 | 2.5 marks |

2-5. Calculate the total volume of HCl required to reach the second equivalence point.
Calculation:

Total volume of HCl required = [(2 x 3.00) + 2.40]/0.300
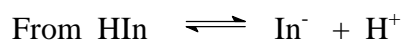= 28.00 mL

1.5 marks

Problem 2

PART B

2-6.   Calculate the absorbance at 400 nm of Solution III.
       Calculation:

Solution III is the indicator solution at 10^{-5} M in a solution containing 1.0 M CH_3COOH.
To obtain the absorbance of the solution, it is necessary to calculate the concentration of the basic form of the indicator which is dependent on the $[H^+]$ of the solution.

$$[H^+] \text{ of solution III} \quad = \quad \sqrt{K_a . C}$$

$$= \quad \sqrt{1.75 \times 10^{-5} \times 1.0}$$

$$= \quad 4.18 \times 10^{-3}$$

$$K_{In} \qquad \qquad (1.0 \text{ mark})$$

$$\text{From HIn} \quad \rightleftharpoons \quad In^- + H^+$$

$$K_{In} \quad = \quad \frac{[H^+][In^-]}{[HIn]} \qquad (0.5 \text{ mark})$$

$$\frac{[In^-]}{[HIn]} \quad = \quad \frac{K_{In}}{[H^+]}$$

$$= \quad \frac{10^{-3.38}}{10^{-2.38}}$$

$$= \quad 0.100$$

$$\frac{[In^-]}{[HIn]} \quad = \quad 0.100 \qquad (1.0 \text{ mark})$$

Whereas $[HIn] + [In^-] = 10^{-5}$
            $10[In^-] + [In^-] = 10^{-5}$
            $[In^-] = 0.091 \times 10^{-5}$

$$(1.5 \text{ mark})$$

$$\therefore \text{ Absorbance of solution III} = \frac{0.091 \times 10^{-5}}{1.00 \times 10^{-5}} \times 0.300$$

$$= \quad 0.027 \qquad (1.0 \text{ mark})$$

-0.5 mark for incorrect unit

The absorbance at 400 nm of Solution III = | 0.027

5 marks

Problem 2

2-7.   Apart from H^+, OH^-, and H_2O, what are all the chemical species present in the solution resulting from mixing Solution II and Solution III at 1:1 volume ratio?

CH_3COOH , CH_3COO^- , Na^+ , HIn , In^-

1.5 marks

2-8.   What is the absorbance at 400 nm of the solution in (2-7) ?
Calculation:

When solutions II and III are mixed at 1:1 volume ratio, a buffer solution of 0.05 M CH_3COO^- / 0.45 M CH_3COOH is obtained.

$$[H^+] \text{ of mixture solution} = K_a \frac{[CH_3COOH]}{[CH_3COO^-]}$$

$$= 1.75 \times 10^{-5} \times \frac{0.45}{0.05}$$

$$= 15.75 \times 10^{-5} \qquad \text{(1.0 mark)}$$

therefore $\quad \dfrac{[In^-]}{[HIn]} = \dfrac{K_{In}}{[H^+]}$

$$= \frac{10^{-3.38}}{15.75 \times 10^{-5}}$$

$$\frac{[In^-]}{[HIn]} = 2.65 \qquad \text{(1.0 mark)}$$

Whereas $\quad [HIn] + [In^-] = 10^{-5}$

$$\frac{[In^-]}{2.65} + [In^-] = 10^{-5}$$

$$[In^-] = 0.726 \times 10^{-5}$$

(1.5 marks)

$\therefore$ Absorbance of solution $\quad = \dfrac{0.726 \times 10^{-5}}{1.0 \times 10^{-5}} \times 0.300$

$$= 0.218$$

(0.5 mark)

-0.5 mark for incorrect unit

The absorbance at 400 nm of the solution $=$ | 0.218 |

4 marks

Problem 2

2-9.   What is the transmittance at 400 nm of the solution in (2-7)?
          <u>Calculation:</u>

> Transmittance of solution   =   antilog (-absorbance)
>
>   =   0.605

                                                    -0.5 mark for incorrect unit

Transmittance of the solution = | 0.605 or 60.5% |

                                                            1 mark

Problem 3 _____ 20 points

3-1.   How many beta decays in this series? Show by calculation.

Calculation:

> A = 232 - 208 = 24; 24/4 = 6 alpha particles   (1)
> The nuclear charge is therefore reduced by 2 x 6 = 12 units, however, the
> difference in nuclear charges is only 90 - 82 = 8 units. Therefore there must be
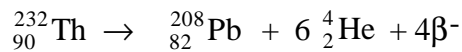>   12 - 8 = 4β⁻ emitted.
>   (1)

2 marks

Number of beta decays = | 4 |

3-2.   How much energy in MeV is released in the complete chain?

Calculation:

> $^{232}_{90}$Th → $^{208}_{82}$Pb + 6 $^{4}_{2}$He + 4β⁻
>   Energy released is Q value
>   Q = [m(^{232}Th)-m(^{208}Pb)-6m(^{4}He)]c^2
>   (the mass of 4e⁻ are included in daughters)   (2)
>   = [232.03805 u - 207.97664 u - 6 x 4.00260 u] x 931.5 MeVu⁻¹
>   = (0.04581u)(931.5 MeVu⁻¹) = 42.67 MeV   (2)

4 marks

Energy released = | 42.67 | MeV

Problem 3

3-3.   Calculate the rate of production of energy (power) in watts ($1W = Js^{-1}$) produced by 1.00 kilogram of ^{232}Th ($t_{1/2} = 1.40 \times 10^{10}$ years).

Calculation:

1.00 kg contains $= \dfrac{1000\,g \times 6.022 \times 10^{23}\,atoms\,mol^{-1}}{232\,g\,mol^{-1}}$

$= 2.60 \times 10^{24}$ atoms   (1)

Decay constant for ^{232}Th

$\lambda = \dfrac{0.693}{(1.40 \times 10^{10}\,y)(3.154 \times 10^{7}\,s\,y^{-1})}$ (1)

$= 1.57 \times 10^{-18}\,s^{-1}$

$A = N\lambda = (2.60 \times 10^{24})(1.57 \times 10^{-18})$ where A is activity

$= 4.08 \times 10^{6}$ dps (disintegrations s^{-1})

Each decay liberates 42.67 MeV   (1)

Rate of production of energy (power)

4.08×10^{6} dis $s^{-1} \times 42.67$ MeV dis$^{-1} \times 1.602 \times 10^{-13}$ J Mev^{-1}

$= 2.79 \times 10^{-5}$ J $s^{-1} = 2.79 \times 10^{-5}$ W   (2)

5 marks

Rate of production of energy $=$ | 2.79×10^{-5} | W

Problem 3

3-4. What volume in cm^3 of helium at 0 °C and 1 atm collected when 1.00 gram of ^{228}Th ($t_{1/2} =$ 1.91 years) is stored in a container for 20.0 years.

Calculation:

$$^{228}\text{Th} \rightarrow {}^{208}\text{Pb} + 5\,^4\text{He} \tag{1}$$
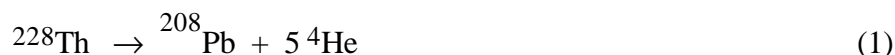
The half-lives of various intermediates are relatively short compared that of ^{228}Th.

$$A = \lambda N = \left(\frac{0.693}{1.91\,\text{y}}\right)\left[\frac{(1.00\,\text{g})(6.02 \times 10^{23}\,\text{mol}^{-1})}{228\,\text{g mol}^{-1}}\right]$$

$$= 9.58 \times 10^{20}\ \text{y}^{-1} \tag{1}$$

Number of He collected

$$N_{\text{He}} = (9.58 \times 10^{20}\ \text{y}^{-1})(20.0\ \text{y})(5\ \text{particles})$$

$$= 9.58 \times 10^{22}\ \text{particles of He} \tag{1}$$

$$V_{\text{He}} = \frac{(9.58 \times 10^{22})(22.4\,\text{mol}^{-1})(10^3\,\text{cm}^3\text{L}^{-1})}{6.022 \times 10^{23}\,\text{mol}^{-1}}$$

$$= 3.56 \times 10^3\,\text{cm}^3 \tag{2}$$

5 marks

Volume of He at 0 °C and 1 atm $=$
$$\boxed{3.56 \times 10^3}\ \text{cm}^3$$

3-5. One member of thorium series, after isolation, is found to contain 1.50×10^{10} atoms of the nuclide and decays at the rate of 3440 disintegrations per minute. What is the half-life in years?

Calculation:

$$A = \lambda N;$$

$$t_{1/2} = \frac{0.693}{\lambda} = \frac{0.693 N}{A} \tag{1.5}$$

$$= \frac{(0.693)(1.50 \times 10^{10}\,\text{atoms})}{3440\,\text{atoms min}^{-1}} \tag{1.5}$$

$$= 3.02 \times 10^6\ \text{min}$$

$$= 5.75\ \text{years} \tag{1}$$

4 marks

Half-life $=$
$$\boxed{5.75}\ \text{years}$$

## Problem 4   28 points

4-1.   The molecular formula of **L** is $C_{10}H_8N_2O_2$ 2 marks

> Knowing that L was synthesized from bipyridine and during the reaction
> bipyridine was simply oxidized to bipyridine oxide. The molecular mass
> of bipyridine is 156 (for $C_{10}H_8N_2$) while the molecular mass of L is 188.
> The difference of 32 is due to 2 atoms of oxygen. Therefore , the
> molecular formula of L is $C_{10}H_8N_2O_2$.

4-2.   The structures of bipyridine and **L**

Structure of bipyridine

2 marks

structure of **L**
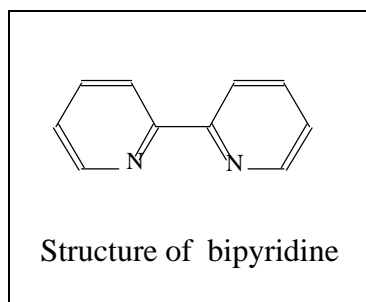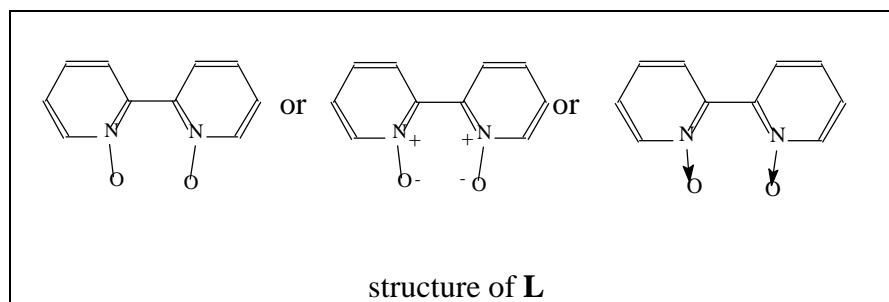
2 marks

4-3.   Does the ligand **L** have any charge, i.e., net charge ? (Please tick).

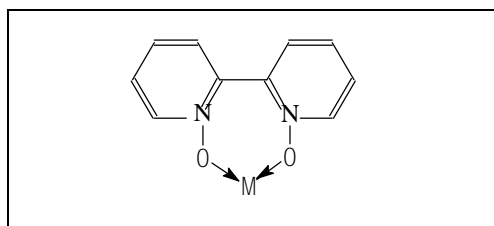| - 2 charge	- 1 charge	no charge	+ 1 charge	+ 2 charge
		√		

1 mark

4-4.   Draw the structure when one molecule of **L** binds to metal ion (M).

2 marks

Problem 4

4-5.   Determine the empirical formula of **A**.

Calculation:

	Fe	C	H	Cl	N	O
%	5.740	37.030	3.090	10.940	8.640	34.560*
mol	0.103	3.085	3.090	0.309	0.617	2.160
mol ratio	1.000	29.959	30.00	2.996	5.992	20.971
atom ratio	1	30	30	3	6	21

(* Percentage of O is obtained by difference.)

The empirical formula of **A** is $FeC_{30}H_{30}Cl_3N_6O_{21}$

3 marks

What are the values of m and n in $FeL_m(ClO_4)_n \cdot 3H_2O$?

m   =   3   n   =   3

1 mark   1 mark

Since the molecular formula contains one atom of Fe , so in this case the empirical formula is equivalent to the molecular formula. The molecular formula of L has been obtained previously in (4a) and (4b) , therefore we can work to find m = 3. Having obtained the value of m , one can work out for n and find that n = 3.

The complete formula of **A** is $[FeL_3](ClO_4)_3 \cdot 3H_2O$.

1 mark

The ratio of cation to anion is   1 : 3   1 mark

Problem 4

The three $(ClO_4)^-$ groups will dissociate as free ion in solution.
So the entire complex will be in the ion forms as $[FeL_3]^{3+}$ and
3 $(ClO_4)^-$ in solution.

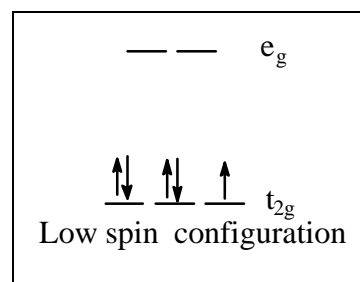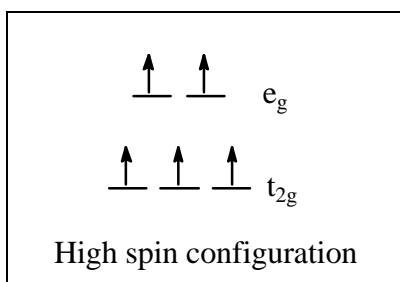4-6.   The oxidation number of Fe in complex **A** is $+3$ or III

0.5 marks

The number of *d*-electrons in Fe ion in the complex =   5

0.5 marks

Write the high spin and the low spin configuration that may exist for this complex.

High spin configuration

Low spin configuration

2 marks

Which configuration , high or low spin , is the correct one (please tick)?

√	High spin
	Low spin

1 mark

Problem 4

The best evidence to support your answer for this high/low spin selection:

	Color
	Elemental analysis data
√	Magnetic moment
	Molar conductance

1 mark

We can use a simple relation between number of unpaired electrons and the magnetic moment as follows.

$$\mu = \sqrt{n(n + 2)}$$

where μ is the so-called 'spin-only' magnetic moment and n is the number of unpaired electrons. Thus , for high spin case ,

$$\mu = \sqrt{5(5 + 2)} = \sqrt{35} = 5.92 \text{ B.M.}$$

And for low spin case , $\mu = \sqrt{1(1 + 2)} = \sqrt{3} = 1.73$ B.M

The measured magnetic moment , μ , of A given in Table 4b is 6.13 B.M. which is in the range for high spin case . Therefore , we can conclude that A would exist as a high spin complex.

4-7. λ_{max} of complex **A** is | 450 | nm.

1 mark

From Table 4c , the color absorbed is complementary to the color seen.

Problem 4

4-8   Calculate the 'spin-only' magnetic moment of complex **B**:

Calculation:

From $ì = \sqrt{n(n+2)}$

For Cr^{3+},   n = 3   1 mark

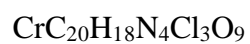Therefore, $m = \sqrt{3(3+2)} = \sqrt{15} = 3.87$ B.M.

The 'spin-only' magnetic moment of complex **B** = | 3.87 | M.

1 mark

4-9   The empirical formula of **B** is | $CrC_{20}H_{18}N_4Cl_3O_9$ | 1 mark

x   = | 2 | 1 mark

y   = | 2 | 1 mark

z   = | 1 | 1 mark
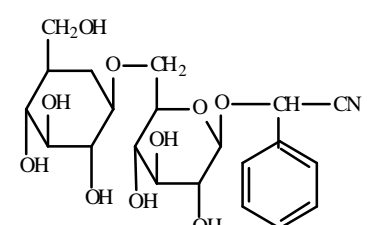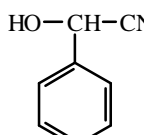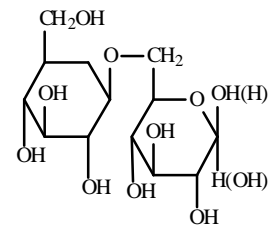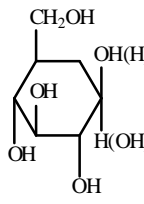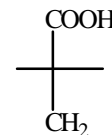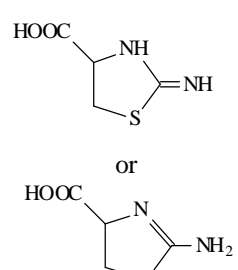
Problem 5 _____ 23 points

5-1.   Write structures of **A - D** with appropriate stereochemistry in Haworth projection, except for **B**.

A
(3 marks)

Remark: 1 for cyanohydrin moiety, 1 for two D-glucose units
and 1 for 1,6-linkage

B
(1 mark)

C
(2 marks)

Remark: 1 for two glucose units
0.5 for 1,6-linkage
0.5 for β-linkage

D
(1.5 marks)

Remark: 0.5 for correct structure
1 for stereochemistry

5-2.   Write molecular formula each for compounds **F** and **G** and structural formula for compound **H** and **I** and indicate stereochemistry of **H**.

Molecular formula of compound **F** = **HCN** (0.5 mark)		
Molecular formula of compound **G** = **H₂S** (0.5 mark)	Remark: 1 mark for structure 1 mark for correct stereochemistry	Compound **I** (2 marks) Remark: 2 marks for structure

(5 marks)

Problem 5

5-3.   Deduce the absolute configuration of (-) **E** and the structure with configuration of each intermediate (**J-O**) in the sequence with the proper R,S-assignment.

COOH H————OH C$_6$H$_5$ (-) **E** ☑ R or ☐ S (2 marks) Remark: 1 mark for structure 0.5 mark for **R, S** 0.5 mark for correct stereochemistry	COOC$_2$H$_5$ H————OC$_2$H$_5$ C$_6$H$_5$ (-) **J** (1.5 mark) Remark: 0.5 mark for ester 0.5 mark for ether 0.5 mark for correct stereochemistry	CH$_2$OH H————OC$_2$H$_5$ C$_6$H$_5$ (-) **K** (1 mark) Remark: 0.5 mark for structure 0.5 mark for correct stereochemistry	CH$_2$OSO$_2$C$_6$H$_5$ H————OC$_2$H$_5$ C$_6$H$_5$ Compound **L** (1 mark) Remark: 0.5 mark for structure 0.5 mark for correct stereochemistry
CH$_3$ H————OC$_2$H$_5$ C$_6$H$_5$ (-) **M** (1 mark) Remark: 0.5 mark for structure 0.5 mark for correct stereochemistry	CH$_3$ H————OH C$_6$H$_5$ (-) **N** ☐ R or ☑ S (1.5 mark) Remark: 0.5 mark for structure 0.5 mark for **R, S** 0.5 mark for correct stereochemistry	CH$_3$ H————OSO$_2$C$_6$H$_5$ C$_6$H$_5$ Compound **O** (1 mark) Remark: 0.5 mark for structure 0.5 mark for correct stereochemistry	CH$_3$ D————H C$_6$H$_5$ (-) **1-phenylethane-** *1-d* ☑ R or ☐ S (0.5 mark) Remark: 0.5 mark for **R, S**

5-4.   The mechanism involved in the conversion of compound **O** to (-) **1-phenylethane-*1-d***
        is   .

	S$_N$1
√	S$_N$2
	S$_N$i
	E1
	E2

1 mark

Problem 6   16 points

6-1.

| 2 |

sulfonic acid groups are formed from oxidation of a disulfide bond.

1 mark

6-2.   Complete structure of DNP-Asp at its isoelectric point is
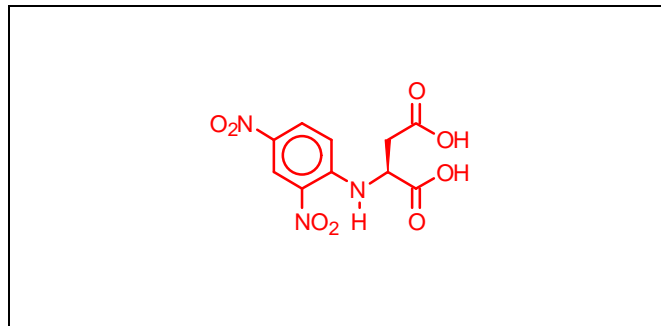
2 marks

Remarks

 2   marks for exactly the same structure
-1   mark for the condensed structure
-0.5 mark for Zwitterionic form
 0   mark for misplaced DNP group

6-3.

The sequence of B8 is   Cya-Tyr-Ile-Glu

2 marks

Remarks
-0.5 marks if the sequence is correct but the symbol "Cys" is used in place of "Cya"
-1   mark if "Cya" is put correctly at N-terminus but the sequence is incorrect
 0   mark for the reverse sequence

6-4.

The sequence of B9 is   Asp-Cya-Pro-Leu

1 mark

Remarks
-0.5 marks if the sequence is correct but the symbol "Cys" is used in place of "Cya"
 0   mark for wrong sequence even if Asp and Leu are placed correctly since the
      information is already provided in the question

Problem 6

6-5.   The *complete* structure of A is

Cys-Tyr-Ile-Glu-Asp-Cys-Pro-Leu-Gly-NH$_2$

5 marks

Remarks
  5   marks for exactly the same sequence with correct placement of disulfide bond
- 1   mark for missing or misplaced the disulfide bond.
- 0.5 marks for missing "NH$_2$" group at C-terminus.
- 0.5 for using the symbol "Cya" is used in place of "Cys".
  0   mark if the sequence wrong.

6-6.   Write the revised structure of A below and circle the site(s) to indicate all the possible
        source of ammonia

Cys-Tyr-Ile-Gln - Asn-Cys-Pro-Leu-Gly- NH$_2$

3 marks

Remarks
0.5   marks for each correct position of the amide group (Glu->Gln, Asp->Asn and at C-
       terminus)
0.5   marks for each circle at appropriate places (circle at Gly is allowed)

6-7.

The isoelectric point of **A** is   9

2 marks

Attention !

At all times while you are in the laboratory you must wear safety eye glasses or your own glasses if they have been approved, and use the pipette filler bulb provided. You will receive only **ONE WARNING** from the laboratory supervisor if you remove your glasses or fill a pipette by mouth.

A second infringement will be considered a major fault incompatible with further experimental work, and you will be dismissed from the laboratory with a resultant zero score for the entire experimental examination.

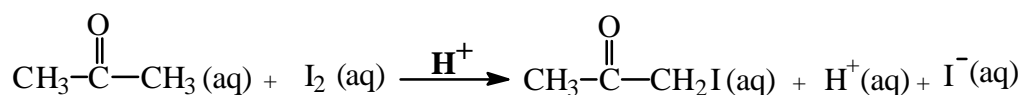Do not hesitate to ask a demonstrator if you have any questions concerning safety issues.

- Please carefully read the text of each experimental task and **study the layout of the answer forms** before you begin your experimental work.

- Write your name and student code (posted at your workstation) on each answer sheet.

- You have 5 hours to complete all of the experimental tasks, and record your results on the answer sheets. In some steps, you have to ask for the demonstrator signature before proceeding to further step. You must stop your work immediately after the **STOP** command is given. A delay in doing this by 3 minutes will lead to cancellation of the current task and will result in zero points for that task.

- All results must be written in the appropriate areas on the answer sheets. Anything written elsewhere will not be marked. Do not write anything on the back of your answer sheets. If you need additional sheets or a replacement answer sheet, request it from the supervisor.

- When you have finished the examination, you must put all papers into the envelope provided, then you must seal the envelope and hand in to your demonstrator with your signature. Only papers in the sealed envelope will be marked.

- Do not leave the examination room until you are directed to do so. A receipt for your sealed envelope will be issued to you as you leave.

- Use only the pen and calculator provided.

- Use only the distilled water, and use the appropriate waste containers for disposal of chemicals and other waste materials.

- The number of significant figures in numerical answers must conform to the rules of evaluation of experimental errors. The inability to perform calculations correctly will result in penalty points, even if your experimental technique is flawless.

- This practical examination contains 2 envelopes. The first envelopes has 8 pages of Task 1 & 2 and 8 pages of answer sheet. The second envelope has 2 pages of answer sheet and 2 pages of spectra.

- Chemicals and/or laboratory wares can be requested if used up or broken. The penalty of each request will be the loss of 1 point.

- The official English version of this examination is available for clarification only on request.

> **Do not start Laboratory Task 2 until you have finished Laboratory Task 1. The experimental part of Laboratory Task 1 can be completed in approximately 1.5 hours (calculation time not included).**

A Kinetic Study of the Acid Catalyzed Reaction Between Acetone and Iodine in Aqueous Solution

INTRODUCTION

The reaction between acetone and iodine in aqueous solution is catalyzed by H^+.

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3\,(aq)\ +\ I_2\,(aq)\ \xrightarrow{\ H^+\ }\ CH_3-\overset{\overset{O}{\|}}{C}-CH_2I\,(aq)\ +\ H^+(aq)\ +\ I^-(aq)$$

In this experiment, the kinetics of the iodination is measured to determine the rate law of the reaction. The rate equation for the loss of $I_2(aq)$ has been shown to have the form

$$Rate\ =\ -\frac{d[I_2]}{dt}\ =\ k[CH_3COCH_3]^x[I_2]^y[H^+]^z$$

where H^+ ions are the catalyst.

In order to determine the rate constant k and the kinetic orders x, y and z, the initial rate of reaction is measured.

$$Initial\,rate\ =\ k[CH_3COCH_3]_0^x[I_2]_0^y[H^+]_0^z$$

Where $[\ ]_0$ are the initial concentrations of acetone, I_2 and H^+, respectively.

If the initial rates are measured for various initial concentrations of the reactants then the order with respect to each reactant can be obtained.

The initial rate is obtained by measuring the decrease in the $I_2(aq)$ concentration after a short time interval (7.0 min. in this experiment) after the start of the reaction. Aqueous sodium acetate solution is added to stop the reaction after 7 minutes. The acetate ion reacts immediately with the H^+ to produce acetic acid and so reducing the concentration of H^+. The reaction is thus stopped as there is no catalyst present.

Since the reaction does not come to a complete halt, the solution **should be titrated immediately after the addition of the sodium acetate solution.**

The remaining iodine I_2 (aq) is determined by titration with sodium thiosulfate, $Na_2S_2O_3$. As the end point of the titration is approached, starch indicator is added and the titration is continued until the blue color disappears.

Equipments

1.	Glass stoppered flask 250 mL	5
2.	Erlenmeyer flask 125 mL	3
3.	Burette 25 mL	1
4.	Pipette 5 mL	4
5.	Pipette 10 mL	3
6.	Pipette filler bulb with tip	1
7.	Beaker 100 mL	1
8.	Beaker 50 mL	3
9.	Beaker 250 mL (labeled waste disposal)	1
10.	Graduated cylinder 10 mL	1
11.	Wash bottle 500 mL	1
12.	Stop-watch	1
13.	Pen	1
14.	Label sheet	1

Chemicals

1.	Aqueous iodine solution in 0.4 M KI	80	mL
2.	0.100 M aq. HCl	50	mL
3.	0.50 M aq. CH_3COONa	80	mL
4.	Standard 0.02xxx M $Na_2S_2O_3$(aq) solution	200	mL
	(the exact concentration will be announced at the beginning of Task 1)		
5.	Aqueous acetone (50% by volume)	50	mL
	(density of pure acetone; 0.787 g/mL, MW. = 58.08)		
6.	Starch indicator	7	mL

Stop-watch Operation
A = Mode button (right bottom)
B = Start/Stop button (right top)
C = Split/Reset button (left top)

Mode is already set. **Do not touch the button A.**
1.   Check that the display is 0.00$_{00}$. If not, call demonstrator.
2.   To start, press **B.**
3.   To stop, press **B**.
4.   To reset, press **C**.

Procedure
A. Standardization of Iodine Solution
1. Pipet 5.00 mL of aqueous iodine into a clean 125 mL Erlenmeyer flask.
2. Add 10 mL of distilled water using graduated cylinder.
3. Titrate the iodine with the standard 0.02xxx M sodium thiosulfate solution until the colour of the solution is pale yellow.
4. Add 3 - 4 drops of starch indicator and continue the titration until the blue colour disappears.
5. Record the initial and the final volumes of the thiosulfate solution and the volume used in the answer sheet.
6. Repeat the titration as necessary (Steps 1 to 5)
7. Give the titre volume for calculation in the answer sheet.
8. Calculate the iodine concentration.

B. <u>A kinetic study of acid catalyzed reaction between acetone and iodine in aqueous solution</u>

  1. Label the stoppered flasks as follows: Flask I, II, III and IV.
  2. To each respective flask add the following volumes of distilled water, 0.100 M hydrochloric acid and 50% acetone:
     Stopper each flask immediately after addition of the solutions.

Flask No.	Volume (mL)		
	water	0.100 M HCl	50% acetone
I	5.00	5.00	5.00
II	0.0	5.00	5.00
III	0.0	5.00	10.00
IV	0.0	10.00	5.00

  3. Measure out 10 mL of 0.50 M aq. CH_3COONa into the graduated cylinder.
  4. Set the stop-watch to 0.00_{00} display.
  5. Pipet **5.00 mL** of iodine solution into the <u>stoppered **Flask No. I**</u>.
     Start the stop-watch as soon as the **first drop of iodine solution is added**.
  6. Stopper the flask and swirl continuously.
  7. Just before 7.0 min, remove the stopper, at **7.0 min**, immediately pour 10 mL of sodium acetate
     solution (from step 3) into the reaction flask. **Shake well.**
  8. Titrate the remaining iodine with standard thiosulfate solution.
  9. Record the volume of the thiosulfate solution.
 10. Repeat the above steps (Steps 3 to 9) for Flask II, III and IV but add in step 5 the I_2(aq) solution to each flask as indicated:

    Flask II: **10.00 mL I_2 solution**
    Flask III: **5.00 mL I_2 solution**
    Flask IV: **5.00 mL I_2 solution**

Calculations

B-1. Calculate the initial concentrations (M) of iodine, acetone and HCl solutions in Flasks I to IV, assuming volumes are additive.

B-2. Calculate concentrations of iodine (M) remaining in Flasks I to IV at 7.0 minutes.

B-3. Calculate the initial reaction rate for Flasks I to IV in $M\ s^{-1}$.

B-4. The rate of reaction has the form

$$Rate = -\frac{d[I_2]}{dt} = k[CH_3COCH_3]^x[I_2]^y[H^+]^z$$

    Calculate the reaction orders x, y and z from the initial rates and the initial concentrations of acetone, iodine and HCl. The values of x, y and z should be rounded off to the nearest integer and fill in the answer sheet. Write rate equation or rate law.

B-5. Calculate the rate constant, k, for Flasks I to IV with proper unit.

B-6. Give the mean value of the rate constant.

Laboratory Task I_____50 points

RESULTS SHEET

A. Standardisation of Iodine Solution

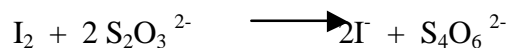Concentration of standard $Na_2S_2O_3$ in bottle : .... 0.01970........... M

	Volume		
Titration Number	**1**	**2**	**3**
aliquot of I_2 (mL)	5.00	5.00	5.00
initial buret reading (mL)	0.00	0.00	0.00
final buret reading (mL)	10.00	10.05	9.95
standard $Na_2S_2O_3$ (mL)	10.15	10.10	10.05

The value of titre = [   ] mL

Calculation for iodine concentration:

mol ratio of $I_2 : S_2O_3^{2-}$ = [1:2]

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

$$[I_2].V_{I_2} = \frac{[S_2O_3^{2-}].V_{S_2O_3^{2-}}}{2}$$

$$[I_2] = \frac{0.01970 \times 10.10}{2 \times 5.00} = 0.0199 \ M$$

1 mark for correct mol ratio.
max 2 marks for correct calculation.
-1 mark for less than 2 or more than 3 significant figures.

Concentration of I_2 [0.0199] M

Accuracy (max 7 marks)-recalculated using student's data   7 marks
Sliding scale 7 marks for 0 to 0.5 % deviation.
          0 mark for greater than 3.0 % deviation.

Laboratory Task I

B. <u>A kinetic study of the acid catalyzed reaction between acetone and iodine in aqueous solution</u>

B-1. <u>Calculation for initial concentrations (M) in the solution mixtures</u>

	Concentration			
Flask No.	**I**	**II**	**III**	**IV**
$[I_2]$, M	0.00498	0.00998	0.00498	0.00498
[acetone], M	1.69	1.69	3.39	1.69
[HCl], M	0.0250	0.0250	0.0250	0.0500

0.25 mark for each correct concentration of I_2 and HCl.
0.5 mark for each correct concentration of acetone.

B-2. <u>Calculation for the concentration (M) of iodine remaining in Flasks I to IV at 7 minutes.</u>

	Volume			
Flask No.	**I**	**II**	**III**	**IV**
initial buret reading (mL)	0.00	0.00	0.00	0.00
final buret reading (mL)	8.35	18.55	6.75	6.85
standard $Na_2S_2O_3$ (mL)	8.35	18.55	6.75	6.85

$[I_2]$ remaining at 7 minutes (M)	0.00412	0.00914	0.00332	0.00338

0.5 mark for each correct calculation of remaining iodine.

B-3. <u>Calculation for initial rate of disappearance of I_2 at 7 minutes for Flasks I to IV (in M s^{-1})</u>

$$\text{Initial rate of disappearance of iodine (M s}^{-1}) = -\frac{d[I_2]}{dt}$$

Flask No.	**I**	**II**	**III**	**IV**
Calculation for rate	$\dfrac{0.00498-0.00412}{7 \times 60}$	$\dfrac{0.00997-0.00914}{7 \times 60}$	$\dfrac{0.00498-0.00333}{7 \times 60}$	$\dfrac{0.00498-0.00338}{7 \times 60}$
Initial rate	2.05×10^6	1.98×10^6	3.95×10^6	3.811×10^6

4 marks for correct calculation.

B-4. Calculation for the kinetic orders x, y and z

$$\text{rate} = -\frac{d\,[I_2]}{dt} = k[CH_3COCH_3]^x\,[I_2]^y\,[H^+]^z$$

Calculation for x	**Calculation for y**	**Calculation for z**
$\dfrac{\text{Rate (III)}}{\text{Rate (I)}} = \dfrac{3.95 \times 10^{-6}}{2.05 \times 10^{-6}}$	$\dfrac{\text{Rate (II)}}{\text{Rate (I)}} = \dfrac{1.98 \times 10^{-6}}{2.05 \times 10^{-6}}$	$\dfrac{\text{Rate (IV)}}{\text{Rate (I)}} = \dfrac{3.81 \times 10^{-6}}{2.05 \times 10^{-6}}$
$2^x = 1.93$	$2^y = 0.965$	$2^z = 1.86$
$x = 0.95$	$y = -0.051$	$z = 0.90$
$x = 1$ (integer)	$y = 0$ (integer)	$z = 1$ (integer)

max 1 mark for each correct calculation

Write rate equation or rate law

$$\text{Rate} = \boxed{k[CH_3COCH_3][H^+]}$$

2 marks

B-5. Calculation for the rate constant, k, for Flasks I to IV with proper unit.

Flask No.	I	II	III	IV
Calculation	$\dfrac{2.05 \times 10^{-6}}{(1.69)(0.0250)}$	$\dfrac{1.98 \times 10^{-6}}{(1.69)(0.0250)}$	$\dfrac{3.95 \times 10^{-6}}{(3.39)(0.0250)}$	$\dfrac{3.81 \times 10^{-6}}{(1.69)(0.0500)}$
Rate Constant k =	4.85×10^{-5}	4.68×10^{-5}	4.66×10^{-5}	4.51×10^{-5}
Unit	$M^{-1}\,s^{-1}$	$M^{-1}\,s^{-1}$	$M^{-1}\,s^{-1}$	$M^{-1}\,s^{-1}$

Max 0.5 mark for each correct calculation.
1 mark for correct unit.

B-6. Mean value of rate constant = $\boxed{4.68 \times 10^{-5}}$

22 marks

Accuracy: (max 22 marks)-recalculated using student's data.
Sliding scale 22 marks for 0 to 6% deviation.
　　　　　　0 mark for greater than 18% deviation.
　　　　　　0 mark for greater than ±10% deviation.

Isolation and Identification of an Essential Oil from Natural Source

In this experiment, you will steam distil and determine the structures of the main essential oil (**S**) from a given natural source and a product from its chemical conversion (unknown **Y**).

To determine the structures, you have to use organic qualitative analysis to identify any functional groups present in the compounds by using the reagents at your station. NMR data will be given only after the functional group test is completed.

Chemicals Available:

Sample (1 g in a vial)
Unknown **Y** (in a vial)

Anhydrous Na_2SO_4 (in a plastic vial)
Dichloromethane
Ceric ammonium nitrate solution
2,4-Dinitrophenylhydrazine (labelled as 2,4-DNP)

2% aq. NH_3
5% aq. $AgNO_3$
5% aq. HCl
5% aq. NaOH
5% aq. $NaHCO_3$

1% $FeCl_3$ in EtOH

0.2% aq. $KMnO_4$ Decolourised with easily oxidised functional groups.

Acetone (for washing)

Equipments and Glasswares

1.	Microscale kit	1	set
2.	Round bottomed flask, 25 mL	1	
3.	Hotplate-stirrer/stand/clamps	1	set
4.	Sand bath	1	
5.	Beaker (250 mL)	1	
6.	Test tube	16	
7.	Test tube rack	1	
8.	Pasteur pipette	8	
9.	Rubber bulb	1	
10.	Microspatula	1	
11.	Rubber tubing (1 m)	2	
12.	Thermometer	2	
13.	Wooden ring	2	
14.	A bag of tissue paper	1	
15.	A bag of cotton/a piece of paper	1 set	
16.	Cotton gloves	1 pair	
17.	Vial (for recovered dichloromethane)	1	
18.	Wooden stick	1	
19.	Ice (in a bucket in each lab)		

Procedure:

Apparatus. Assemble a distillation apparatus (as shown in the diagram 1) using a 25 mL round bottomed flask for distillation and a 10 mL round bottomed flask to collect the distillate. **Heat the sand bath to approximately 150 °C before proceeding the next step.**

Simplified Steam Distillation: Mix 1 g of ground sample with 15 mL of water in the 25 mL round bottomed flask and allow the sample to soak in the water for about 10 minutes before distillation. Do not forget to put in a magnetic bar, turn on the water in the condenser and stirring motor, heat the mixture (the temperature of the sand bath should not be below 170°C) to provide a steady rate of distillation. **At least 5 mL** of distillate must be collected. Hot plate must be turned off after distillation is finished. Disassemble the apparatus and rinse the condenser with acetone. **Be sure that the condenser is dry before using in the next step**

> **Q.1) Show the <u>distillate</u> to your demonstrator and ask for his or her Signature on your answer sheet before proceeding to the next Step.**

Extraction of the Essential Oil: Transfer the distillate to a 15 mL capped centrifuge tube and add 1 mL of dichloromethane to extract the distillate. Cap the tube securely and shake vigorously, cool in ice. Allow the layers to separate.

Using a Pasteur pipette, transfer the dichloromethane layer to a 10 mL test tube. Repeat this extraction with fresh 1 mL dichloromethane twice and combine with the first extract.

Drying: Dry the dichloromethane extract by adding anhydrous Na_2SO_4 and stir occasionally for 10 minutes.

Evaporation: With a clean, dry cotton plugged Pasteur pipette transfer the organic layer to a dry 5 mL conical vial. Use approximately 1 mL of clean dichloromethane to wash Na_2SO_4 using the dry cotton plugged Pasteur pipette, then transfer into the vial. Be careful not to transfer any of the Na_2SO_4 into the vial. Use Hickman still head and **dry** condenser (see diagram 2) to distil the dichloromethane from the solution until the volume is reduced to 1 mL. Discard the distilled dichloromethane from the Hickman still head with a Pasteur pipette or a syringe to a vial (for recovered dichloromethane) and keep the residue for functional group analysis.

Functional Group Analysis: Carry out the functional group analysis of the residue solution (1 mL) by using the appropriate reagents at your station. (Note: dichloromethane is immiscible with water.)

Tollen's Reagent: add 1 drop of 5% aq. $AgNO_3$ in a small test tube followed by 1 drop of 5% aq. NaOH, brown precipitate will appear. Add 2% aq NH_3 to the tube until all the precipitate dissolved. The solution is ready for the test.

Q.2) **Fill in your results in the answer sheet and indicate the functional group(s) present or not present.**

Structure elucidation of the main essential oil (S): Reaction of the main essential oil (**S**) with CH_3I in the presence of K_2CO_3 gives compound **X** ($C_{11}H_{14}O_2$). Oxidation of **X** gives unknown **Y** ($C_{10}H_{12}O_4$) as the main product and CO_2.

Q.3) **Identify the functional groups of unknown Y (provided in a conical vial) by using the reagents at your station and fill in your results in the answer sheet. Indicate the functional group(s) present or not present.**

Hand in your copy of **answer sheet PART I (Demonstrator copy)** of functional group analysis with your signature **and ask for ^{1}H NMR spectra and answer sheet PART II**. ^{1}H NMR spectra will be given only when the functional group analysis is completed.

Q.4) **Draw the structure which represents the main component in the essential oil (S) that was distilled from the sample. Assign each proton from the provided ^{1}H NMR spectra by labelling the peak number on the proton in the structure in the answer sheet.**

Q.5) **Draw the structures of compound X and unknown Y. Assign each proton of unknown Y from the provided ^{1}H NMR spectra in the same manner as Q.4.**

Laboratory Task II

RESULTS SHEET: **28.6 points**

PART I

Q.1) Show the distillate ($\geq$5 mL) to your demonstrator and ask for his/her signature.

Demonstrator Signature:………………………………………………

(0 or 5 marks)

Q.2) Functional Groups Analysis of the distilled essential oil (S):   **(5.5)**
Tick ($\sqrt{}$) where appropriate.

Reagents	Positive test	Negative test	
0.2% $KMnO_4$	$\sqrt{}$		
1% $FeCl_3$	$\sqrt{}$		
2,4-DNP		$\sqrt{}$	
Ceric ammonium nitrate	$\sqrt{}$		2.5 marks
Tollen's Reagent		$\sqrt{}$	0.5 for each correct result

Functional groups in **S**	Present	Not present	
-C=C-	$\sqrt{}$		
-OH (alcoholic)		$\sqrt{}$	
-OH (phenolic)	$\sqrt{}$		
-CHO		$\sqrt{}$	
-CO-		$\sqrt{}$	3 marks
-COOH		$\sqrt{}$	0.5 for each correct result

Q.3) Functional Groups Analysis of unknown Y: **(7)**
Tick ($\sqrt{}$) where appropriate.

Reagents	Positive test	Negative test	
5% HCl		$\sqrt{}$	
5% NaOH	$\sqrt{}$		
5% $NaHCO_3$	$\sqrt{}$		
0.2% $KMnO_4$		$\sqrt{}$	
1% $FeCl_3$		$\sqrt{}$	
2,4-DNP		$\sqrt{}$	
Ceric ammonium nitrate		$\sqrt{}$	4 marks
Tollen's Reagent		$\sqrt{}$	0.5 for each correct result

| Name: | | | Student code: |

Functional groups in **Unknown Y**	Present	Not present
-C=C-		√
-OH (alcoholic)		√
-OH (phenolic)		√
-CHO		√
-CO-		√
-COOH	√	

3 marks

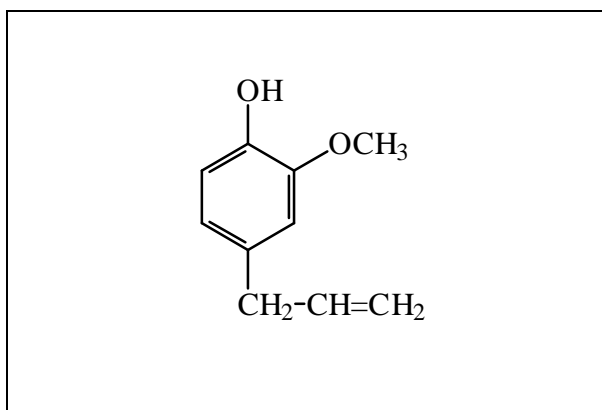0.5 for each correct result

Student signature:…………………………………………………………………..

Laboratory Task II

PART II

Q. 4) Structure Elucidation: (6)

The structure which represents the main essential oil (**S**):

OH
OCH$_3$
CH$_2$–CH=CH$_2$

2 marks
0.5 mark for OH, 0.5 mark for OCH$_3$, 0.5 mark for CH$_2$CH=CH$_2$,
0.5 mark for 1, 2, 4-trisubstituted benzene

NMR Assignment of the main essential oil (S):
(See peak number in the given ^{1}H NMR spectrum)

Peak No.	Chemical shift (δ, ppm)	No. of proton(s)	Multiplicity	^{1}H NMR Assignment
1	3.31	2H	d (0.25 mark)	
2	3.84	3H	s (0.25 mark)	
3	5.0-5.1	2H	m (0.25 mark)	
4	5.6	1H	s (0.25 mark)	
5	5.9-6.0	1H	m (0.25 mark)	
6	6.7	2H	s (0.25 mark) d or m (0.5 mark)	Draw a structure of the essential oil (**S**) with peak no. assignment at each proton.
7	6.87	1H	d (0.25 mark)	

4
OH **2**
OCH$_3$
6 or **7** or **7** or **6** **6**
CH$_2$–CH=CH$_2$
1 **5** **3**

4 marks
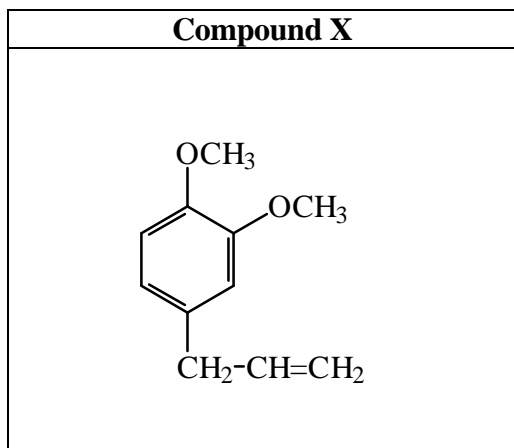2 marks for multiplicity assignment
2 marks for chemical shift assignment
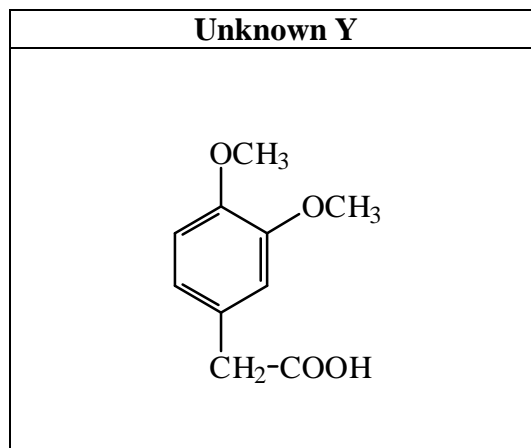(0.25 mark for each proton assignment)

Laboratory Task II

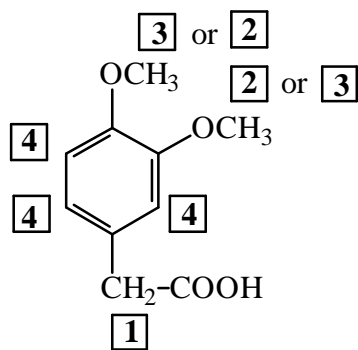## Q.5) The structure of compound X and unknown Y: (5)

Compound X	Unknown Y

OCH$_3$

OCH$_3$

CH$_2$-CH=CH$_2$

OCH$_3$

OCH$_3$

CH$_2$-COOH

1 mark
 0.5 mark for 2(OCH$_3$)
 0.5 mark for CH$_2$CH=CH$_2$

1 mark
 0.5 mark for 2(OCH$_3$)
 0.5 mark for CH$_2$COOH

NMR Assignment of Unknown Y:
(See peak number in the given ^{1}H NMR spectrum, labile proton does not appear in the spectrum)

Peak No.	Chemical shift (δ, ppm)	No. of proton(s)	Multiplicity	^{1}H NMR Assignment
1	3.59	2H	s (0.25 mark)	
2	3.86	3H	s (0.25 mark)	
3	3.88	3H	s (0.25 mark)	
4	6.81	3H	s (0.25 mark) d (0.5 mark) m (0.75 mark)	

[3] or [2]

OCH$_3$ [2] or [3]

OCH$_3$

[4]

[4]   [4]

CH$_2$-COOH

[1]

Draw a structure of the unknown **Y** with peak no. assignment at each proton.

3 marks
1.5 marks for multiplicity assignment
1.5 marks for chemical shift assignment
(0.25 for each proton assignment)